

## CHAPTER 5

# Chemistry and properties of metal-complex and mordant dyes

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### 5.1 INTRODUCTION

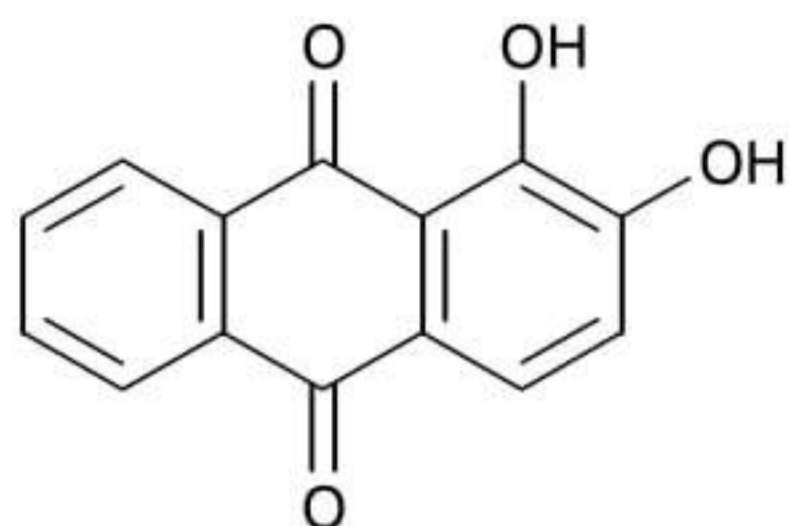
The complexing of chelatable organic compounds with transition-metal atoms is widely exploited in catalytic reactions, biological systems, metal recovery and sequestration of trace metals. Such complexes are important in many non-textile applications, including solvent dyes of high fastness, charge-control agents in photocopying, dye developers in instant colour photography and specific reagents in colorimetric analytical chemistry. This chapter is mainly concerned with the interaction between organic chromogenic systems and chromium or copper (or occasionally iron, cobalt or nickel) to give acid dyes for amide fibres and direct or reactive dyes for cellulosic fibres [1–3].

It has been recognised for centuries that certain natural dyes, including alizarin, kermes, cochineal and fustic, now known to contain *o*-dihydroxy phenolic or anthraquinonoid residues in their structures, can be fixed on natural fibres using oxides or salts of transition metals as mordants. Although mordanted wool dyed with alizarin showed excellent fastness, reproducibility of shade was difficult to achieve because of the variable composition of the raw materials available. The famous Turkey red, in which alizarin was applied to aluminium-mordanted wool in the presence of calcium salts, formed a metallised complex the nature of which remains in considerable doubt.

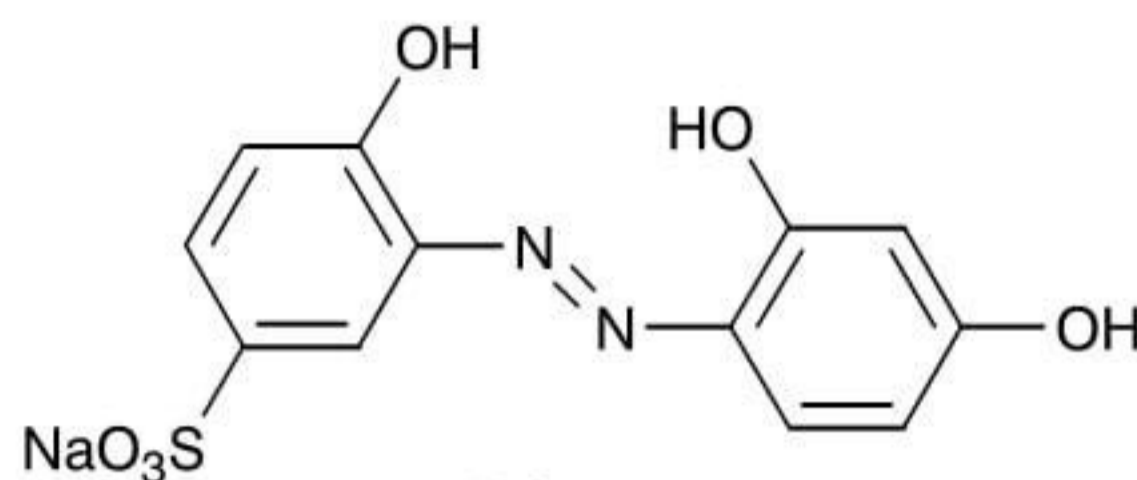
The research of Werner at Zürich in the early 1900s on the theory of coordination valency [4] established the concept of a metal-complex dye and was the key to understanding of the mordanting process. He concluded that a metal ion was characterised by two types of valency, which he called primary and secondary. The primary valency satisfied the chemical equivalence (the number of positive charges on the metal cation) and the secondary valency took part in coordination bonding. We now refer to the primary valency as the oxidation number or state of the central metal atom and the secondary valency as the number of associated ligand atoms required to complete the coordination number. It must be borne in mind that the concept of bond angles, such as the tetrahedral configuration of the C-H bonds in methane, was then unknown and knowledge of the mode of attachment of a ligand to the central metal atom was extremely vague.

Synthetic alizarin (5.1), CI Mordant Red 5 (5.2) and CI Mordant Orange 1 (5.3), the first azo dye capable of forming a metal complex, in this case via the salicylic acid residue, are examples of the simple mordant dyes in widespread use at the time when Werner propounded his theory. The first metal-complex dyes to be prepared in substance, rather than within the fibre, were discovered by Bohn of BASF in 1912 by treating hydroxyanthraquinonesulphonic acids with a warm solution of a chromium(III) salt. In the

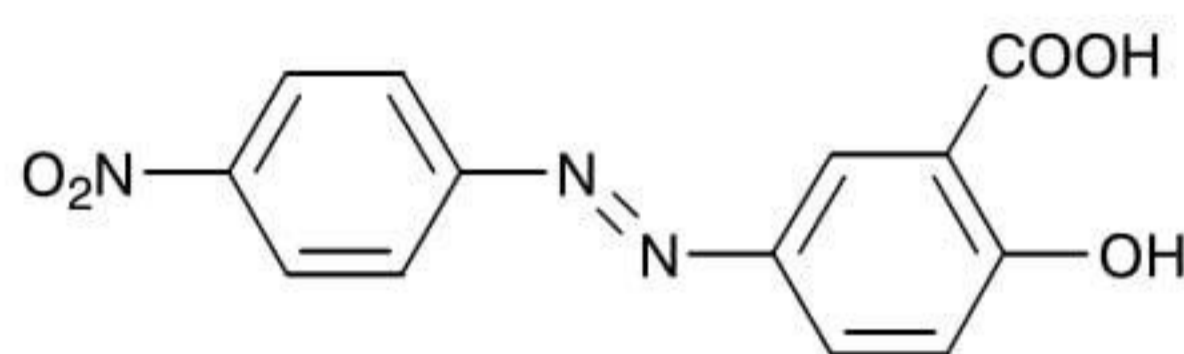
same year chromium complexes of mordant azo dyes were also patented. However, it was not until Ciba in 1915 proposed applying these sulphonated 1:1 chromium-dye complexes to wool from a sulphuric acid solution at low pH that economic exhaustion values could be attained. CI Acid Yellow 104 is a typical example of these mono- or disulphonated azo dye complexes still in current use.



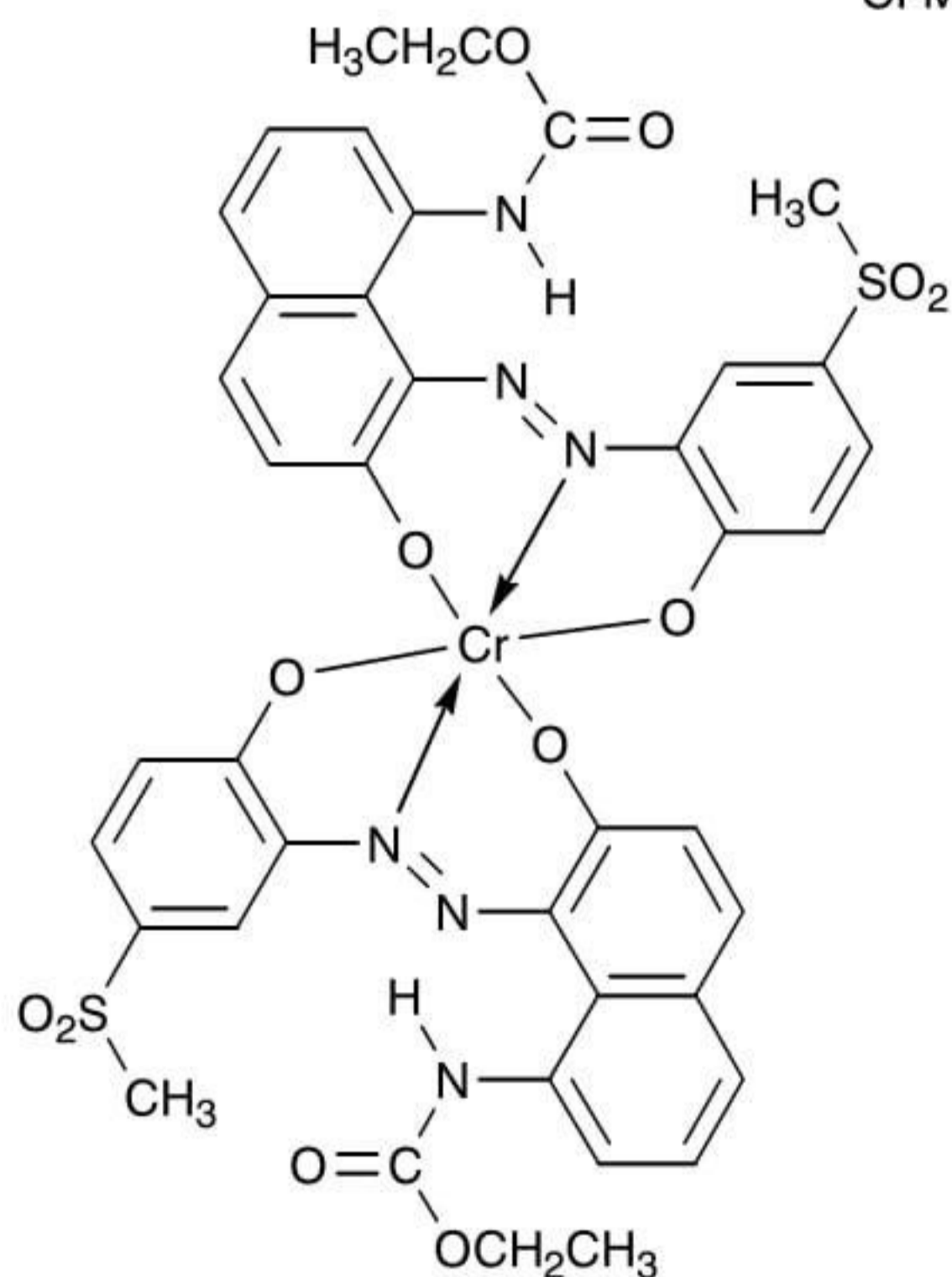
5.1  
Alizarin



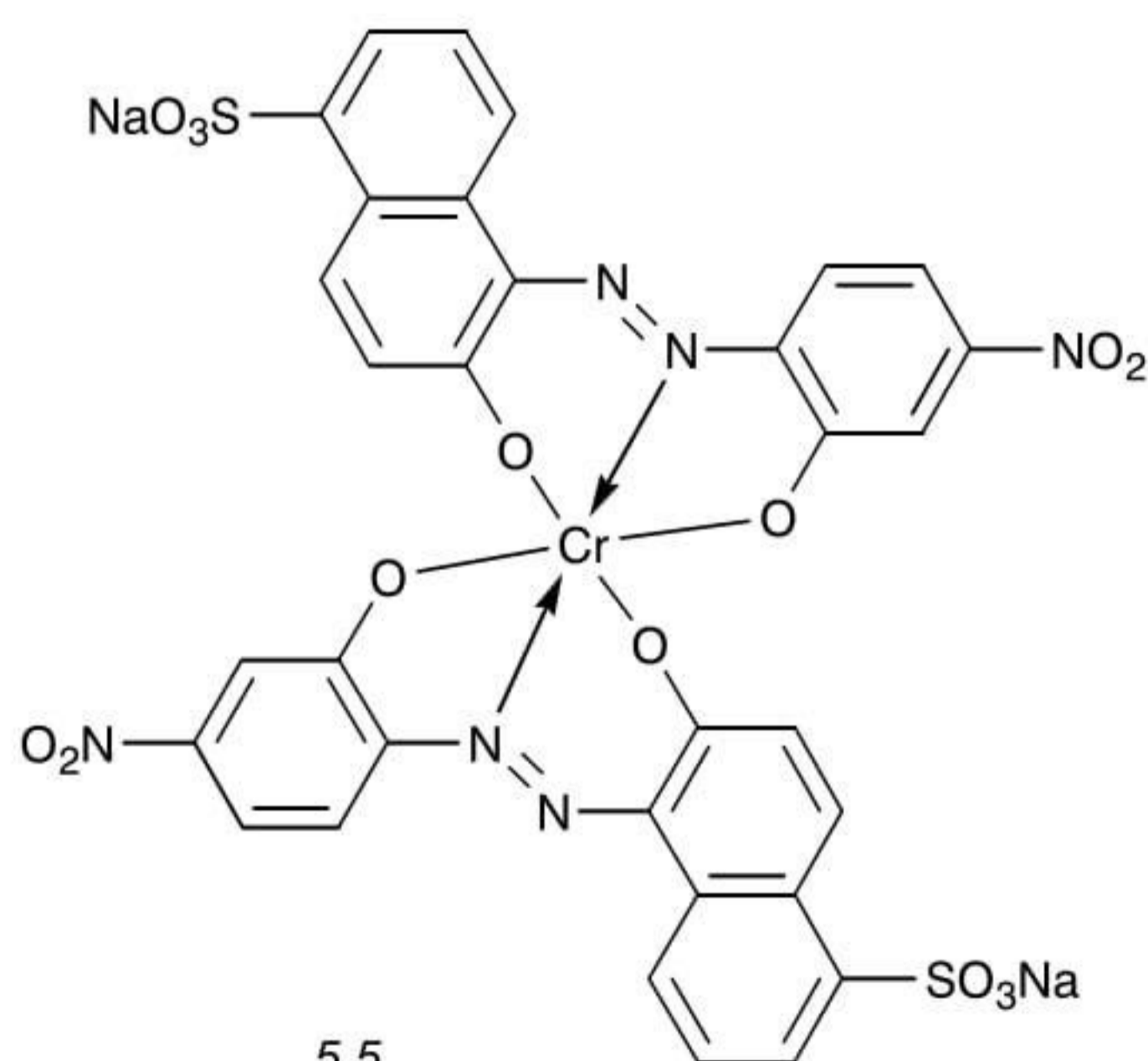
5.2  
CI Mordant Red 5



5.3  
CI Mordant Orange 1



5.4  
CI Acid Black 58

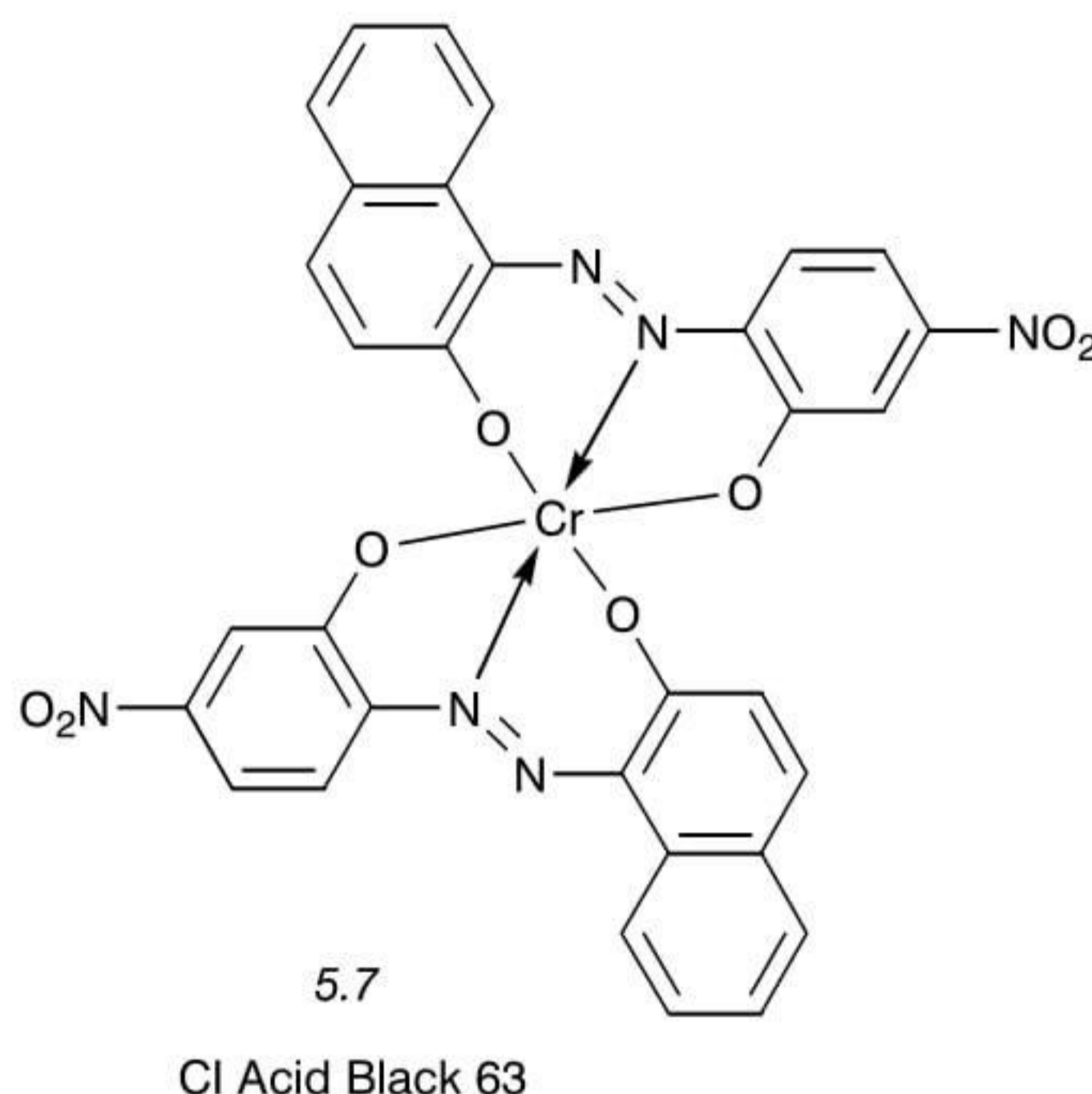
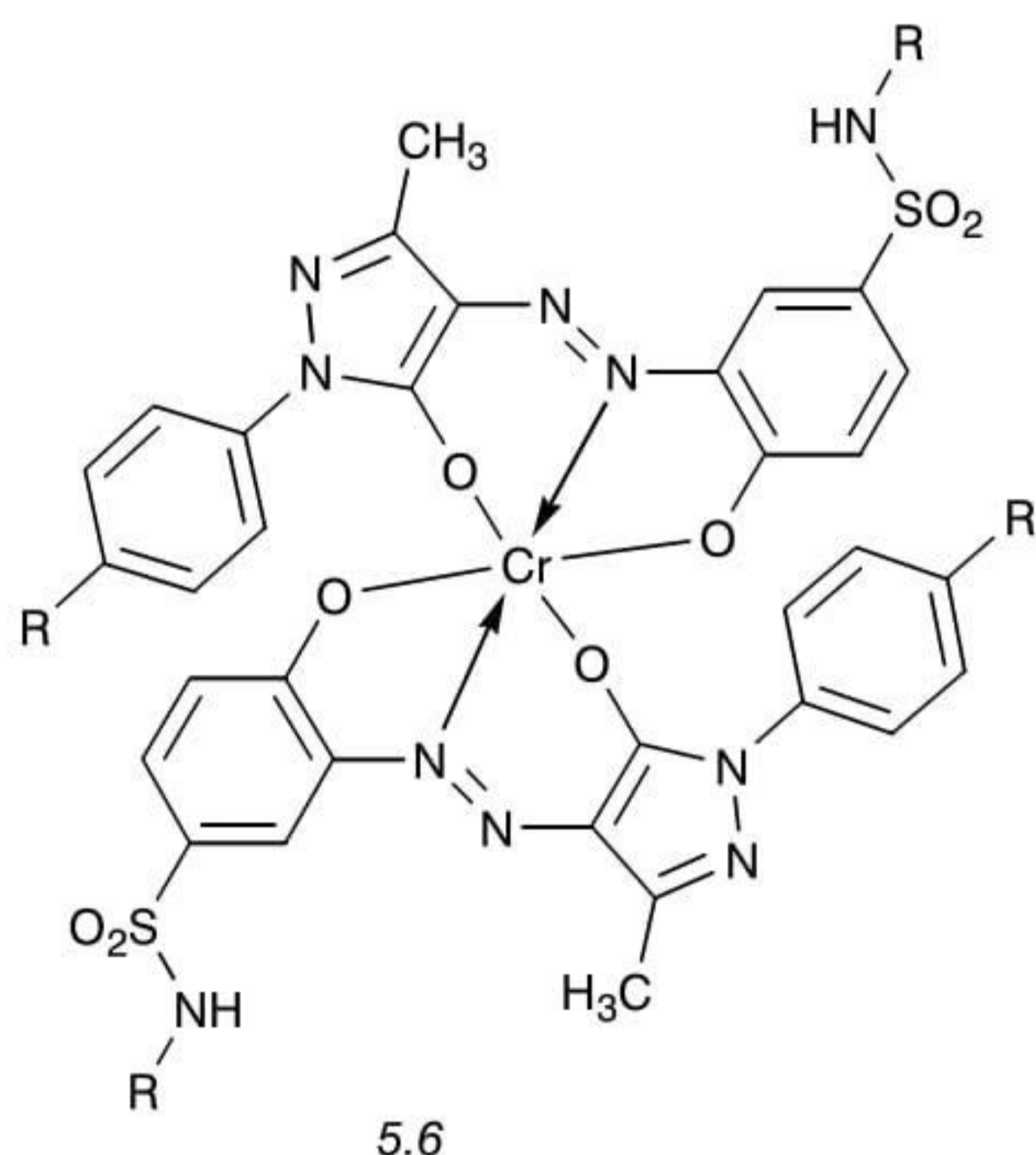


5.5  
CI Acid Green 12

The first water-soluble symmetrical 1:2 metal-complex dye, which contained no sulpho groups and was solubilised by a polar methylsulphonyl group on each organic ligand, was described by Schetty of Geigy for application to wool under neutral dyeing conditions [5]. This dye was CI Acid Black 58 (5.4), still an important basis for grey shades in wool dyeing. If sulphonated intermediates were used to form symmetrical disulphonated 1:2 metal-

complex analogues, such as CI Acid Green 12 (5.5), unlevel dyeing remained a problem because of the low pH necessary to achieve satisfactory exhaustion.

This difficulty was gradually overcome by the use of nonionic or weakly cationic levelling agents, but the most important factor was the introduction of a range of polar but nonionised solubilising groups [1,6]. These included alkylsulphonyl ( $\text{RSO}_2-$ ), as in structure 5.4, mono- and dialkylsulphonamides ( $\text{R}_2\text{NSO}_2-$ ) and cyclic sulphones. Typical sulphonamido-substituted dyes include CI Acid Orange 60 (5.6;  $\text{R} = \text{H}$ ) and 87 (5.6;  $\text{R} = \text{CH}_3$ ). Insoluble 1:2 metal-complex dyes devoid of polar solubilising groups are also available, such as CI Acid Black 63 (5.7). They are mainly of interest for the dyeing of nylon from aqueous dispersion.



## 5.2 FUNDAMENTAL CONCEPTS

Metal-complex formation entails the interaction of one or more organic ligands with a multivalent metal cation. This brings about certain fundamental changes in the characteristics of the components of the complex.

### 5.2.1 Ligand systems

A ligand system is any charged or uncharged polar entity or atomic component of a substituent group containing an excess electron or electron pair. The nature of the bond between the ligand and the metal atom depends on the ligand acting as an electron-pair donor and the metal as an electron-pair acceptor. The size of the atom and the electron distribution in the outermost shell of a transition element of the first series are especially conducive to the formation of metal complexes. The donation of an electron pair from ligand atom to metal gives rise to a covalent or sigma bond, in molecular orbital terminology. It is often convenient to distinguish between conventional covalent bonds arising from the sharing of electrons, denoted by a straight line, and coordinated sigma bonds arising by electron-pair donation from a ligand system, denoted by an arrow. However, there is no real difference between them once the bonds are formed.

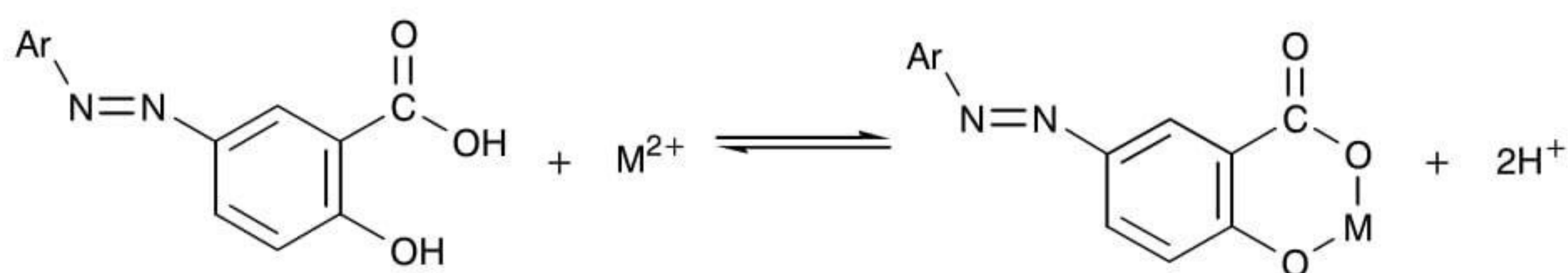
In the synthesis of metal-complex dyes the organic ligand may form part of either a basic or an acidic functional group. A basic ligand carries a lone pair of electrons that may interact with the metal ion. Examples include  $-\text{NH}_2$  (amino),  $=\text{NH}$  (imino),  $=\text{N}-$  (in azo or azomethine),  $=\text{O}$  (in carbonyl) or  $-\text{S}-$  (in thioether). An acidic ligand, such as  $-\text{OH}$  (from carboxylic, phenolic or enolic groups),  $-\text{SH}$  (from thiophenolic or thioenolic groups) or  $-\text{NH}-$  (from amino or imino groups), loses a proton during metallisation to give a formal negative charge.

In the case of a ligand molecule such as ammonia or water, only one pair of electrons is utilised in forming a coordinated sigma bond with the metal. Ligand systems of this type are said to be unidentate and are found in many metal-complex dye structures, satisfying sites around the central metal atom not already sterically occupied by coordinated dye ligands. Bi- or tridentate ligand systems form respectively two or three coordinated or covalent bonds with the central atom. Dye molecules used as intermediates in synthesising metal complexes have at least two ligand donor groups arranged so that it is geometrically possible to coordinate at two or more positions in the coordination shell of a single metal ion. Examples found throughout this chapter contain from two to six ligand groups bound to the one transition-metal ion. Where two groups originating in the same bidentate molecule combine with the same metal ion, a heteroatomic ring is formed.

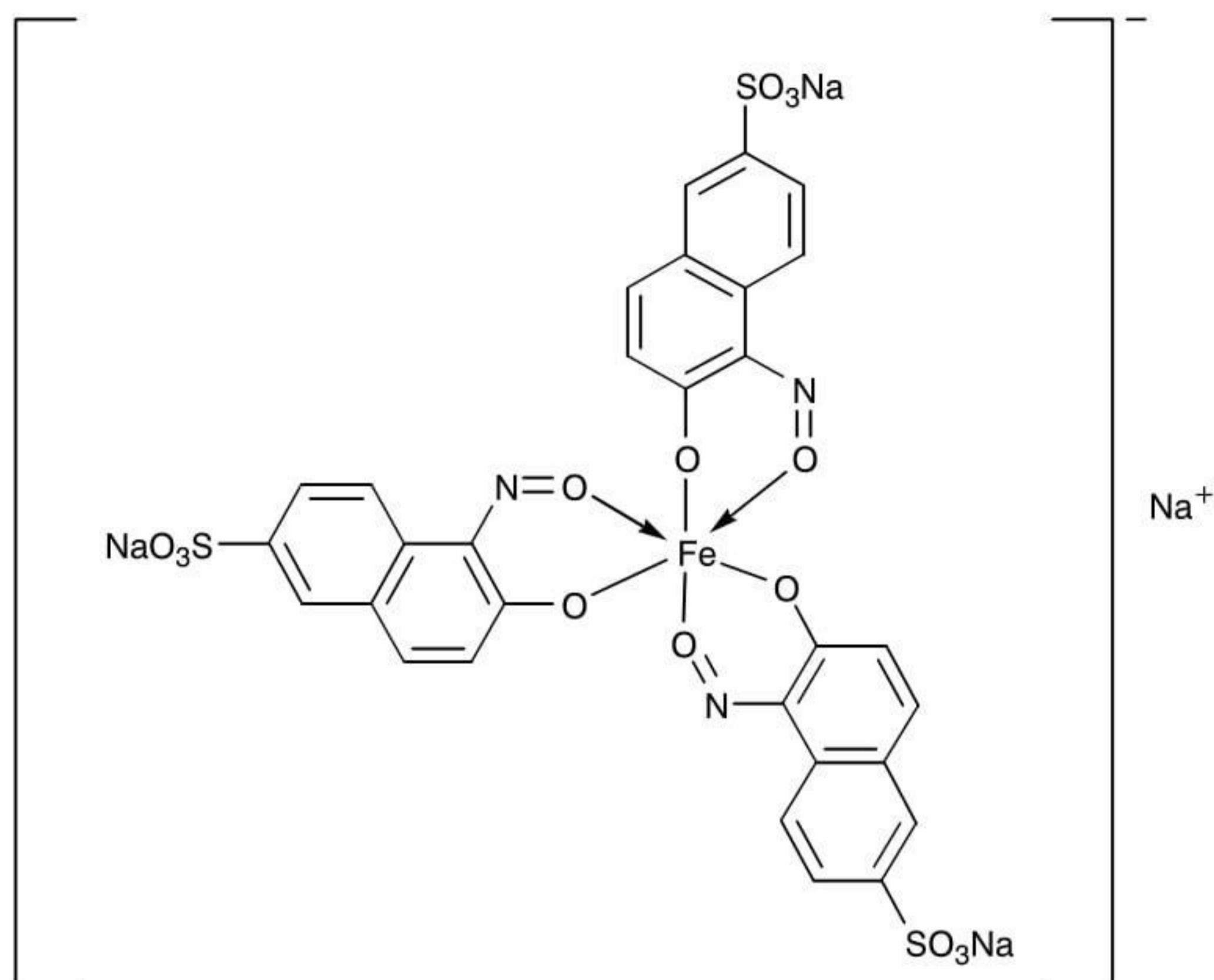
Ring formation between the metal  $M$  and a salicylic acid residue (in a dye structure such as 5.3) containing two donor groups is shown in Scheme 5.1. This process was first described by Morgan and Drew [7] as chelation, which profoundly affects the chemical and physical properties of both the ligand system and the metal atom. Although the formation of a single heterocyclic ring imparts some stability to the complex, this is not generally sufficient to be directly useful in dyeing. Scheme 5.1 is a reversible reaction, so that demetallisation can take place to an extent that depends on the severity of the conditions. The metal chelate may be thermodynamically stable yet kinetically labile. The chromogenic ligand system may be replaced by other electron-pair donors, such as water molecules. This sensitivity to hydrolysis is shown by certain complexes of *o*-nitrosonaphthols, such as the 1:3 iron(II) complex (5.8) of 1-nitroso-2-naphthol-6-sulphonic acid, although this dye is still of some interest for the dyeing of wool. On the other hand, multidentate ligands form numerous complexes with copper, chromium or cobalt that contain two condensed heteroatomic ring systems. These are much more stable, both thermodynamically and kinetically, undergoing ligand exchange reactions extremely slowly.

### 5.2.2 Coordination number

The number of ligand systems associated with a metal atom in a complex is known as the coordination number, often abbreviated to CN. For transition metals in their lower oxidation states ( $1+$ ,  $2+$  or  $3+$ ) the CN is usually 4 or 6. The metals used in complex formation with



Scheme 5.1



5.8

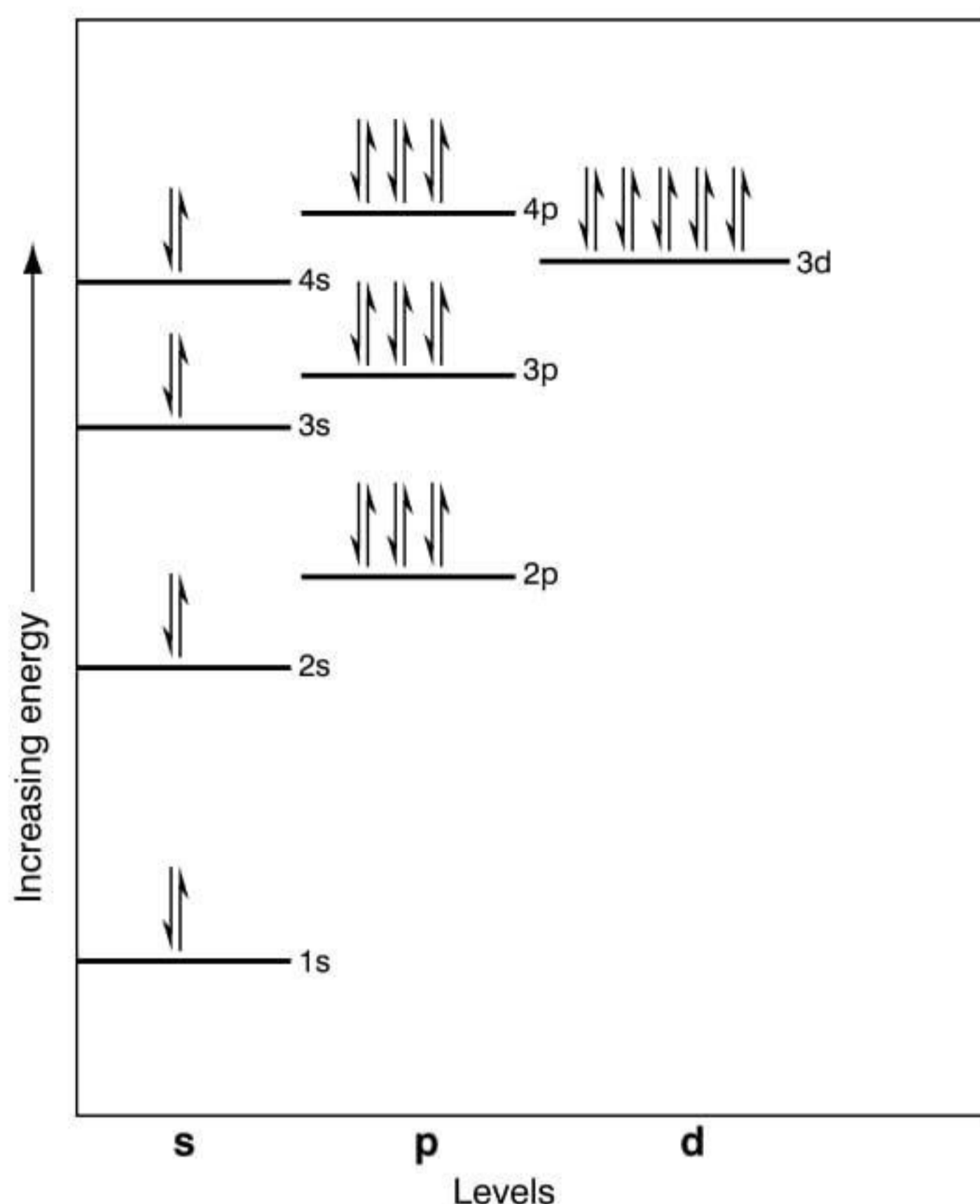
CI Acid Green 1

dye molecules fall into this category. In less common complexes the CN can range from 2 to 10. This value depends on the size and geometry of the ligand system relative to the size of the metal ion. The larger the central cation, the greater the number and variety of ligand systems that can be accommodated. The charge on the cation also influences the CN. Metals in a higher oxidation state (such as 6+ or 7+) generally have low CN values, since the removal of six or seven electrons reduces the ionic size and so the accommodation of many ligand systems simultaneously around the ion becomes sterically impossible.

### 5.3 ELECTRONIC STRUCTURE OF TRANSITION-METAL IONS

The structures of metal-complex dyes, which must exhibit a high degree of stability during synthesis and application, is limited to certain elements in the first transition series, notably copper, chromium, iron, cobalt and nickel. The remaining members of the transition series form relatively unstable chelated complexes. The following description of the influence of electronic structure, however, is applicable to all members of the series.

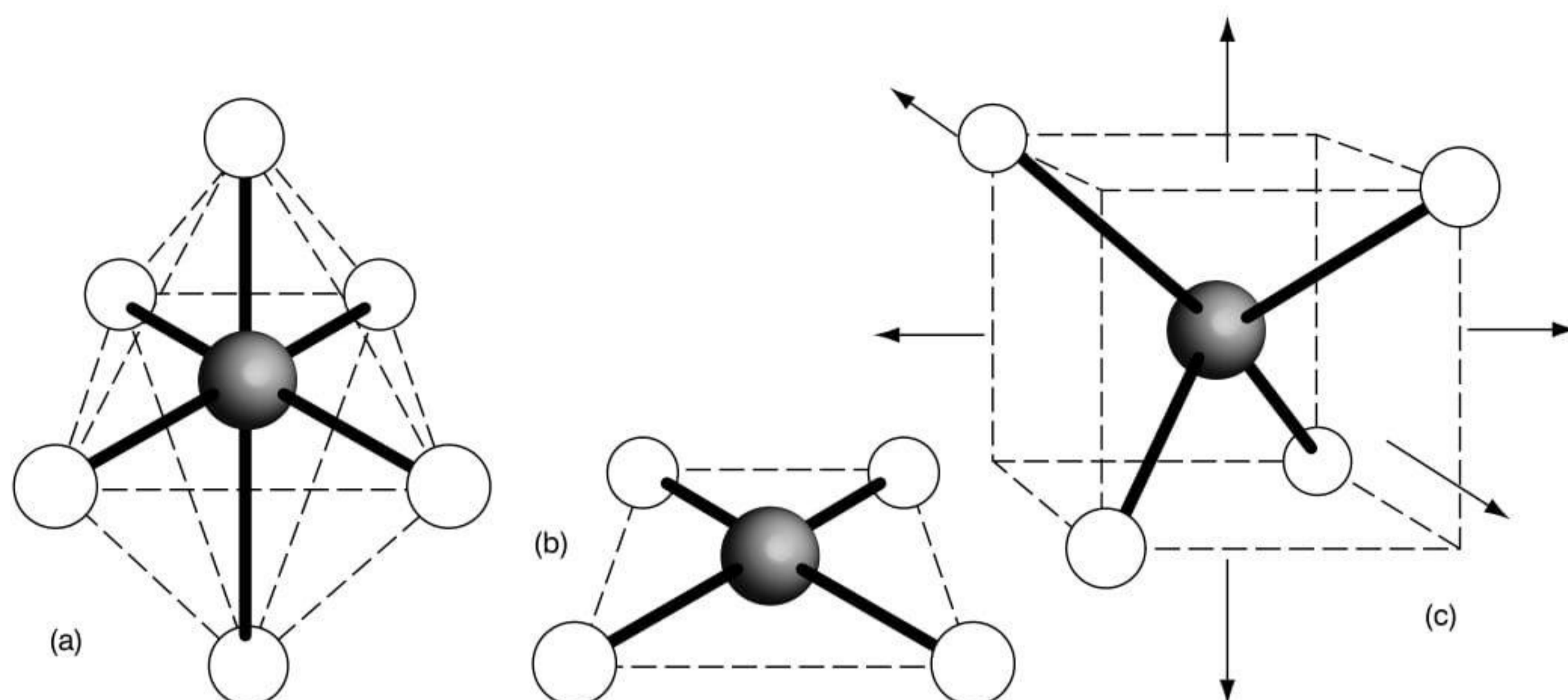
The principal characteristic of the transition elements is an incomplete electronic subshell that confers specific properties on the metal concerned. Ligand systems may participate in coordination not only by electron donation to the 3d levels in the first transition series but also by donation to incomplete outer 4s and 4p shells. Figure 5.1 shows that the differences in orbital energy levels between the 4s, 4p and 3d orbitals are much smaller than, for example, the difference between the inner 2s and 2p levels. Consequently, transitions between the 4s, 4p and 3d levels can easily take place and coordination is readily achieved. The manner in which ligand groups are oriented in surrounding the central metal atom is determined by the number and energy levels of the electrons in the incomplete subshells.



**Figure 5.1** Relative energy levels up to atomic number 36

The first transition series of elements with atomic number from 21 to 29 (scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper) is built up by the addition of electrons to the outer 3d shell, which can accommodate a total of ten electrons in five subshells of equal energy, each capable of containing two electrons. The influence of the electrical fields originating from the ligand atoms as they approach the electrons of these outermost 3d, 4s and 4p shells is described by ligand field theory. On approach, hybridisation between available ligand electrons and metal electrons takes place as bonds are formed. It is this and the strength of the ligand field that determines the final arrangement of the ligand systems around the central metal atom.

For trivalent elements of  $CN_6$ , such as chromium(III) or cobalt(III), the most stable spatial arrangement of six identical ligand groups is that of an octahedron with four of the groups situated in equatorial quadrants and the other two directly above and below the central metal atom, as shown in Figure 5.2(a). It is possible to obtain a distorted octahedral or tetragonal configuration by an increase in the distance of separation of the ligand groups in the pole positions of the octahedron. In the extreme, when the two pole positions are ligand-free, this leads to a square planar arrangement. For divalent elements of  $CN_4$ , such as copper(II), there are two possibilities: a square planar distribution on the equatorial plane, as in Figure 5.2(b), or the tetrahedral configuration shown in Figure 5.2(c). In early objections to the electrostatic theory of bonding in metal complexes it was argued that the symmetrical arrangement of four ligands about a spherical central atom was best explained in terms of a tetrahedral structure. It was not appreciated that in fact the d shell electrons of the metal atom are symmetrical, so that stable square planar arrangements are possible.



**Figure 5.2** Ligand arrangements about a central nucleus

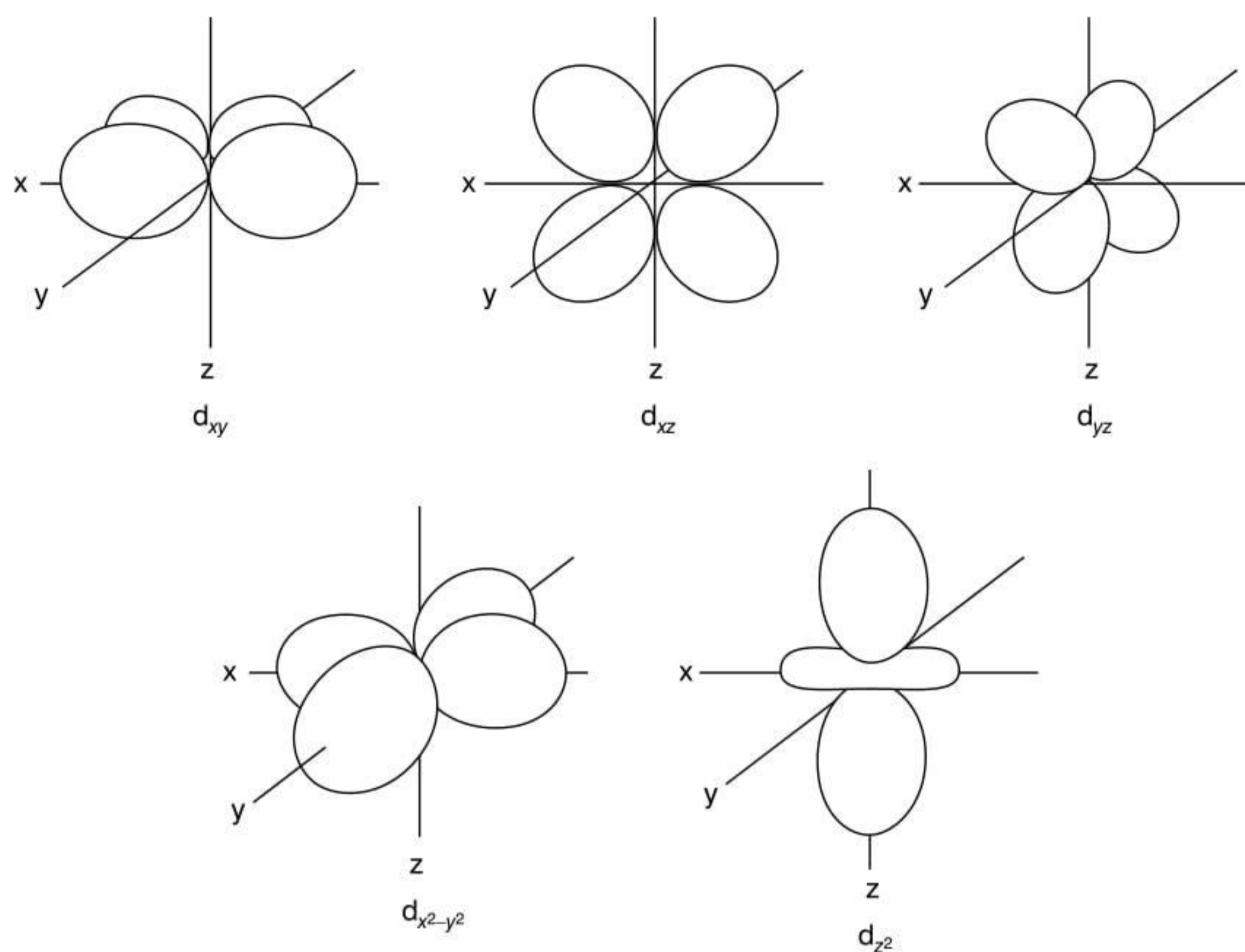
### 5.3.1 Octahedral arrangement

As described above, in each transition-metal atom there are five d orbitals, each of which can accommodate two electrons. These orbitals are arranged spatially in two groups, one acting between the main x-, y- and z-axes of the metal ion and the other acting along these axes. In an octahedral weak ligand field environment, the influence of the six electronegative ligand atoms is to cause the ligand electrons to avoid those regions where the charge density associated with the d electrons is greatest. This charge density distribution is shown in Figure 5.3. Each line of closest approach is therefore along a line of minimum charge repulsion. For the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals, this is along the main x-, y- and z-axes. The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, on the other hand, have maximum charge densities along these main axes, Hence they conflict with the line of approach of the ligand atoms and are destabilised. The five orbitals are thus split into two groups of different energy: an upper doublet referred to as  $e_g$  and a lower triplet level known as  $t_{2g}$ .

The distribution of the d electrons between these various orbitals is determined by the differences in energy level between them. The energy difference is directly proportional to the electric field strength of the ligand systems taking part in complex formation. Since the transition-metal ions do not exist in isolation, they must be evaluated in association with counter-ions or solvents such as water or other ligand systems present.

In isolation the electron distribution in the trivalent chromium(III) ion consists of three unpaired electrons in the d shell, as indicated in line (a) of Table 5.1. In line (b) the six electron pairs donated to the central chromium atom by oxygen atoms of water molecules give rise to  $sp^3d^2$  hybridisation. This is characteristic of an octahedral structure. A similar situation arises with the trivalent cobalt(III) complex in line (e), where each of the three  $t_{2g}$  levels is doubly occupied by an electron pair from each cyano ligand.

With the divalent chromium(II) ion there are two distinct possibilities, shown in lines (c) and (d). With such an isolated ion having four electrons in the d shell the fourth electron may occupy either an  $e_g$  level (c) or a  $t_{2g}$  level (d), depending on whether the energy required to cause spin pairing is less or greater than the difference between these energy



**Figure 5.3** Atomic d orbitals in transition elements

levels. These alternatives result in a high-spin (c) or low-spin (d) complex respectively, the field strength of the ligand systems determining which is actually formed. The unpaired electrons in the chromium(II) ion are unstable, so divalent chromium cannot be utilised in preparing dye complexes. Invariably a  $d^2$  electron is lost and oxidation to chromium(III) ensues, with concurrent reduction of the ligand chromogenic system [8]. The oxidation state and electron distribution in the 3d shell at least partly accounts for the fact that most metal-complex dyes of value for wool or nylon dyeing are based on chromium(III) or cobalt(III) ions.

The presence of unpaired electrons in a complex can be detected by the study of its magnetic properties. A single spinning electron has an associated magnetic moment. When an organometallic complex is weighed in a magnetic field any unpaired electrons contribute to an apparent increase in mass compared with that observed in the absence of the field. The magnitude of attraction of the complex to a magnet is a measure of the content of unpaired electrons. Such a complex is described as paramagnetic. Where there is no detectable difference in mass, the complex contains no unpaired electrons and is said to be diamagnetic. Thus these results are of value in determining the electronic distribution around the central metal atom.

### 5.3.2 Tetrahedral arrangement

Depending on the ligand field strength and the number of ligand systems that can be accommodated, hybridisations other than octahedral are possible. The tetracyanocuprate ion in line (f) of Table 5.1 has a tetrahedral configuration arising from  $sp^3$  hybridisation, as



**Table 5.1** Electron distribution in some transition-metal ions (1s, 2s, 2p, 3s and 3p shells are complete in all cases)

Ion	3d	4s	4p	
(a) Cr <sup>3+</sup>	↓ ↓ ↓			
(b) Cr(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	↓ ↓ ↓	↓ ↑	↓ ↑ ↓ ↑ ↓ ↑	sp <sup>3</sup> d <sup>2</sup>
(c) Cr <sup>2+</sup>	↓ ↓ ↓			high spin
(d) Cr <sup>2+</sup>	↓ ↑ ↓ ↓			low spin
(e) Co(CN) <sub>6</sub> <sup>3-</sup>	↓ ↑ ↓ ↑ ↓ ↑	↓ ↑	↓ ↑ ↓ ↑ ↓ ↑	sp <sup>3</sup> d <sup>2</sup>
(f) Cu(CN) <sub>4</sub> <sup>3-</sup>	↓ ↑ ↓ ↑ ↓ ↑	↓ ↑	↓ ↑ ↓ ↑ ↓ ↑	sp <sup>3</sup>
(g) Cu(NH <sub>3</sub> ) <sub>2</sub> <sup>2+</sup>	↓ ↑ ↓ ↑ ↓ ↑	↓ ↑	↓ ↑ ↓ ↑ ↓	sp <sup>2</sup> d



denotes electron-pair donation to metal ion

in the case of bonding to a saturated carbon atom. The copper(I) ion has a completely filled d shell and electron-pair donation from the four cyano ligands occurs in the 4s and 4p levels. In a tetrahedral arrangement, the  $e_g$  orbitals are more stable than the  $t_{2g}$  orbitals because they are situated at the maximum distance from the influence of the four ligand systems. Conversely, the  $t_{2g}$  orbitals become destabilised. The ligands are best visualised as occupying alternate corners of a cube, the main axes of which represent those of the metal ion, as shown in Figure 5.2(c). The energy difference between  $e_g$  and  $t_{2g}$  orbitals in a tetrahedral structure is approximately half that for the octahedron. This effect favours formation of an octahedral rather than a tetrahedral configuration.

### 5.3.3 Square planar arrangement

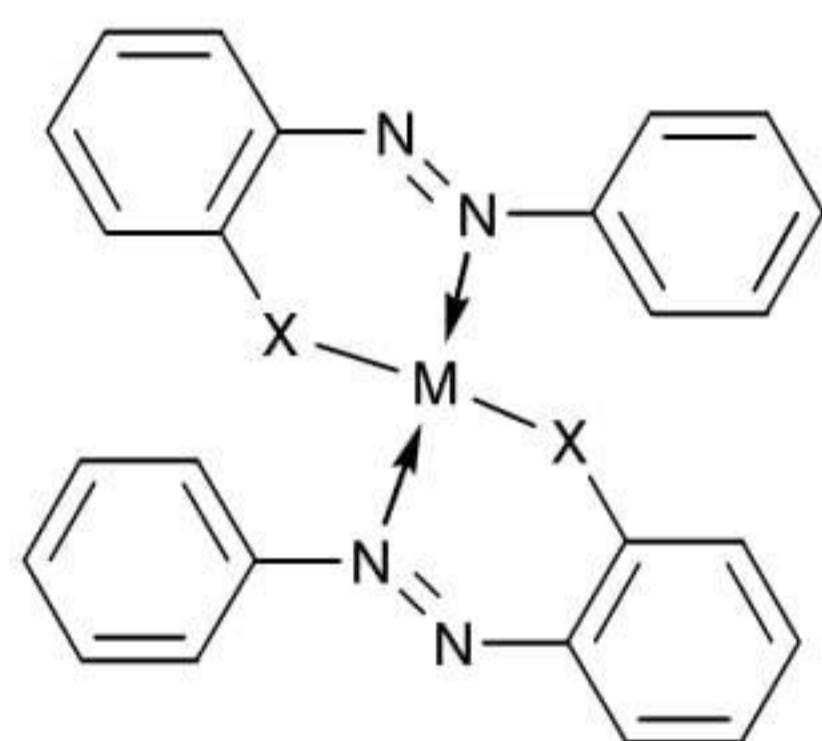
The square planar configuration illustrated in Figure 5.2(b) can be considered as an octahedral structure in which any opposing pair of ligands on a common axis are completely removed from the sphere of influence of the central metal atom. If two such ligands are moved outwards only slightly, the result is a distorted octagonal or tetragonal structure.

## 5.4 STRUCTURAL CHARACTERISTICS NECESSARY FOR COMPLEX FORMATION

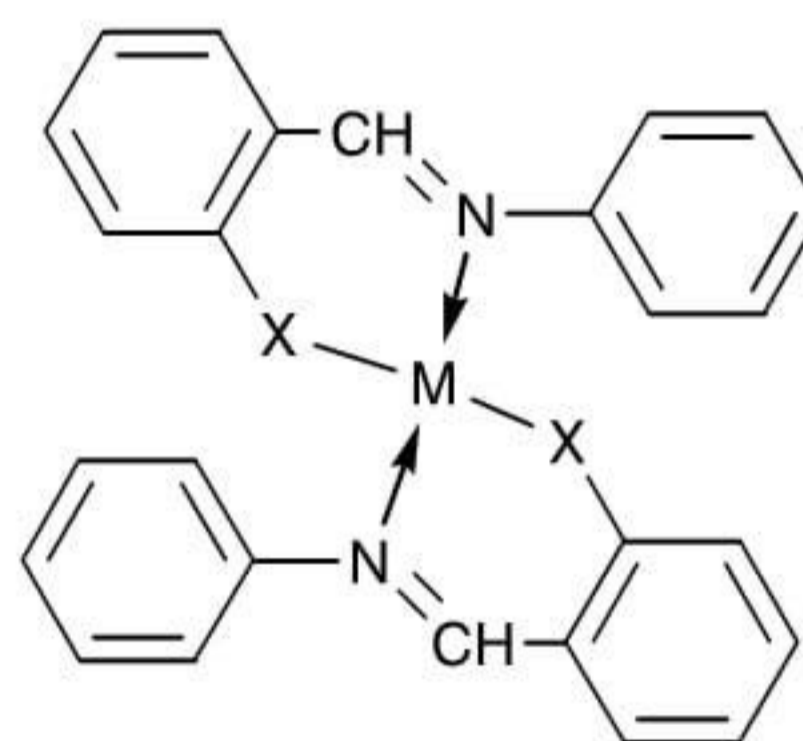
### 5.4.1 Bidentate ligand systems

In a bidentate ligand system, three molecules of a dye containing either a terminal salicylic acid unit (as in 5.2) or an *o*-nitrosonaphthol residue are able to chelate simultaneously with a trivalent metal ion of CN6, such as chromium(III) or iron(III), to form a 1:3 metal–dye complex (as in 5.8). Historically, the most important bidentate ligand system was alizarin (5.1). It has been suggested that both hydroxy groups and the keto group in the *peri* position are all involved with the metal atom in the chelation mechanism.

Most metal-complex dyes of commercial significance belong to the azo class. In practice, tridentate ligand systems incorporating the azo group and both *o,o'*-substituents are necessary to achieve adequate stability and fastness. Each nitrogen atom in an azo (–N=N–) or azomethine (–CH=N–) grouping carries a lone electron pair that can participate in coordination. There is no evidence, however, that the azo group in unsubstituted azobenzene, even the *cis* isomer, can yield a stable complex with any first-series transition metal. On the other hand, an *o*-aminoazo or *o*-hydroxyazo grouping can act as a bidentate ligand system with the azo group participating in coordination. Such 1:2 complexes containing divalent cobalt, nickel or copper were synthesised from *o*-substituted azobenzenes (5.9; M = Co, Ni or Cu, X = O or NH) and the analogous azomethine derivatives (5.10), demonstrating that the  $\beta$ -nitrogen of the azo linkage normally acts as the donor atom [9].



5.9

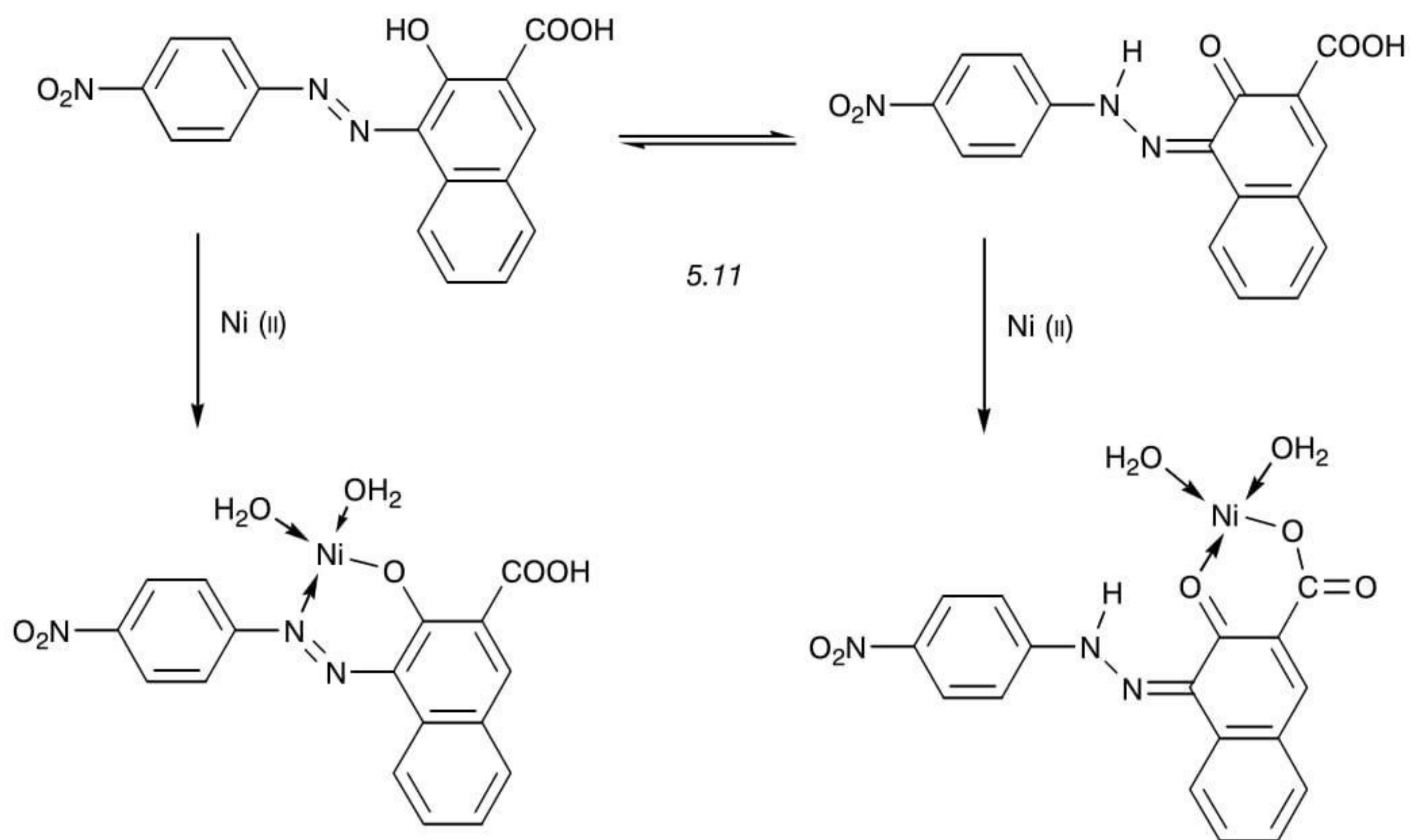


5.10

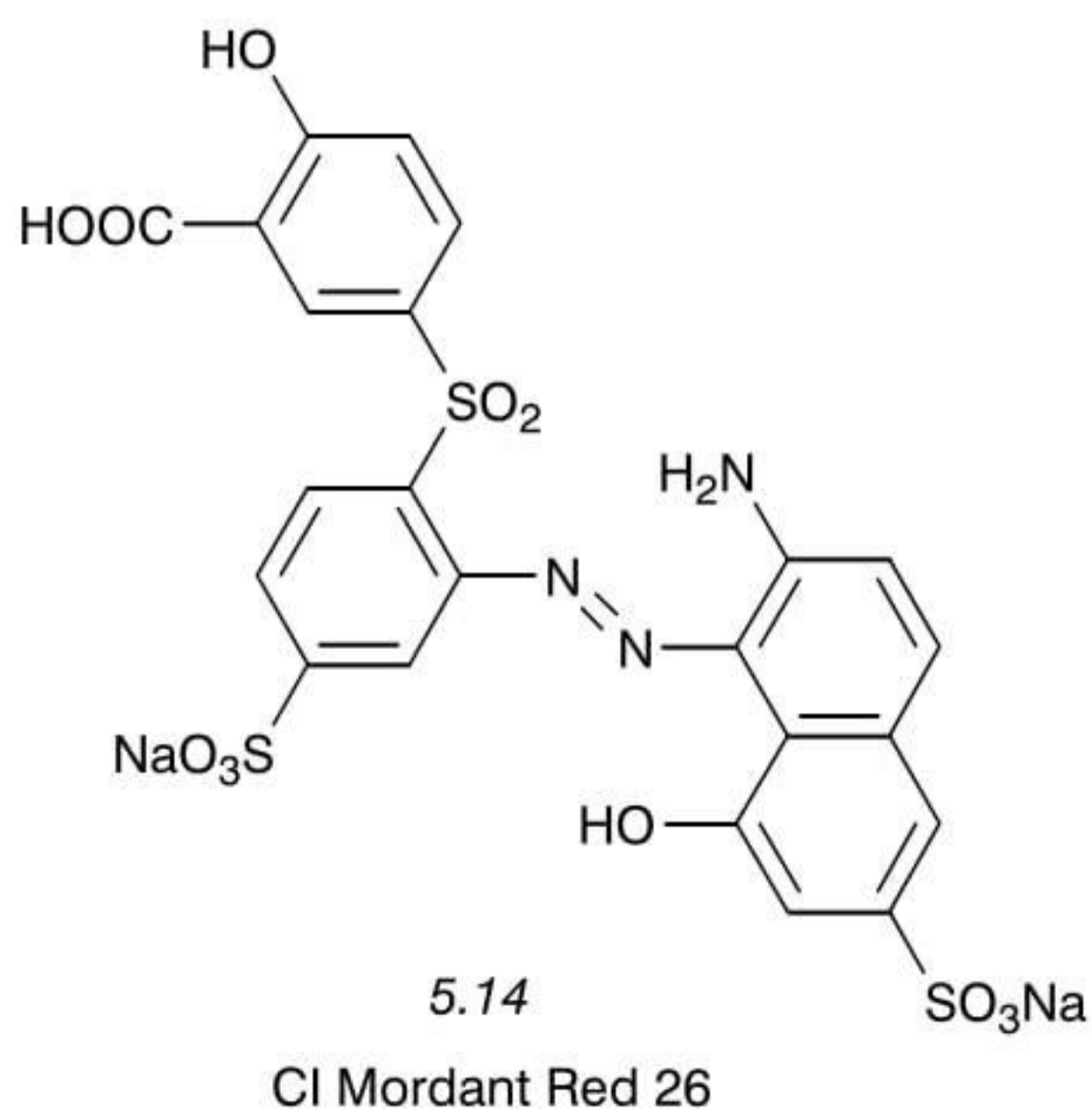
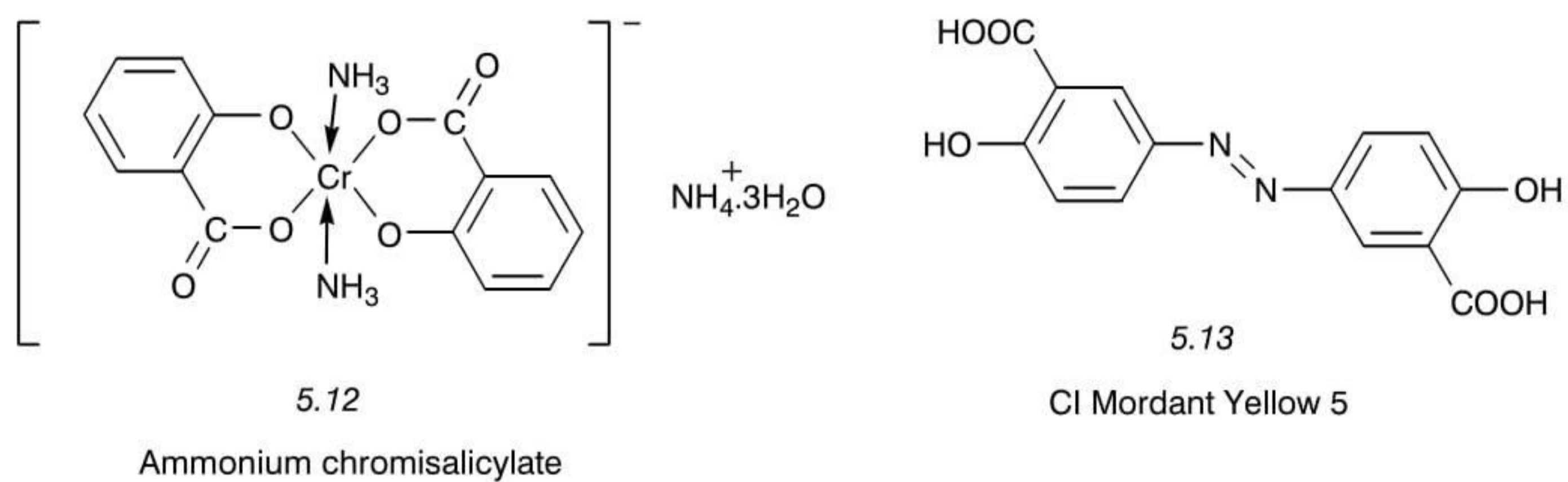
In general, metal complexes formed from bidentate azo chromogens are little used as dyes but do find important applications as pigments (section 2.3.2). Rare exceptions exist, however, such as the nickel(II) complex of *p*-nitroaniline→BON acid (5.11). This has been used for bordeaux prints of high light fastness on cotton fabrics. Two possible modes of bidentate attachment to the nickel atom can be envisaged (Scheme 5.2).

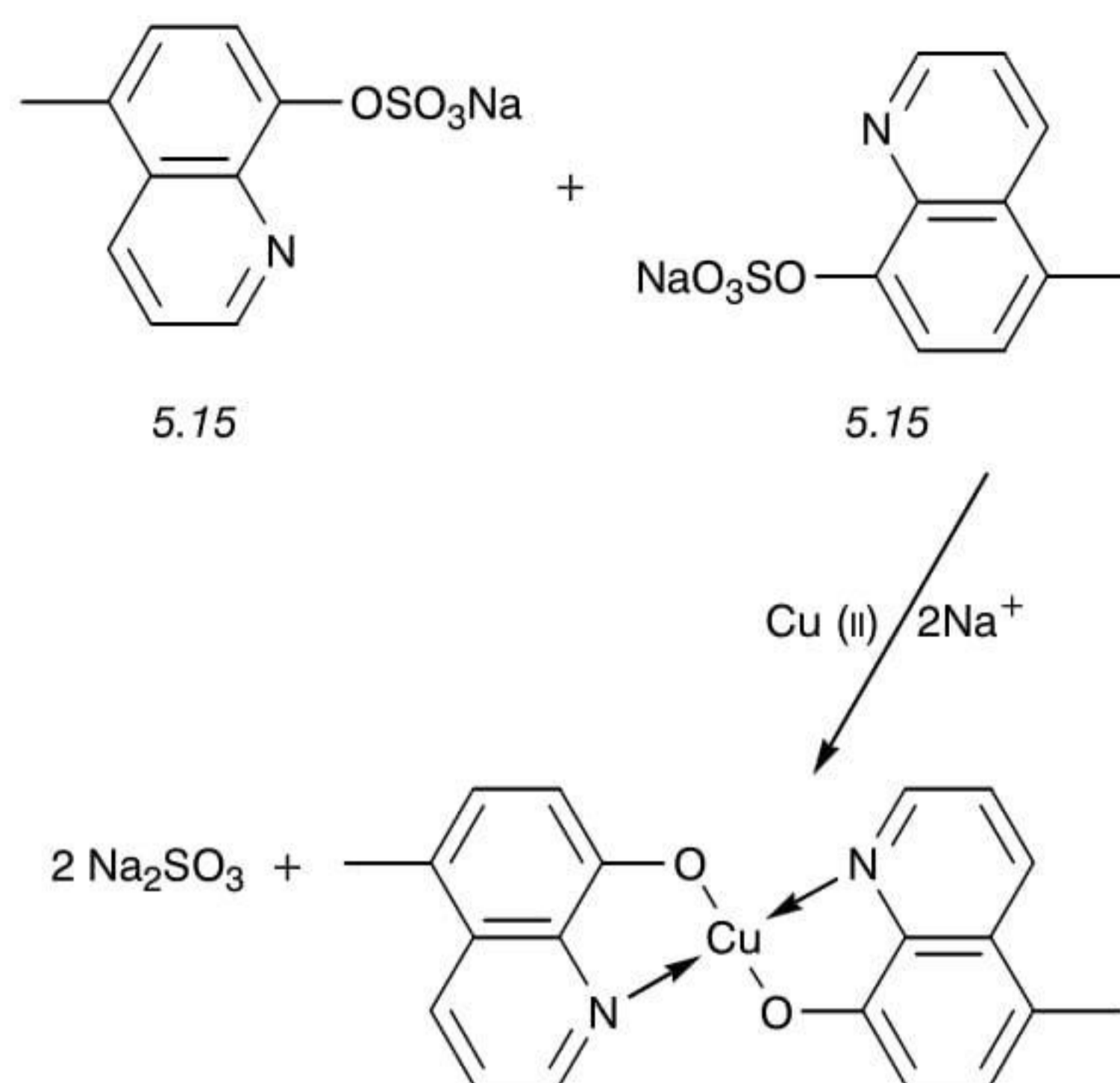
#### Metallisation of terminal coupling components

Salicylic acid has been found useful as a terminal coupling component in direct or mordant dyes to provide a bidentate site for metallisation. The free acid is also capable of complexing and ammonium chromisalicylate (5.12) is used as an intermediate in the synthesis of metal–dye complexes. CI Mordant Orange 1 (5.3) and Yellow 5 (5.13) are examples of dyes



Scheme 5.2





Scheme 5.3

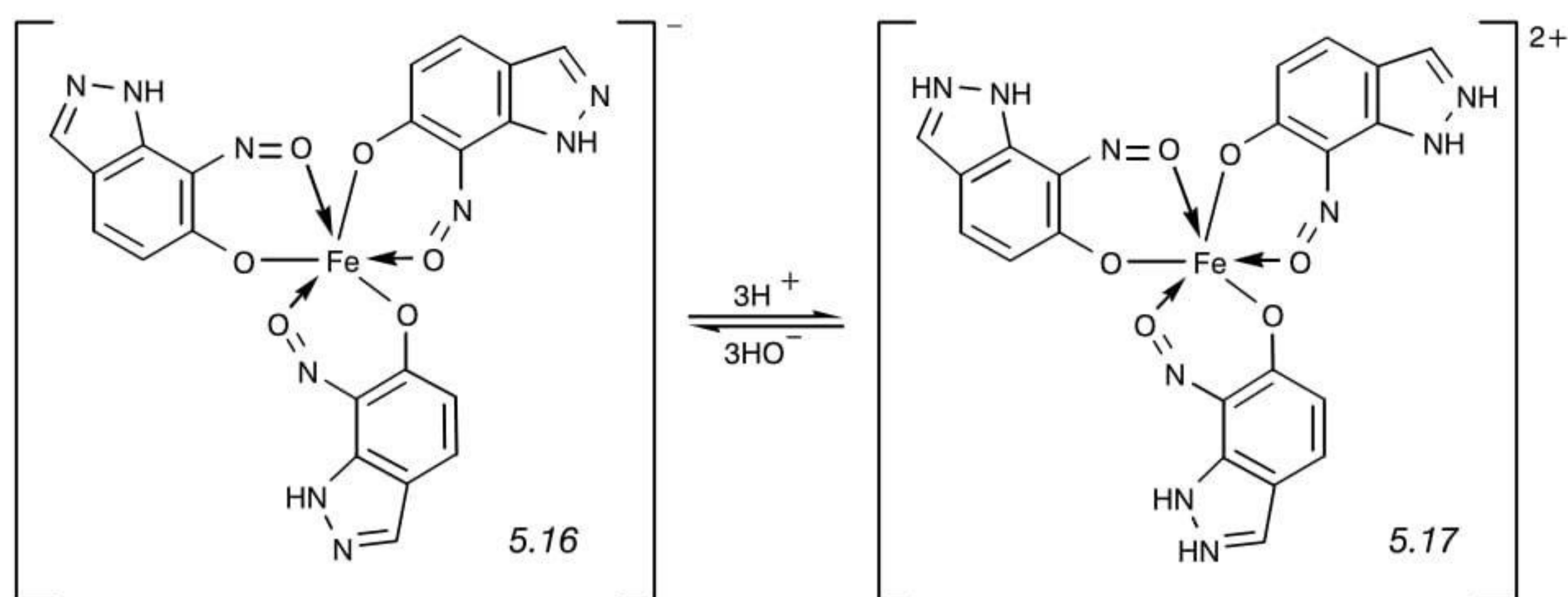
containing terminal salicylic acid residues. Since both ligands in these residues are electronically associated with the azo chromogen, changes in hue on metallisation can be dramatic. Difficulties in shade matching are particularly evident when afterchroming such dyeings. This effect may be minimised by introducing an insulating group, such as methylene, sulphonyl or sulphonamido, between the salicylic acid residue and the chromogen. CI Mordant Red 26 (5.14) is a typical example.

Another terminal bidentate ligand that has been exploited occasionally in bright disazo direct dyes is the sulphated 8-hydroxyquinoline residue (5.15). On aftercoppering, fastness to light and wet tests is enhanced by hydrolysis catalysed by the copper(II) ion and formation of a bidentate 1:2 complex (Scheme 5.3). Apparently, electron withdrawal by sulphur facilitates removal of the sulphite grouping and approach of the copper(II) cation [10].

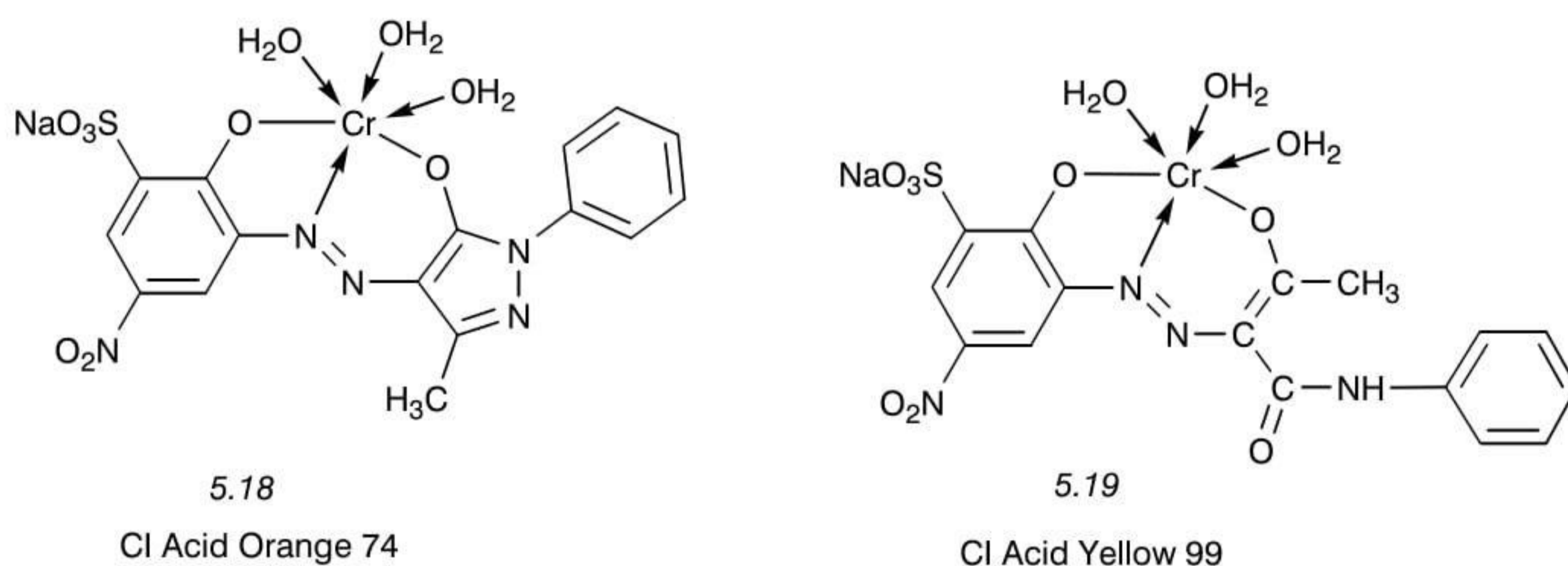
The *o*-nitrosonaphthol ligand system also belongs to the terminal bidentate category (as in structure 5.8). If the sulpho group in each ligand is replaced by a nonionised polar solubilising group, such as methylsulphonyl (as in 5.4) or sulphonamido (as in 5.6), the overall negative charge on the 1:3 metal–dye complex is reduced from -4 to -1, so that dyeing can take place from neutral or weakly acidic dyebaths. Similarly, green to olive hues can be obtained on wool or nylon using 1:3 iron(II) complexes of 6-hydroxy-7-nitroso-indazoles. The amphoteric nature of the three heterocyclic rings in such complexes accounts for their solubility. Protonation of the N atom in each indazole ring (Scheme 5.4) depends on the pH, so that the charge on the complex can vary from -1 for the unprotonated form (5.16) to +2 for the fully protonated form (5.17). The use of iron(III) salts in their synthesis initiates partial oxidation of the hydroxynitroso-indazole with consequent reduction to iron(II), which then interacts to form the 1:3 metal–dye complex [11].

#### 5.4.2 Tridentate ligand systems

Many of the premetallised 1:1 chromium–dye complexes introduced from 1915 onwards for the one-bath dyeing of wool at low pH were *o,o'*-dihydroxyazo compounds containing chelated chromium(III) ions. Typical examples still in use today include CI Acid Orange 74 (5.18) and other azopyrazolones ranging in hue from yellow to bluish red, as well as

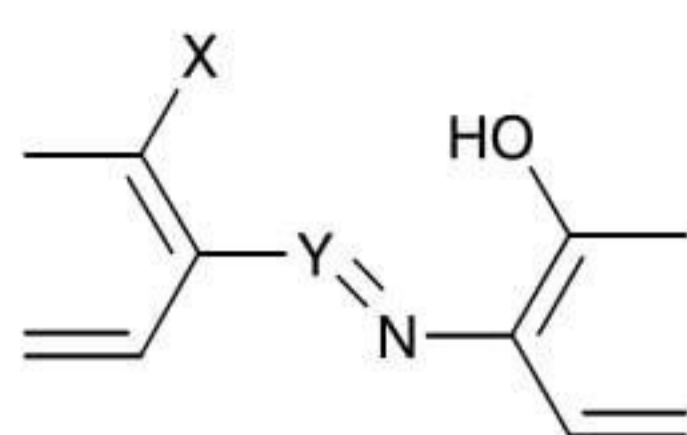


Scheme 5.4

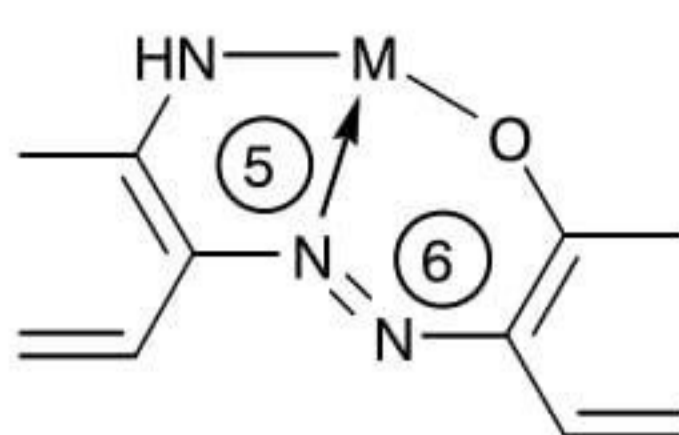


azoacetoacetanilides such as CI Acid Yellow 99 (5.19). For some time after their introduction these dyes were formulated as bidentate systems, utilising only one of the hydroxy groups in conjunction with the azo group. This misconception may have arisen by analogy with true bidentate ligands such as salicylate complexes [7] and the *o*-substituted azo and azomethine analogues [9]. Only in 1939 were these 1:1 chromium complexes of *o,o'*-dihydroxyazo dyes unequivocally confirmed to be tridentate structures, in which both hydroxy groups and the azo linkage are coordinated with the metal atom. The remaining three sites are taken up by unidentate ligands such as water molecules [12].

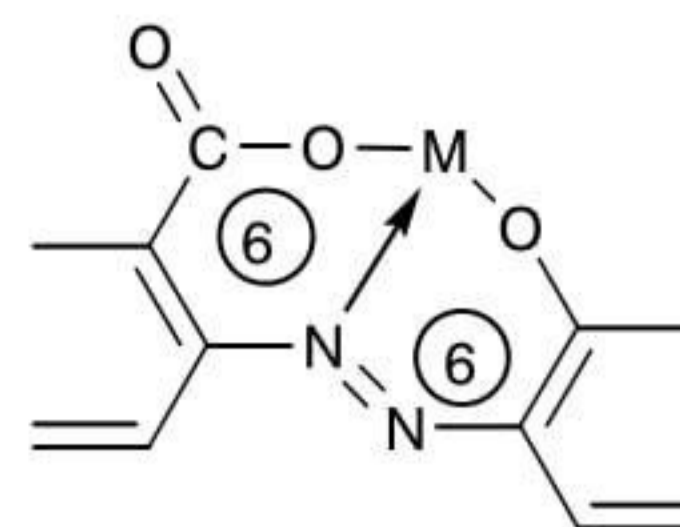
The tridentate azo systems have proved to be the most important of all possible multidentate chromogenic ligand systems available for metal-complex formation. Those capable of coordination with metals of CN6 (trivalent chromium or cobalt) or CN4 (divalent copper) are mainly limited to *o*-hydroxy-*o'*-substituted diaryl azo or azomethine derivatives (5.20; X = OH, NH<sub>2</sub>, or COOH, Y = N or CH). The more important dyes for wool or nylon are chromium complexes in which X is usually a hydroxy group but may be an amino, carboxyl or other ligand group from which a proton is lost during complex formation. Coordination of these systems leads to a bicyclic ring system with the N→M bond shared. If the *o*-substituent X is hydroxy or amino that ring is five-membered (5.21), but if it is carboxyl both annelated rings are six-membered (5.22). This difference has an important bearing on the physical properties of these complexes (section 5.6.1). Annelated-ring formation enhances the stability of the resultant metal-dye complex to an extent that is fully adequate for conventional dyeing conditions. Single-ring bidentate systems, on the other hand, seldom exhibit this degree of stability.



5.20



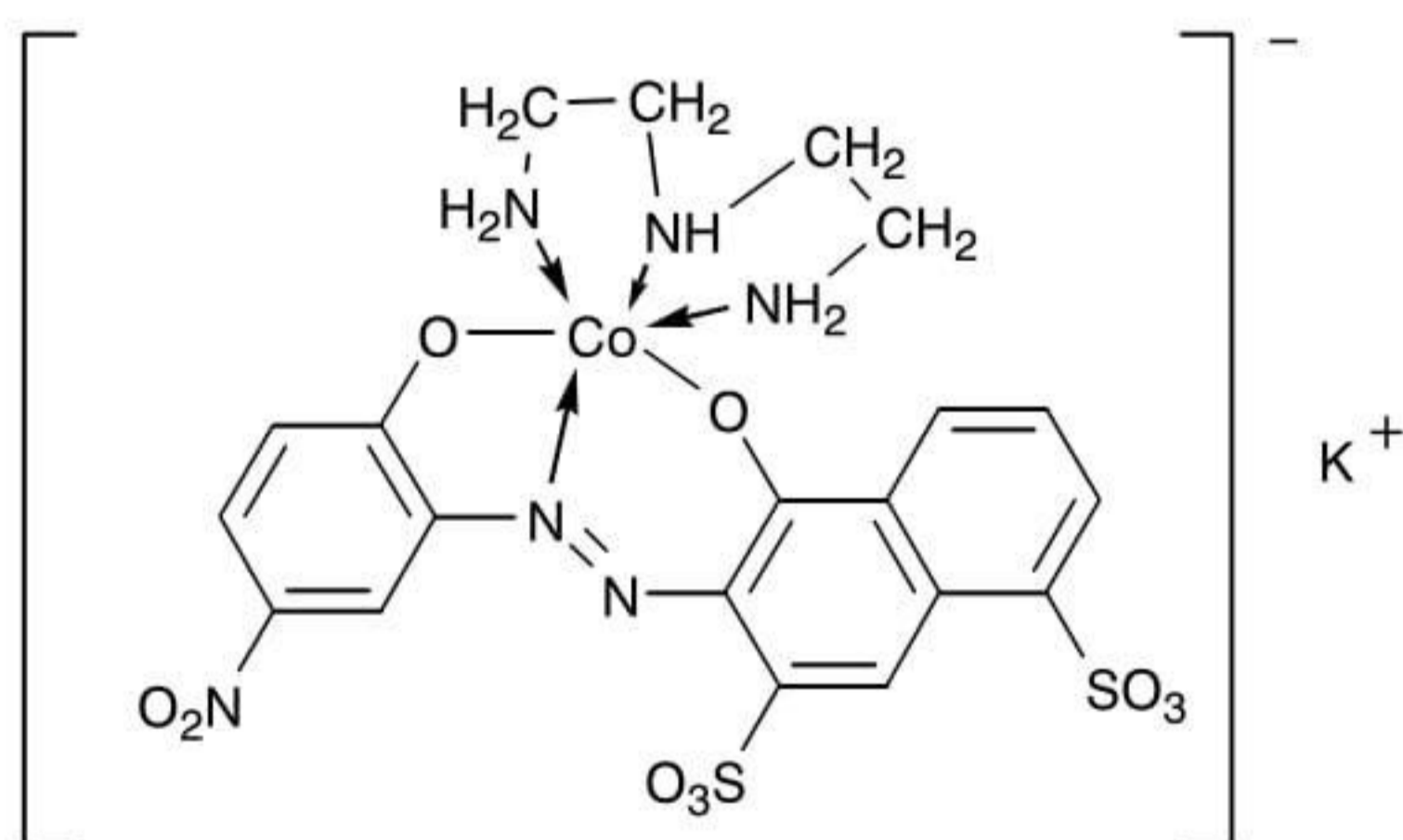
5.21



5.22

### 1:1 Metal-dye complexes

As already described, these are tridentate structures in which the three remaining sites on the chromium(III) ion are occupied by colourless monodentate ligands (as in 5.18). These are quite stable at low pH values, whereas similar cobalt complexes are generally unstable. However, 1:1 cobalt-dye complexes have been obtained by heating a tridentate dye with a cobalt(II) salt in the presence of excess ammonia, the monodentate ligand groups being three ammonia molecules. The reaction involved oxidation of the cobalt(II) ion to cobalt(III) prior to complex formation [13]. Even so, the resulting complexes were insufficiently stable for use as dyes. Stable 1:1 cobalt-dye complexes suitable for dyeing can be prepared, however, by replacing the colourless monodentate ligands by a tridentate molecule such as diethylenetriamine (as in 5.23). By varying the number of sulpho groups in the chromogenic ligand from zero to three, the net charge on the complex varies from +1 to -2.



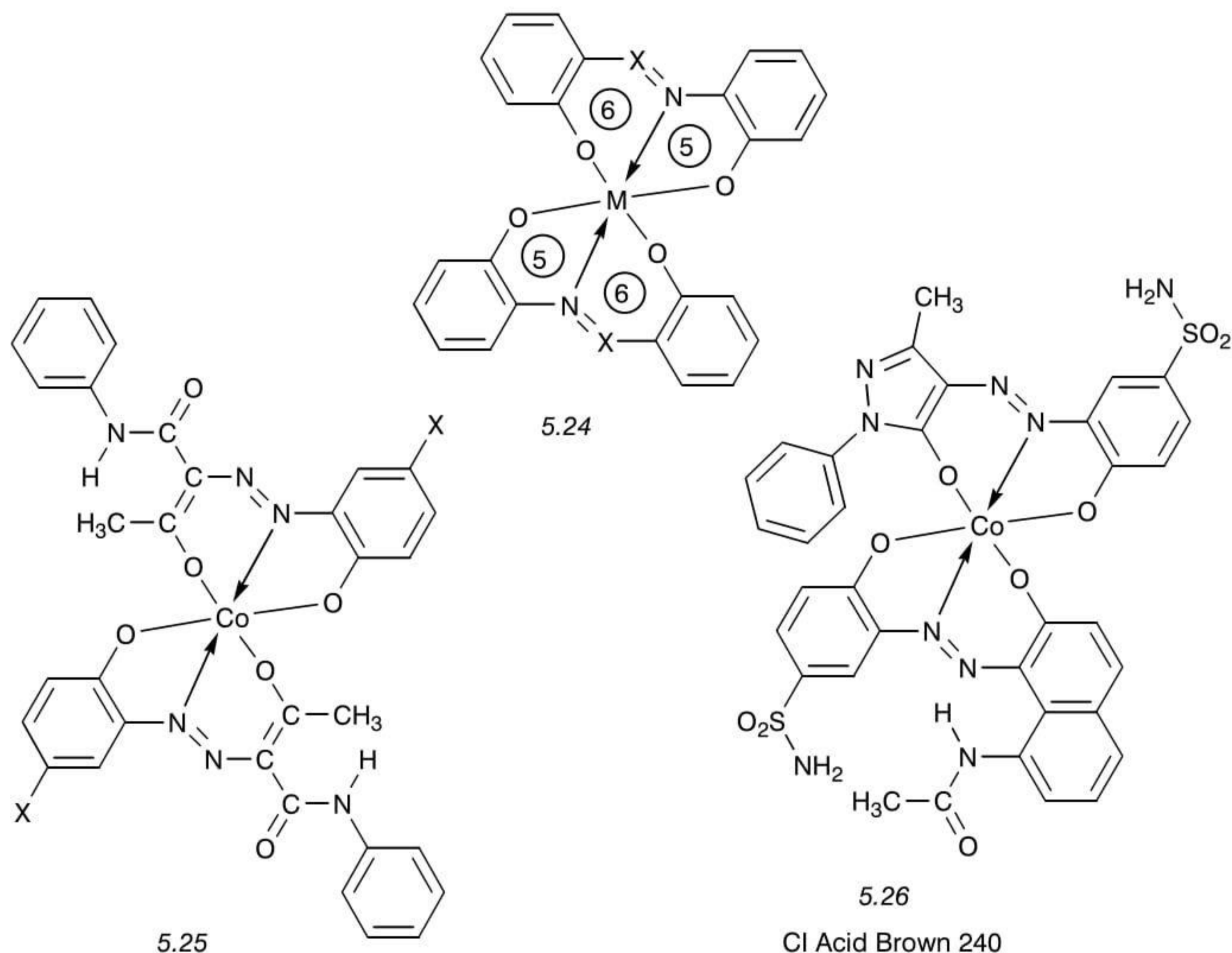
5.23

The presence of sulphonic acid groups in 1:1 chromium or cobalt complexes enhances solubility in water and permits electrostatic bonding to protonated amino groups in wool (section 3.2.2). Strongly acidic conditions are necessary to achieve high substantivity and some degradation of the wool is unavoidable. The relatively low  $M_r$  (400–500) of these 1:1 premetallised dyes ensures good level dyeing properties under these conditions. The presence of ionised sulpho groups in these complexes can give rise to anomalous conclusions when trying to elucidate structure from elemental analysis data, since simple metal salts may also be formed between transition-metal cations and these anionic sulpho groups.

### 1:2 Metal-dye complexes

The unfilled sites in 1:1 metal-dye complexes of chromium(III) or cobalt(III) ions can be

occupied by colourless ligands (three mono-, mono-/bi- or one tridentate). Such a triad of sites can generally be replaced by a second tridentate chromogen, as shown by Drew and Fairbairn [12]. This results in a more stable configuration consisting of two bicyclic ring systems as in the general formula 5.24 ( $M = \text{Co}$  or  $\text{Cr}$ ,  $X = \text{N}$  or  $\text{CH}$ ). Colour, solubility, dyeing and fastness properties can be controlled by selection from a wide range of sulphonated or unsulphonated azo or azomethine tridentate ligand systems.

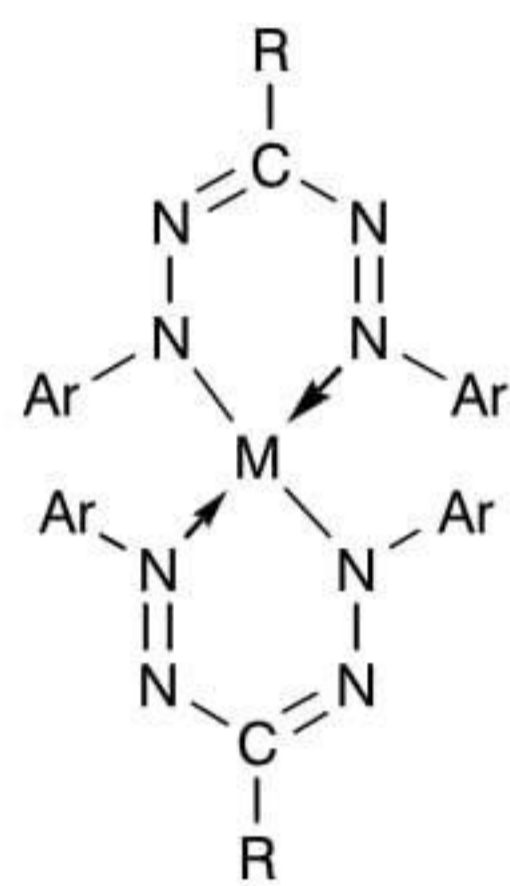


Symmetrical 1:2 cobalt complexes of phenylazoacetanilides, such as CI Acid Yellow 119 (5.25;  $X = \text{NO}_2$ ) or Yellow 151 (5.25;  $X = \text{SO}_2\text{NH}_2$ ), are important in the yellow to orange sector. Many orange and red dyes of this class are symmetrical 1:2 chromium complexes of phenylazopyrazolones, like CI Acid Orange 60 (5.6;  $R = \text{H}$ ). Browns are often unsymmetrical chromium or cobalt types with azopyrazolone and azonaphthol ligands, CI Acid Brown 240 (5.26) being a good example. Dyes in the violet, blue, green and black sectors may be symmetrical or unsymmetrical but often contain two arylazonaphthol ligands, as in C.I. Acid Black 58 (5.4).

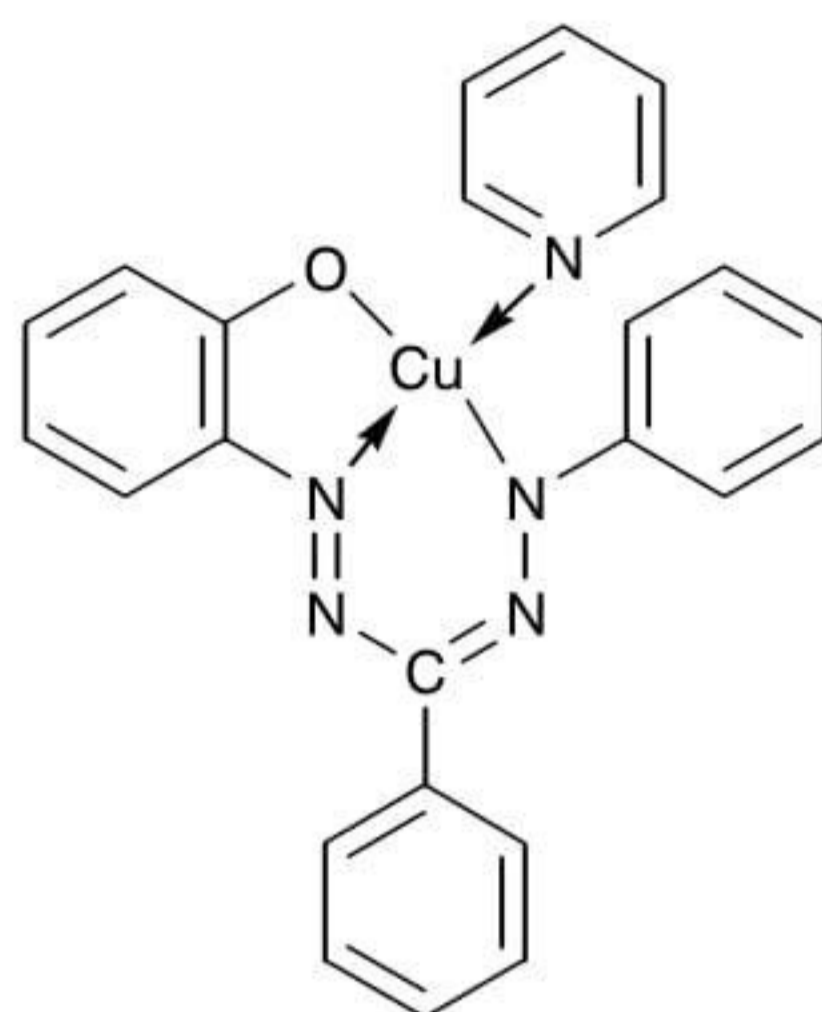
The reaction of two moles of a tridentate chromogen (A) with one equivalent of the metal M leads exclusively to the symmetrical AMA structure. Reaction with two different chromogenic ligands A and B simultaneously yields a mixture of structures: AMA, AMB and BMB. Such mixtures are commercially important, as they are less expensive to produce than the specific unsymmetrical product AMB, which can be obtained in a pure form only by the reaction of a pure 1:1 complex (AM) with the other ligand (B). Monosulphonated unsymmetrical chromium complexes with two negative charges per molecule are particularly important because they have good neutral-dyeing affinity for wool or nylon.



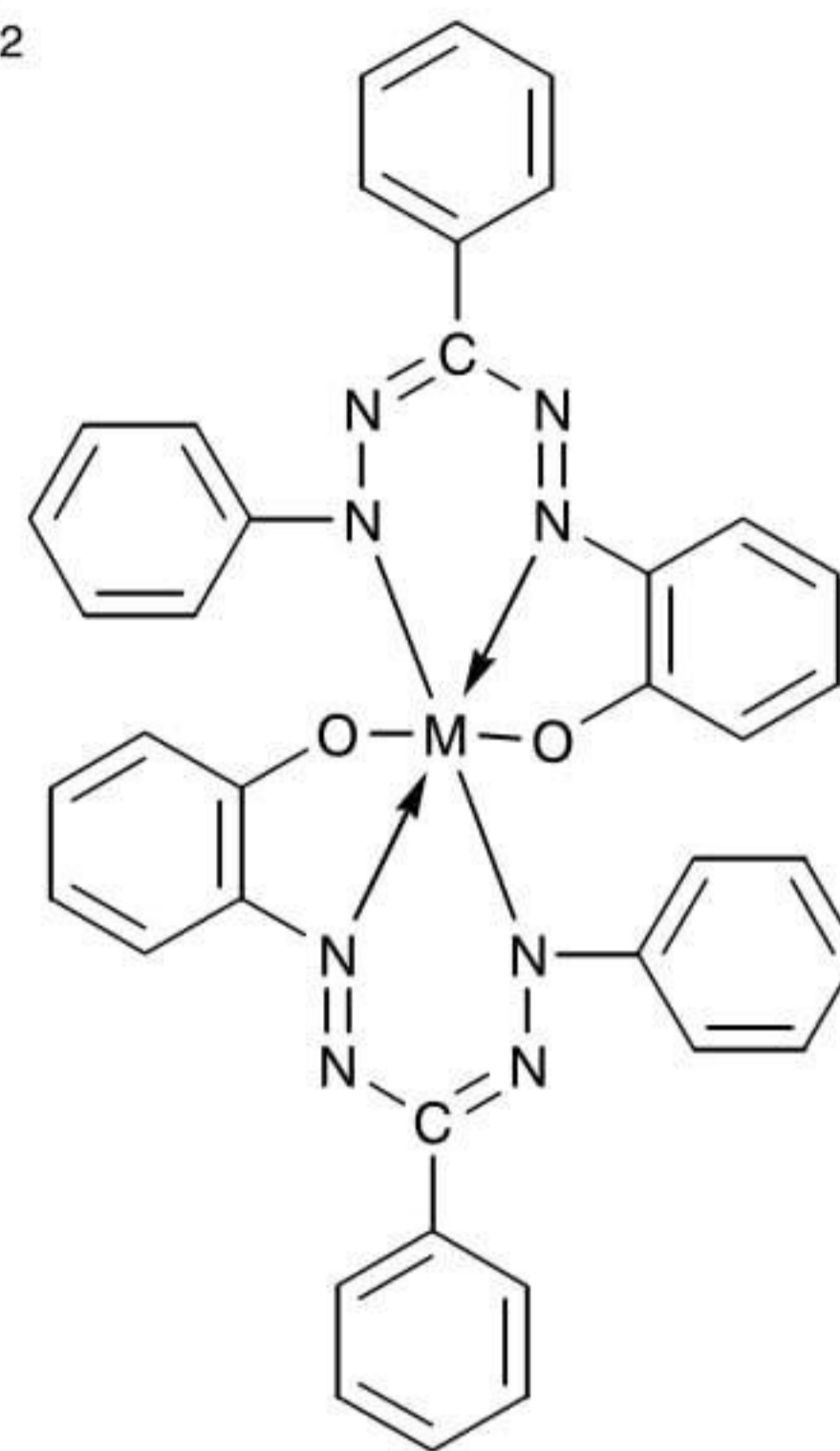
Scheme 5.5



5.27



5.28



5.29

### Tridentate formazans

Formazans may be synthesised by the selective coupling under alkaline conditions of two identical or different diazonium cations with an activated methylene group in a suitable coupling component such as acetone or nitromethane, as shown in Scheme 5.5. By coordination with both of the two azo groupings, divalent metals such as copper, nickel or cobalt will give monocyclic 1:2 metal complexes (5.27) of relatively low stability [14]. Formazans containing an *o*-hydroxy or *o*-carboxy substituent in one of the phenylazo groupings can be used to give intensely coloured neutral bicyclic 1:1 metal-dye complexes [15]. Thus the red tridentate ligand shown becomes violet on metallisation with copper(II) ions. On completing the CN<sub>4</sub> by coordination with an aryl monodentate ligand such as pyridine (5.28), a further bathochromic shift to reddish blue is observed. With trivalent metals of CN<sub>6</sub>, tridentate formazans give 1:2 complexes with two bicyclic ring systems (5.29).

### 5.4.3 Quadridentate ligand systems

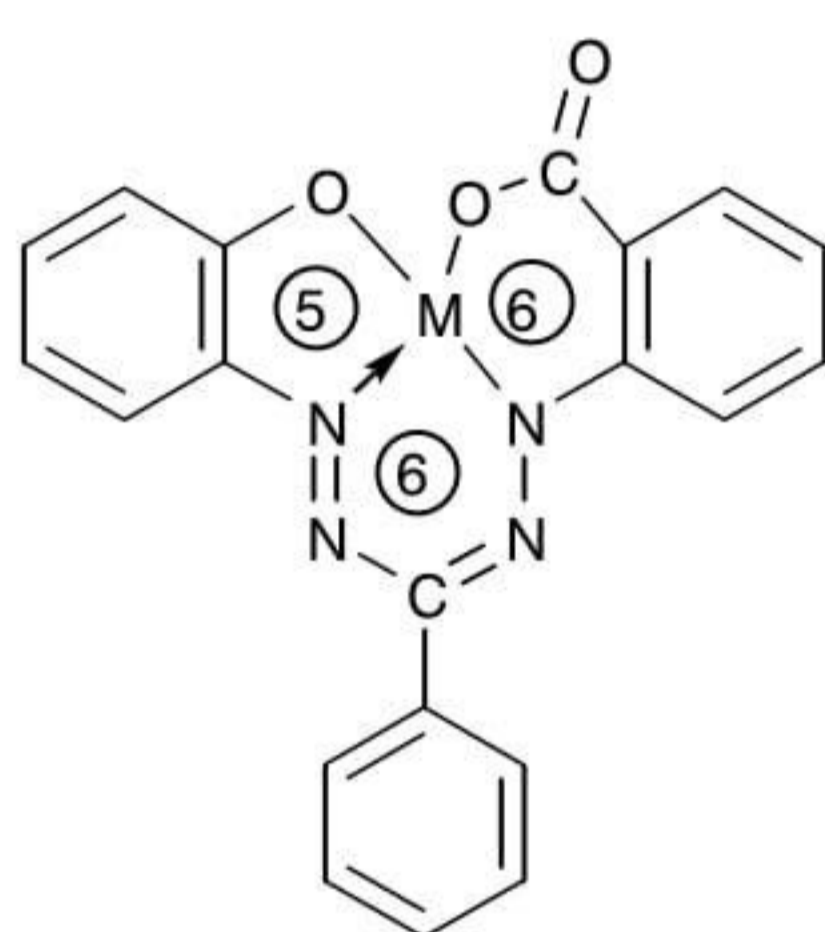
#### Quadridentate formazans

If both of the phenylazo groupings in the formazan chromogen contain an *o*-hydroxy or *o*-carboxy substituent, coordination with a divalent metal atom such as copper yields a highly stable annelated tricyclic ring system (5.30). Only a 1:1 metal:dye ratio is possible in this case. For trivalent metals of CN<sub>6</sub> the coordination sphere is completed using a colourless ligand molecule such as pyridine, ammonia or water. Solubility and dyeing properties may be varied by the introduction of a sulpho group or an uncharged solubilising group such as sulphonamido. In a recent evaluation of a series of quadridentate formazan complexes with

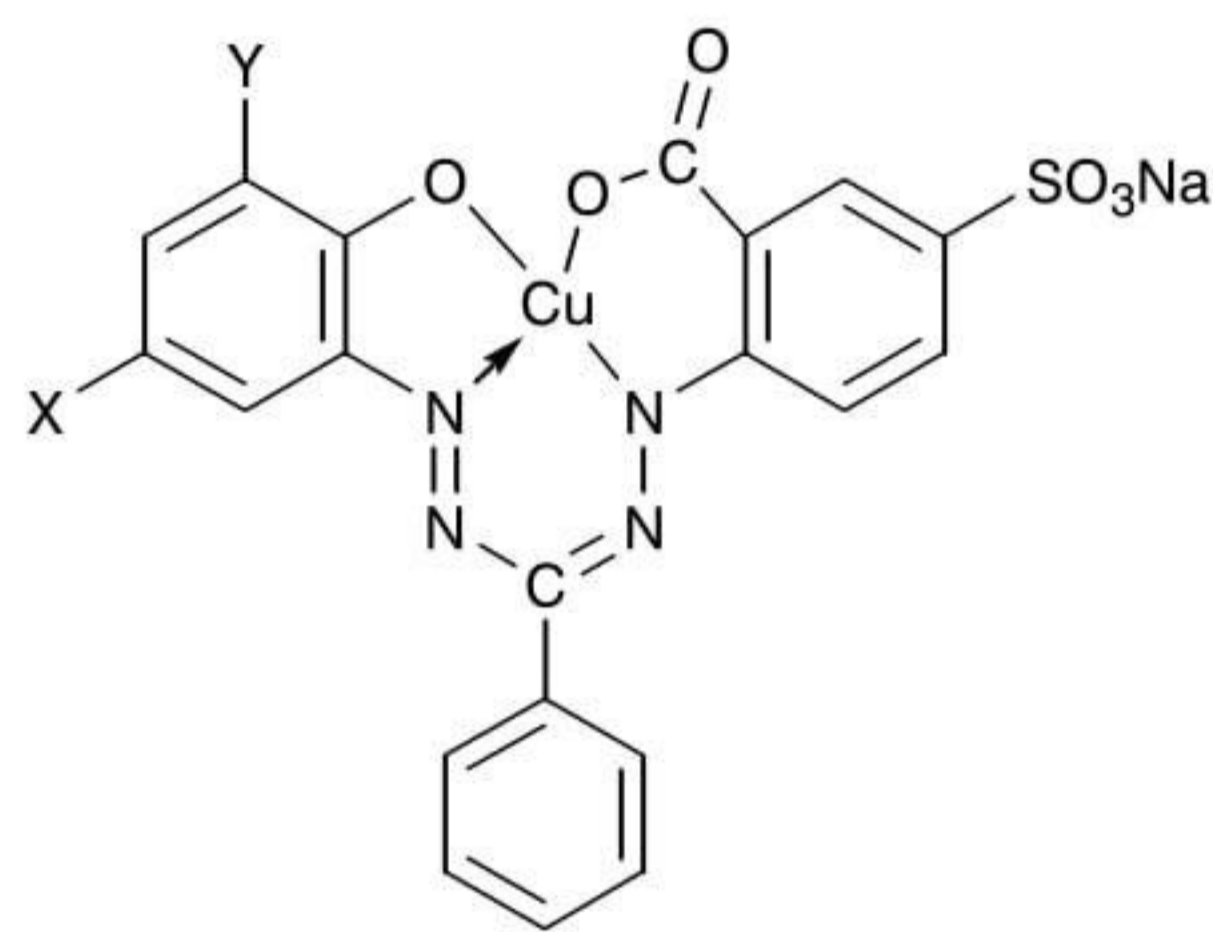


copper(II) of the 5.30 type, the colours of the products obtained from a given formazan were found to vary according to the method of synthesis [16].

Similar blue formazan–copper complexes that are sufficiently solubilised by the introduction of sulphonic acid substituents in the phenyl rings have become established as important members of most ranges of reactive dyes. In general, they are redder than the turquoise blue copper phthalocyanines, less costly than the anthraquinone blues and exhibit higher fastness to light than the twice-coupled H acid blues. Many of them have the general structure represented by 5.31. Those that react with cellulose by nucleophilic addition mostly have the substituents  $X = \text{vinylsulphone}$  or precursor,  $Y = \text{sulpho}$ , whereas those reacting by a nucleophilic substitution mechanism have  $X = \text{sulpho}$ ,  $Y = \text{NH-Z}$ , where Z is the haloheterocyclic reactive system.



5.30



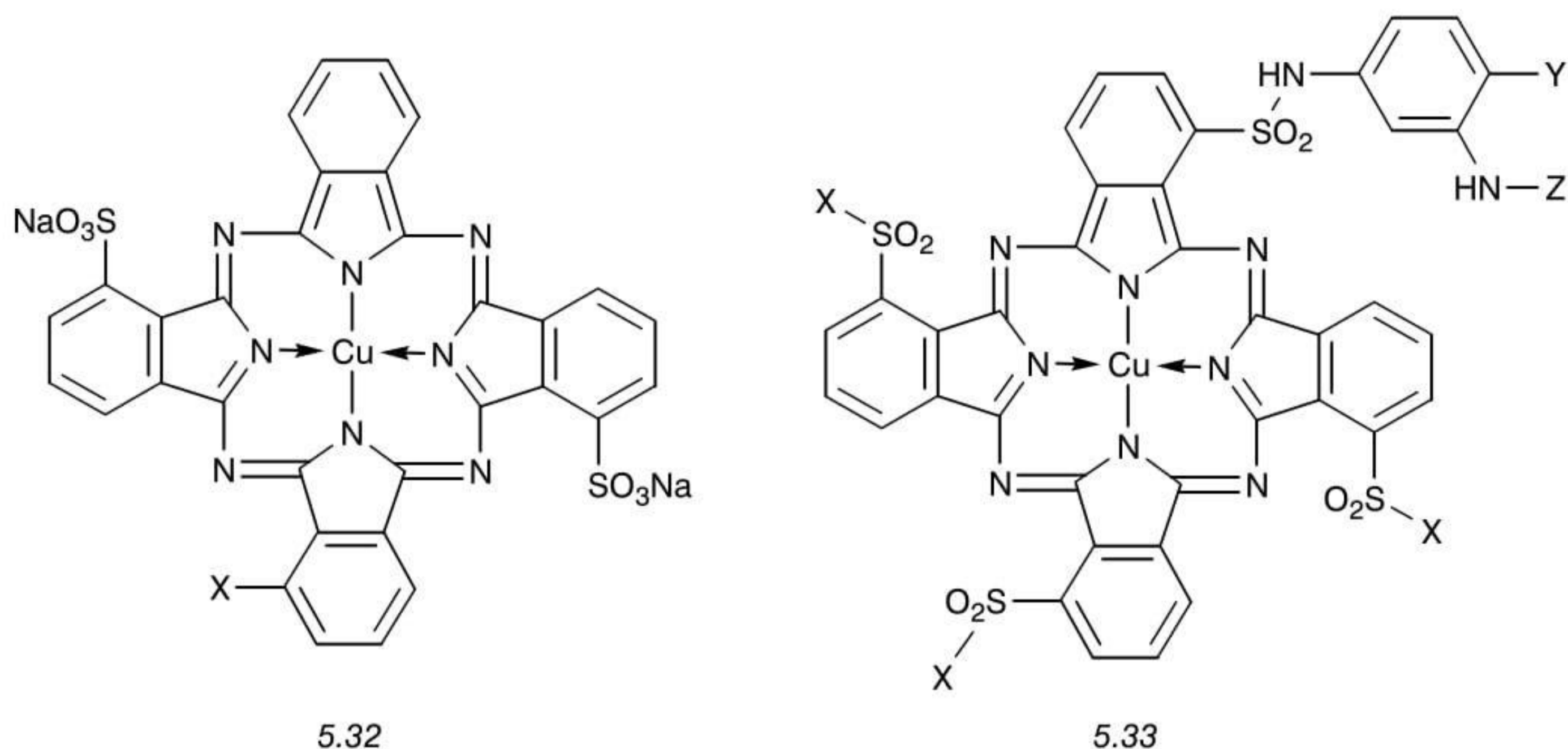
5.31

#### Phthalocyanine metal-complex colorants

Copper phthalocyanine is another important representative of a quadridentate ligand system. It is predominant as a turquoise blue pigment of outstanding light fastness and its halogenated derivatives are important green pigments (section 2.4). The copper phthalocyanine chromogen is a tetracyclic annelated ring system of exceptionally high kinetic and thermal stability. It can be sublimed without decomposition *in vacuo* at temperatures as high as 550 °C, although the solid form may undergo polymorphic change at 250 °C under atmospheric conditions. Many other transition metals and rare-earth elements are able to form 1:1 complexes with phthalocyanine but the brilliant colour and outstanding stability of the copper complex ensure its predominance. A series of 3- and 4-hydroxylated phthalocyanine complexes of tri- or tetravalent metals (Al, Cr, Ge, In and Sn) has been prepared recently. The stabilities of these complexes to thermal oxidation in air have been compared and the effects of the position of the hydroxy group on the electronic spectra in various solvents were studied [17].

Copper phthalocyanine derivatives are well established as turquoise blue direct and reactive dyes for cellulosic fibres. Chlorosulphonation at the 3-position, followed by hydrolysis, yields sulphonated direct dyes such as CI Direct Blue 86 (5.32;  $X = \text{H}$ ) and Blue 87 (5.32;  $X = \text{SO}_3\text{Na}$ ). Solubility and dyeing properties can be varied by introducing four chlorosulphonyl groups, some of which are hydrolysed and some converted to sulphonamide by reaction with ammonia or alkylamines. This approach is also the main route to reactive dyes of the copper phthalocyanine type. The reactive system Z is linked to a 3-sulphonyl site

by means of an aryldiamine, as in structure 5.33 where  $Y = \text{H}$  or  $\text{SO}_3\text{Na}$ , and the dyeing characteristics varied by the nature of  $X$ , which may be  $\text{NH}_2$  or  $\text{ONa}$ . Nickel phthalocyanine is the basis of some brilliant green reactive dyes, into which a similar range of 4-sulphonyl substituents can be introduced.



In an interesting study, phthalocyanine complexes containing four anthraquinone nuclei (5.34) were synthesised and evaluated as potential vat dyes and pigments [18]. Anthraquinone-1,2-dicarbonitrile or the corresponding dicarboxylic anhydride was reacted with a transition-metal salt, namely vanadium, chromium, iron, cobalt, nickel, copper, tin, platinum or lead (Scheme 5.6). Substituted analogues were also prepared from amino, chloro or nitro derivatives of anthraquinone-1,2-dicarboxylic anhydride.

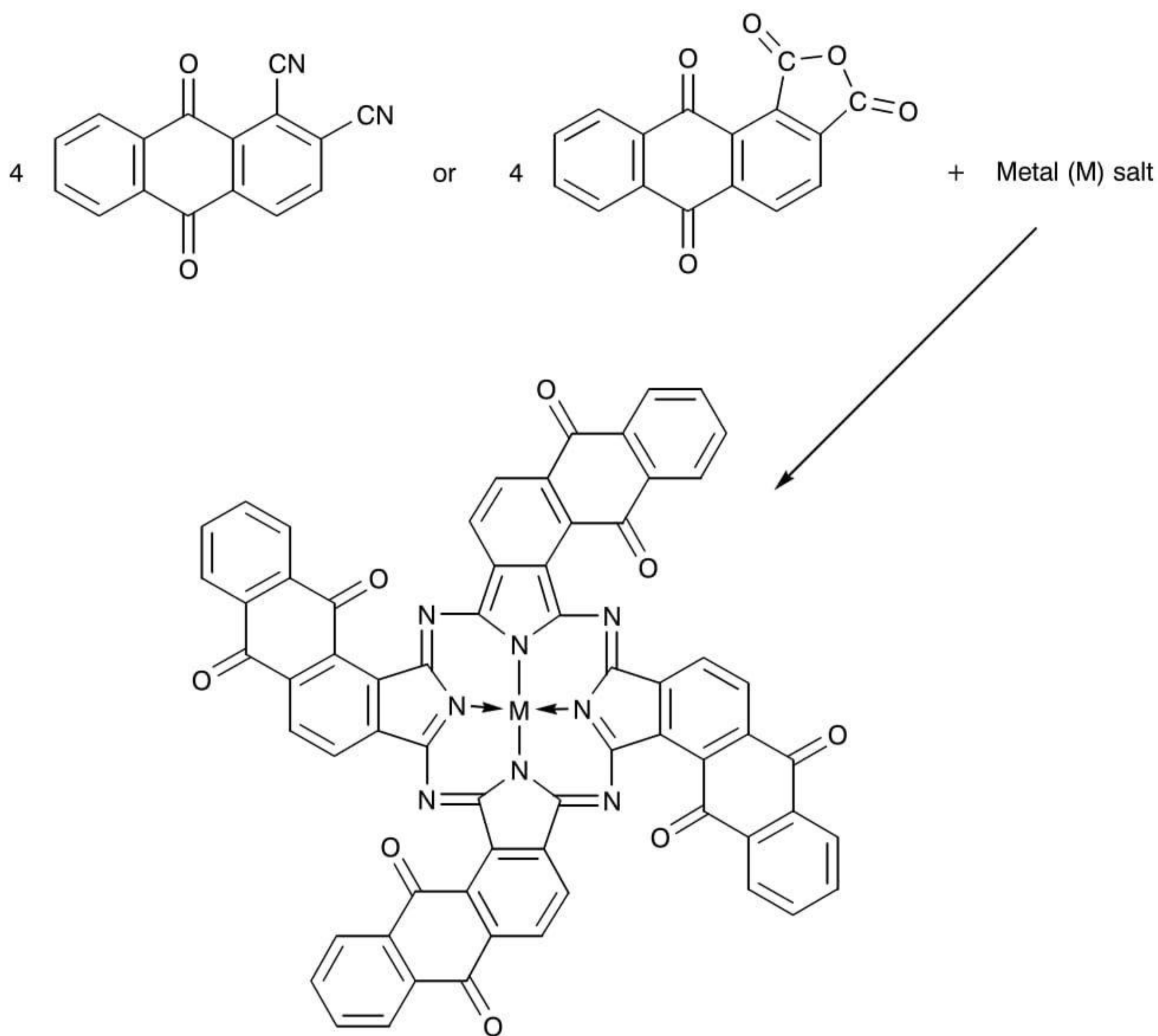
## 5.5 PREPARATION OF METAL-COMPLEX COLORANTS

There are numerous ways in which a metal atom can be incorporated into a dye molecule to form a metal complex. Most attention has been given to complexes of chromium, cobalt and copper. There are essential differences in the conditions of preparation of these compounds.

### 5.5.1 Chromium complexes

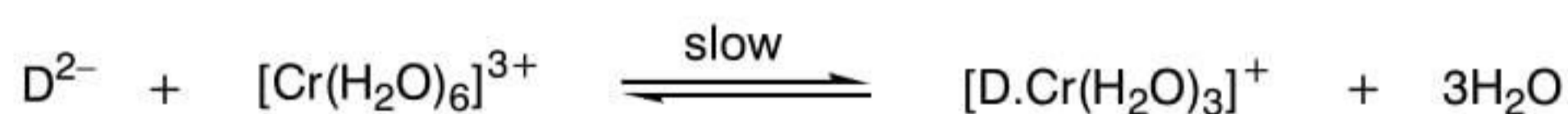
Table 5.1 in section 5.3.1 reveals that the trivalent hexa-aquo chromium complex cation possesses three low-energy  $t_{2g}$  orbitals, each singly occupied. Consequently, the ligand field stabilisation energy is considerable. Since this energy has to be overcome, replacement of the coordinated water molecules by other ligand groups is a slow process. The most successful practical methods are designed to take this into account.

The replacement reactions may be represented generally by a two-stage process. Introduction of the first tridentate monoazo dye ligand  $D^{2-}$  is the rate-determining step (Scheme 5.7). Where a typical *o,o'*-dihydroxyazo dye ligand is used in excess with a hydrated chromium(III) salt under alkaline conditions ( $\text{pH} > 9$ ) favouring 1:2 metal-dye complex formation, none of the 1:1 complex remains. This indicates that the presence of one

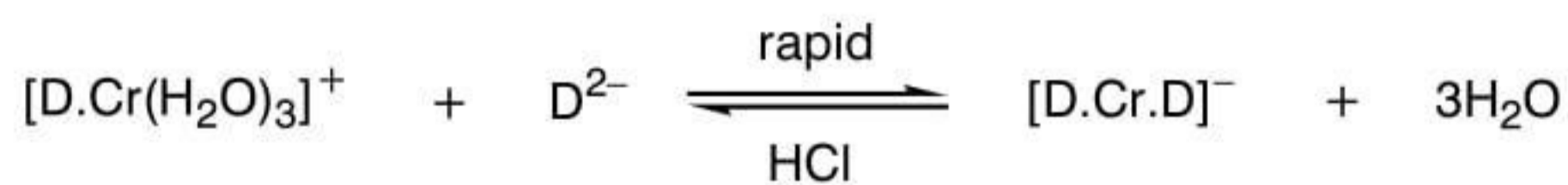


Scheme 5.6

5.34



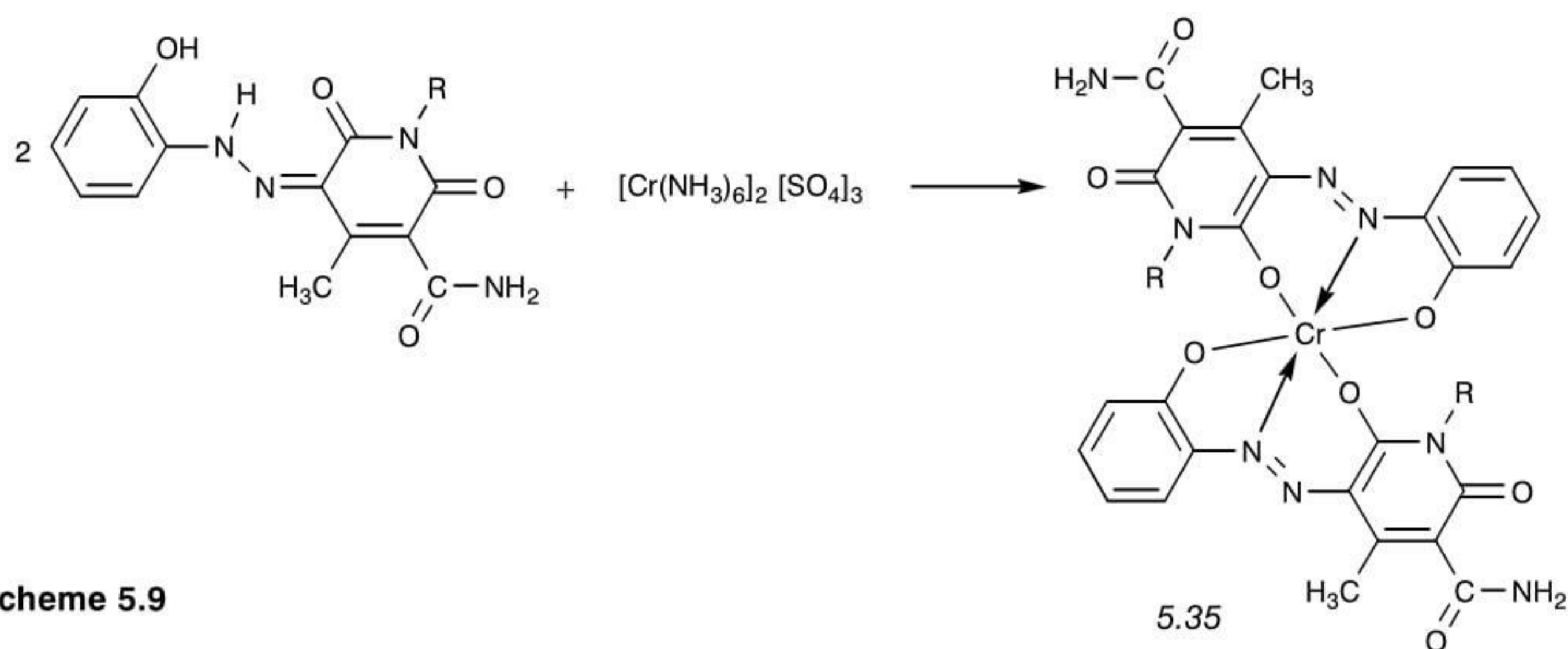
Scheme 5.7



Scheme 5.8

chelated dye ligand favours attachment of the other and the forward reaction in Scheme 5.8 is more rapid than that in Scheme 5.7. In order to obtain a 1:1 complex in high yield, therefore, it is necessary first to synthesise the 1:2 complex in alkaline medium and then to treat this product under strongly acidic conditions. The reverse reaction in Scheme 5.8 then yields the desired 1:1 complex. The chromium salt used can be the acetate, chloride or sulphate, the reactions being carried out in aqueous media at the boil.

Various chromium-complex dyes were prepared recently by reacting ammonium chromium sulphate with a series of chelatable *o,o'*-dihydroxyazopyridone structures (Scheme 5.9). Elemental analyses corresponded to a 1:2 metal-dye ligand ratio (5.35). The



Scheme 5.9

substituted azopyridone chromogens are more stable in the keto-hydrazone form. The dyeability and fastness properties of these unmetallised yellow mordant dyes and their derived chromium complexes were evaluated for the dyeing of wool and polyester/wool blends [19].

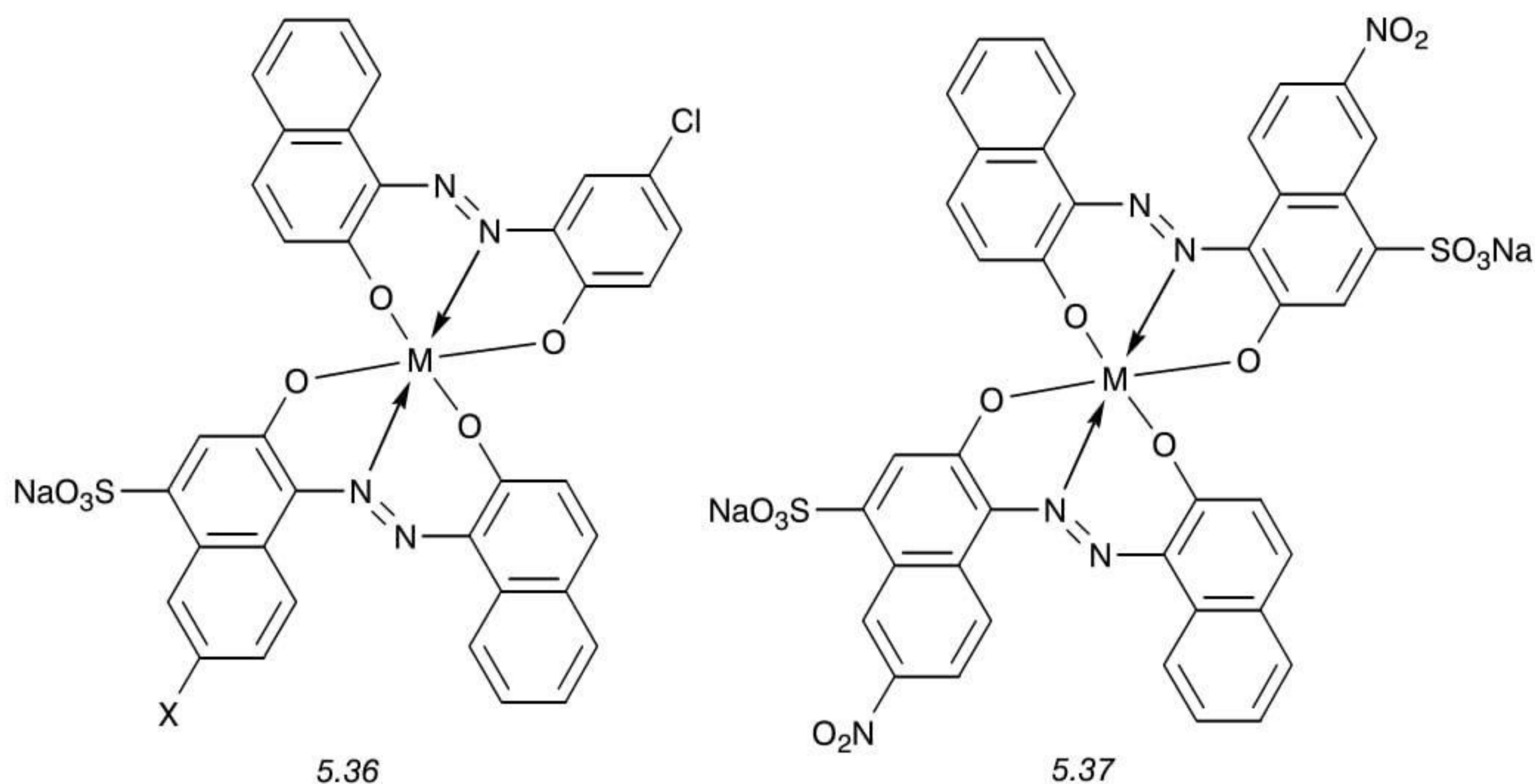
If the metallisable dye is insoluble in water, a miscible solvent such as ethanol or ethylene glycol may be added. Polar solvents such as formamide or molten urea have sometimes been preferred. It is likely that such solvents will preferentially displace water molecules and coordinate with the chromium(III) ion as the first step in the reaction. If colourless organic chelates of chromium, such as those derived from oxalic or tartaric acid, are used instead of or in addition to hydrated chromium(III) salts, the difficulty of replacing the strongly coordinated water molecules in the first stage of the reaction is eliminated. In this way the initial reaction can be carried out at high pH without contamination by the precipitation of chromium hydroxide. Use of the complex ammonium chromisalicylate (5.12) in this connection should also be noted (section 5.4.1).

### 5.5.2 Cobalt complexes

Like trivalent chromium the hexa-aquo cobalt(III) cation contains three low-energy  $t_{2g}$  orbitals, this time each doubly occupied. In general, trivalent cobalt complexes are easier to prepare than their chromium analogues and often exhibit significantly higher fastness to light. Chromium complexes normally absorb at longer wavelengths than the corresponding cobalt compounds, however. This bathochromic shift is evident from comparisons between, for example, either CI Acid Violet 128 (5.36;  $M = \text{Co}$ ,  $X = \text{NO}_2$ ) and Blue 335 (5.36;  $M = \text{Cr}$ ,  $X = \text{H}$ ), or Brown 403 (5.37;  $M = \text{Co}$ ) and Black 172 (5.37;  $M = \text{Cr}$ ).

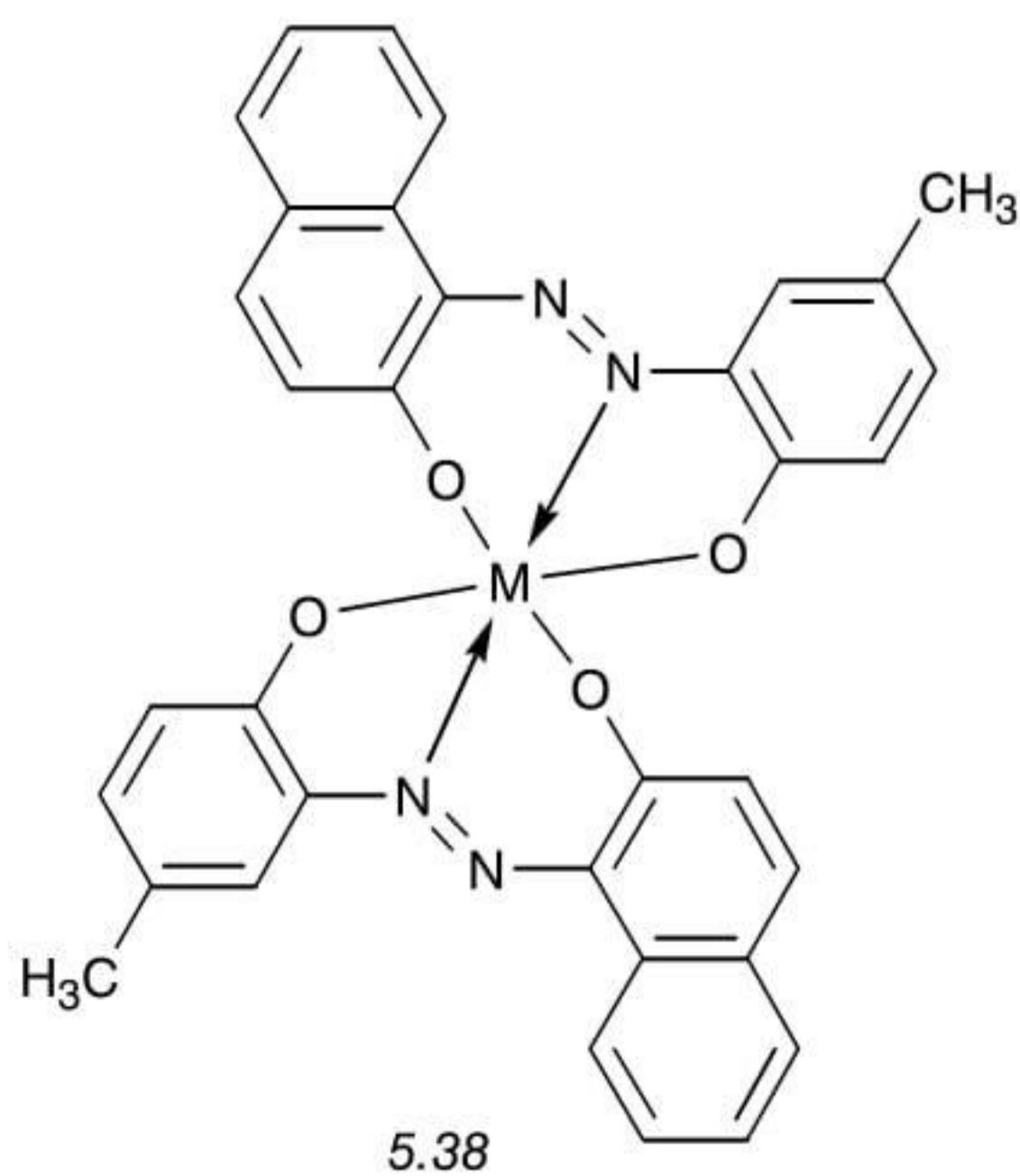
Direct use of cobalt(III) salts in the synthesis of metal-dye complexes is generally avoided because the cobalt(III) ion is strongly oxidising and slow to react with dye ligands. Most 1:2 cobalt-dye complexes are prepared by the reaction between the chelatable dye and a cobalt(II) salt at a relatively high pH. The dominant product is invariably the diamagnetic cobalt(III) complex, oxidation of the cobalt(II) ion taking place by reduction of some of the azo dye molecules present. This can be avoided, however, by adding a less stable oxidant.

Unlike the corresponding 1:1 chromium complexes, the stability of 1:1 cobalt-dye complexes is inadequate for them to be obtained in acceptable yield at low pH. However, advantage can be taken of the strong affinity for cobalt ions of ammonia or amines as



electron donors. Reaction of the cobalt(II) ion with a tridentate dye molecule in an excess of aqueous ammonia yields a 1:1 complex in which the coordination sphere is completed by three ammonia molecules. This again is diamagnetic, indicating the absence of unpaired electrons necessary to achieve an  $sp^3d^2$  octahedral structure. Although 1:1 cobalt-dye complexes have little significance as potential premetallised acid dyes for wool or nylon, they are widely used as intermediates in the synthesis of unsymmetrical 1:2 cobalt-dye complexes, especially when the asymmetry arises from the presence of a sulphonic acid group in one of the chelatable dye ligands.

The dyeing and fastness properties of chromium and cobalt symmetrical 1:2 complexes (5.38) of the mordant dye 2-amino-4-methylphenol→2-naphthol were compared recently on nylon 6 and wool fabrics [20]. The dyebath exhaustion and fastness performance were consistently higher on nylon than on wool. The chromium-complex dyeings were slightly more bathochromic, especially on wool, than those of the cobalt complex but the latter showed marginally higher fastness to washing on wool. Fastness to wet rubbing on wool favoured the chromium complex, however (Table 5.2).



**Table 5.2** Dyeing and fastness properties of 1:2 metal-complex dyes on nylon 6 and wool [20]

Dye Complex 5.38	Exhaustion (%)		$\lambda_{\max}$ (nm) on Fibre	Fastness properties					
	Nylon 6 (80 °C)	Wool (90 °C)		Light (C arc)	Washing			Rubbing	
					E	C	W	Dry	Wet
M = Cr	93		569	>5	5	5	5	5	5
M = Co	93		565	>5	5	5	5	5	5
M = Cr		88	572	5	3-4	4	4	4-5	4
M = Co		88	551	5	4	5	4-5	4-5	3

E Effect on pattern

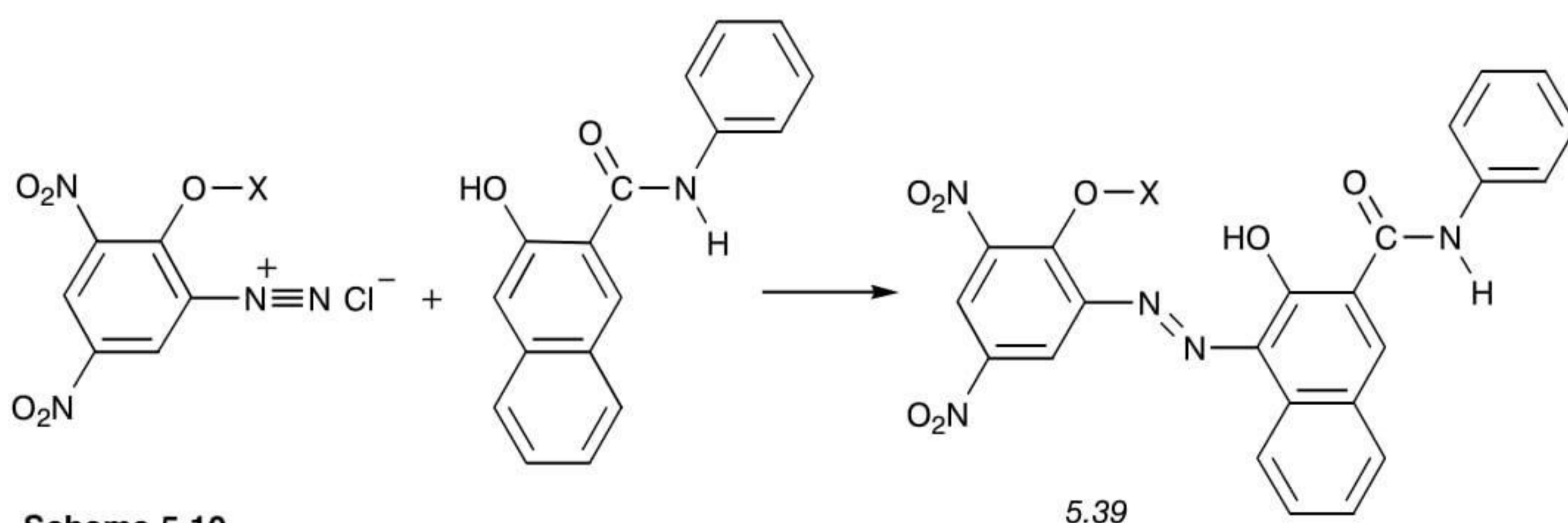
C Cotton stain

W Wool stain

*Chromium and cobalt complexes of azoic dyes*

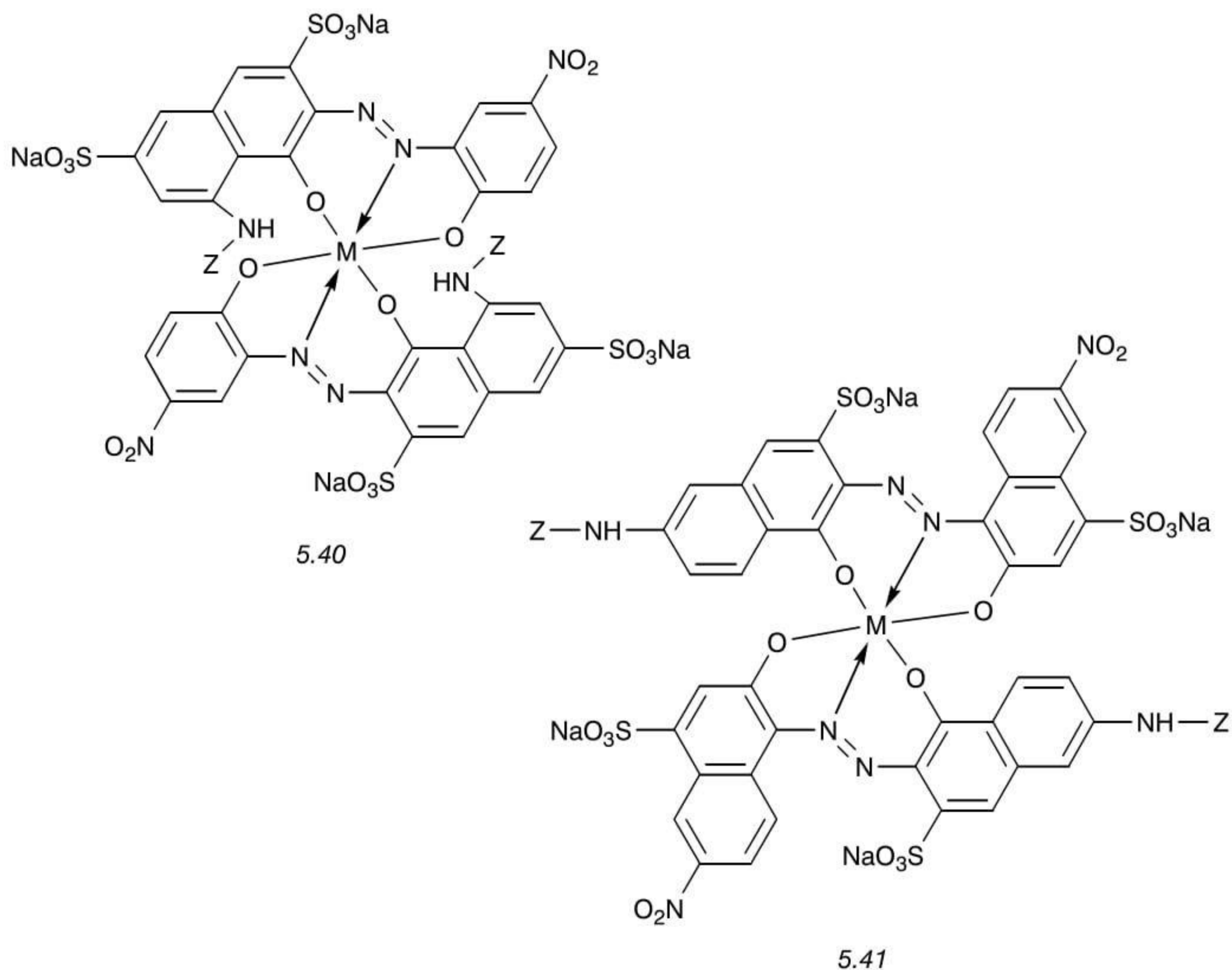
Complexes of chromium(III) and cobalt(III) ions with insoluble azoic dyes, such as that (5.39) prepared by coupling Naphtol AS (CI Azoic Coupling Component 2) with diazotised picramic acid (Scheme 5.10), were synthesised recently for use as negative charge control agents in photocopying [21–23]. The aggregation behaviour and tautomerism of structure 5.39 as the free acid ( $X = H$ ) and the ionised phenolate ( $X = Na$ ) were studied by UV/visible spectrophotometry in polar solvents. Monomer–dimer equilibria were detected in dimethylformamide and in dimethylsulphoxide. Analysis of the deconvoluted absorption bands attributed the spectral changes to a distribution in favour of dimerised aggregates in the ketohydrazone form, with the monomeric species being more stable in the azo form (5.39).

The coupling of Naphtol AS or its phenyl-substituted derivatives with diazonium salts from variously substituted anilines in aqueous alkaline solution (section 4.11) gave incomplete reactions and impure products in some instances, probably because these coupling components have inadequate solubility in aqueous media. Pure dyes in ca. 90% yields were obtained by reaction in dimethylformamide in the presence of sodium acetate. Metallisation of these *o,o'*-dihydroxyazo ligands with sodium chromium salicylate or a cobalt(II) salt gave metal-complex dyes in 80–100% yields [22]. Specific structural isomers of these complexes were identified by i.r., n.m.r., Raman and UV/visible spectroscopy [23].

**Scheme 5.10**

*Mixed chromium/cobalt complexes in reactive dyes*

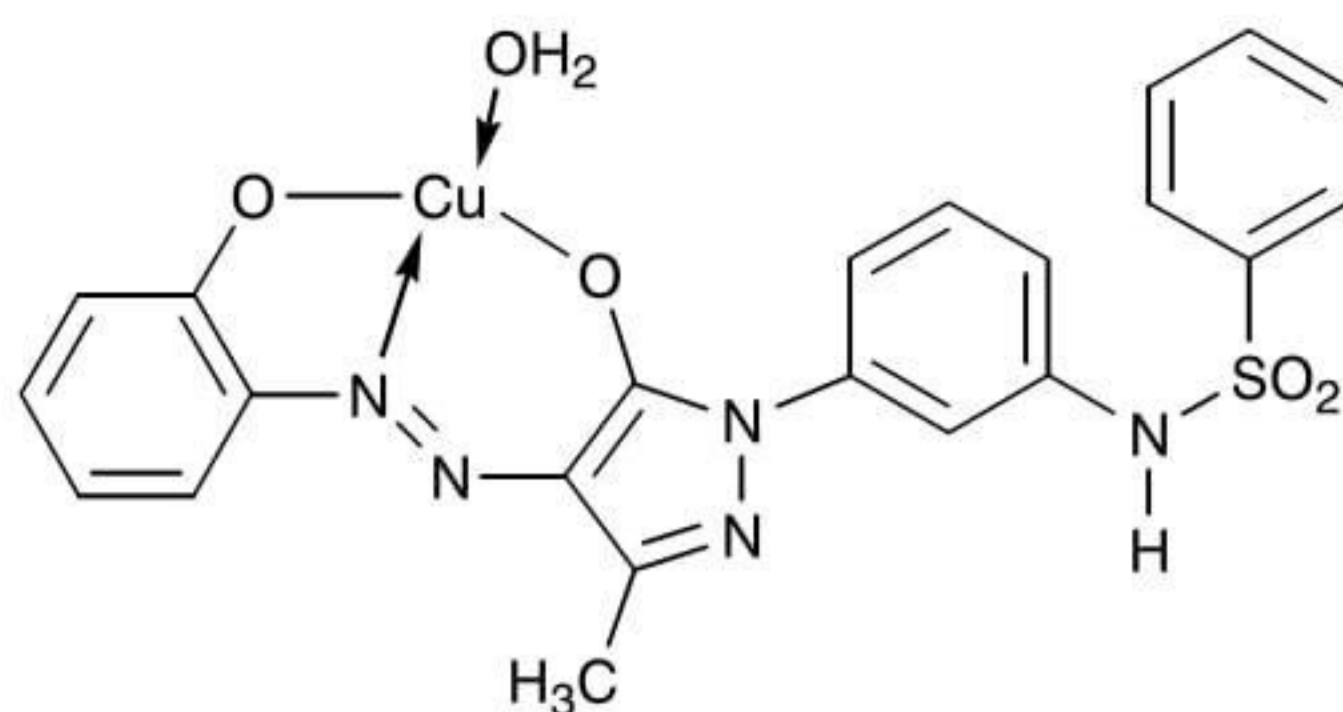
An important subclass of black reactive dyes for the dyeing of cellulosic fibres consists of symmetrical 1:2 metal–dye complexes in which the metal content is a deliberate mixture of chromium(III) and cobalt(III) ions, usually rich in the chromium component. The two most important structural types are the nitrophenylazo H acid complex 5.40 and the nitronaphthylazo J acid complex 5.41. In both cases, each reactive system Z is linked to the NH site in each coupling component.

**5.5.3 Copper complexes**

The only copper complexes of tridentate azo compounds are 1:1 structures, since copper(II) has a CN of 4. They can be prepared by the reaction of the azo compound with a copper(II) salt in an aqueous medium at 60 °C. The major application for copper-complex azo dyes is as direct or reactive dyes for the dyeing of cellulosic fibres. They are seldom developed for use on wool or nylon, although various orange and red 1:1 copper-complex azopyrazolones (5.42) were synthesised recently and evaluated on these fibres by application from a weakly acidic dyebath [24].

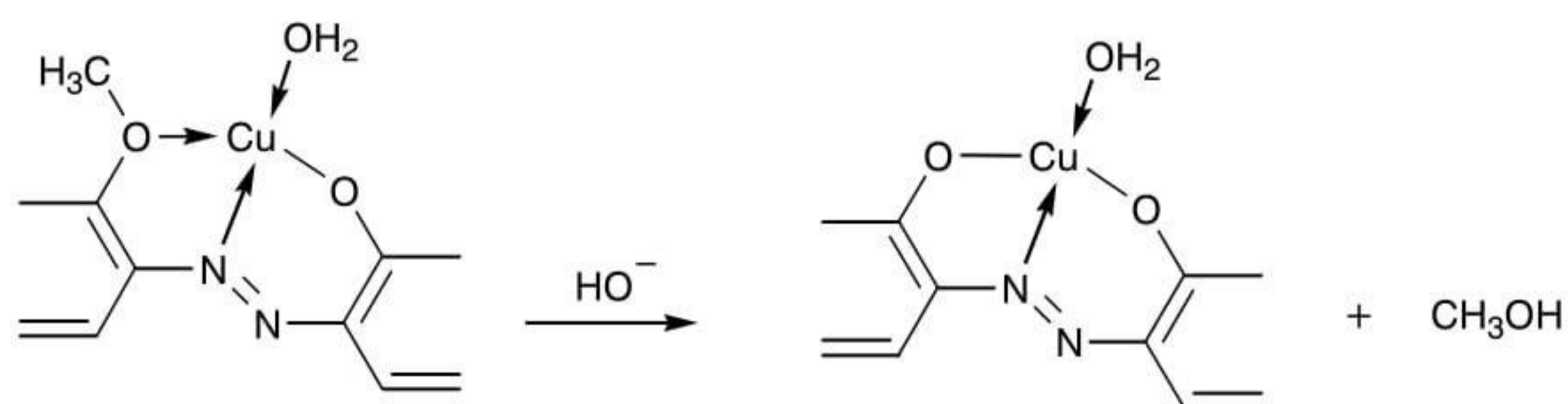
*Copper-complex azo direct dyes*

Almost all of these depend on the availability of two *o,o'*-dihydroxyazo ligands in the unmetallised direct dye molecule, although these may be present as the *o*-methoxy-*o'*-hydroxyazo precursor system. In the manufacture of these dyes it is often easier to synthesise



5.42

the latter grouping because the *o*-methoxyarylamines are diazotised and coupled more efficiently than the corresponding *o*-hydroxyarylamines. Metallisation of the chromogen can be achieved using cuprammonium sulphate in the presence of an alkanolamine such as diethanolamine. During this reaction the methoxy groups present become demethylated. It is probable that coordination occurs between the copper ion and the electron-rich oxygen of the methoxy group. Simultaneously or subsequently the methyl group is lost as a carbonium ion that reacts immediately with hydroxide ion to form methanol, as in Scheme 5.11. Removal of the methyl group is probably assisted by coordination of the methoxy oxygen.



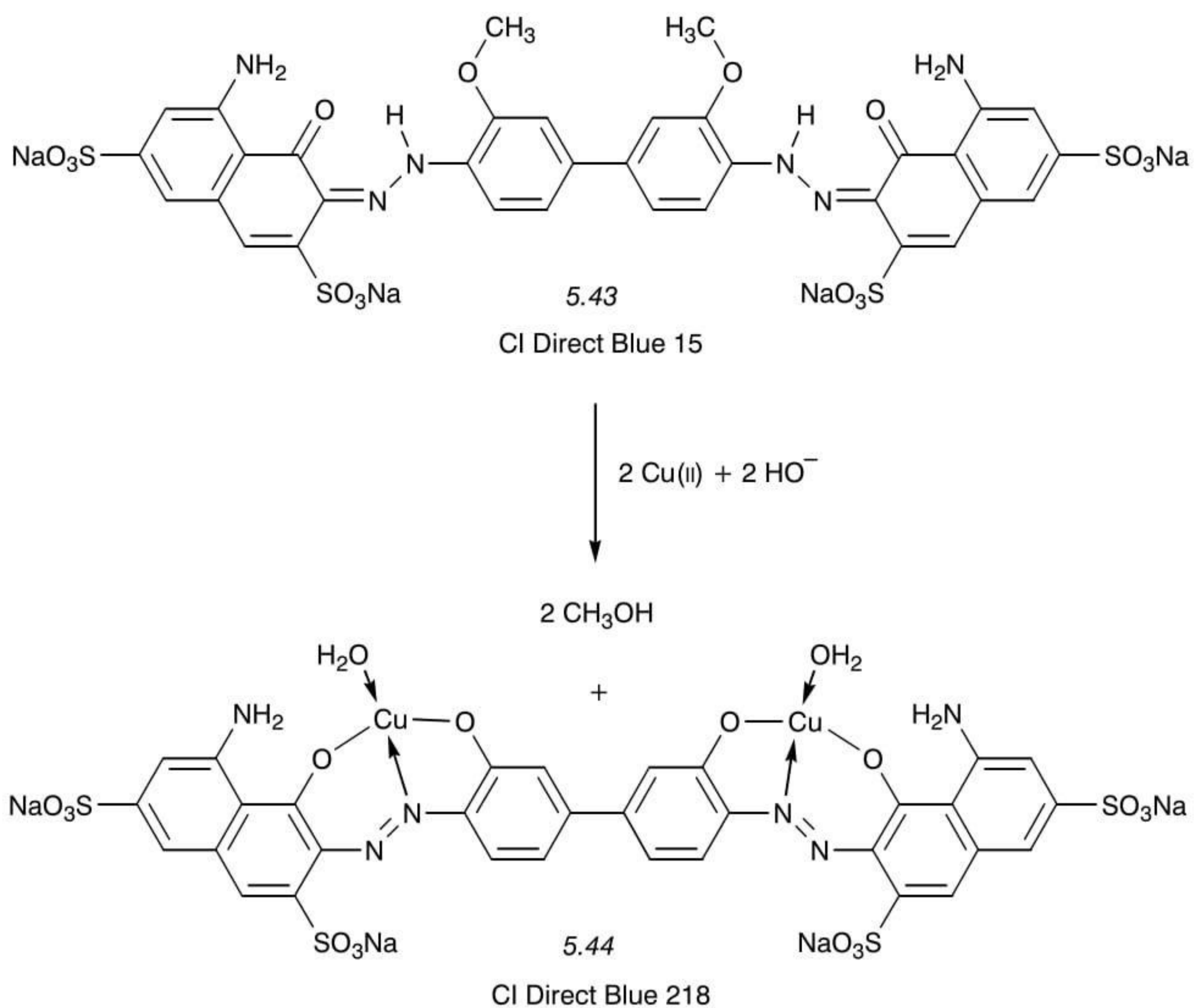
Scheme 5.11

Many of the premetallised direct dyes are symmetrical structures in the form of bis-1:1 complexes with two copper(II) ions per disazo dye molecule. Scheme 5.12 illustrates conversion of the important unmetallised royal blue CI Direct Blue 15 (5.43), derived from tetrazotised dianisidine coupled with two moles of H acid, to its much greener copper-complex Blue 218 (5.44) with demethylation of the methoxy groups as described above. Important symmetrical red disazo structures of high light fastness, such as CI Direct Red 83 (5.45), contain two J acid residues linked via their imino groups. Unsymmetrical disazo blues derived from dianisidine often contain a J acid residue as one ligand and a different coupler as the other, such as Oxy Koch acid in CI Direct Blue 77 (5.46), for example.

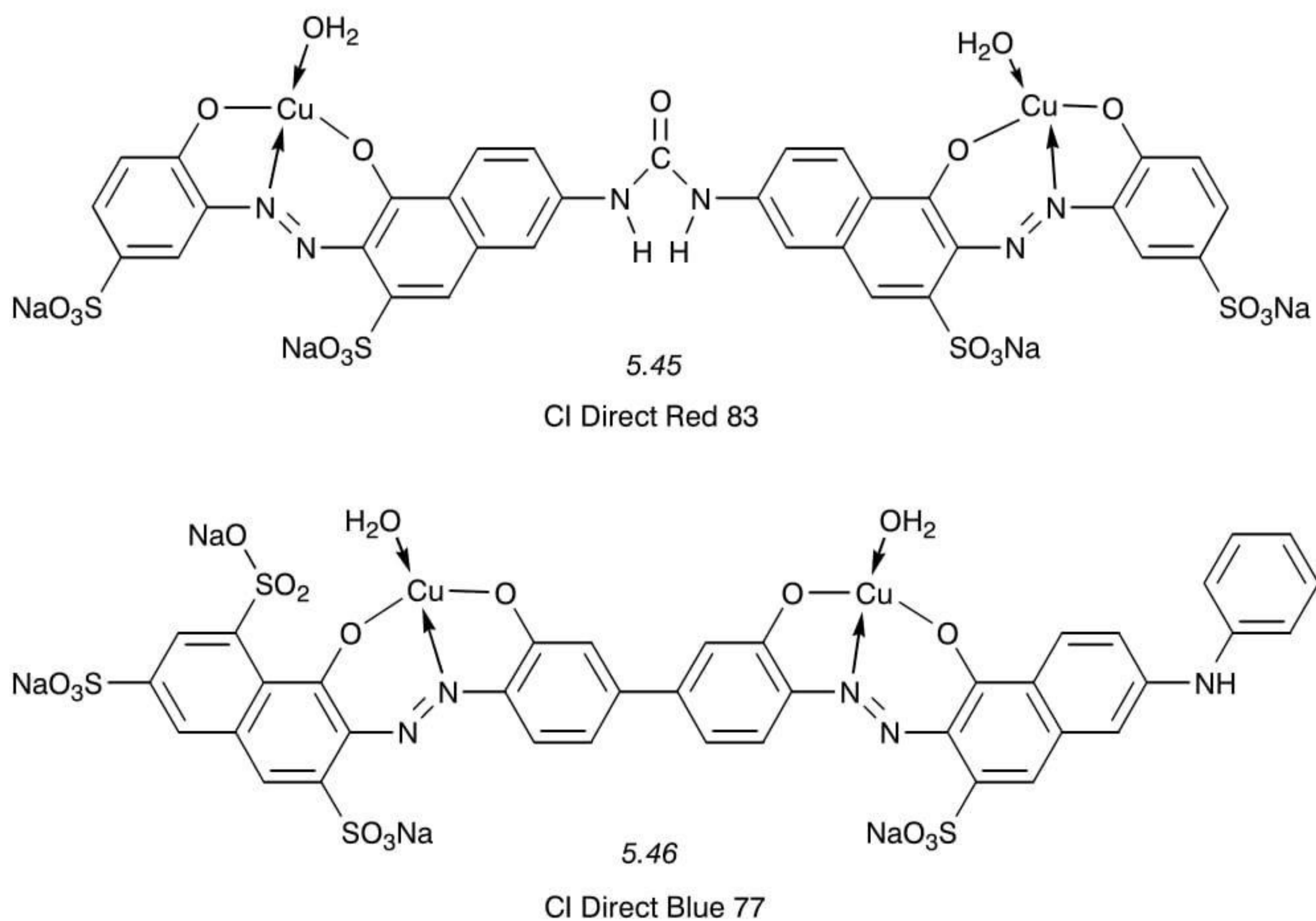
#### *Copper-complex azo reactive dyes*

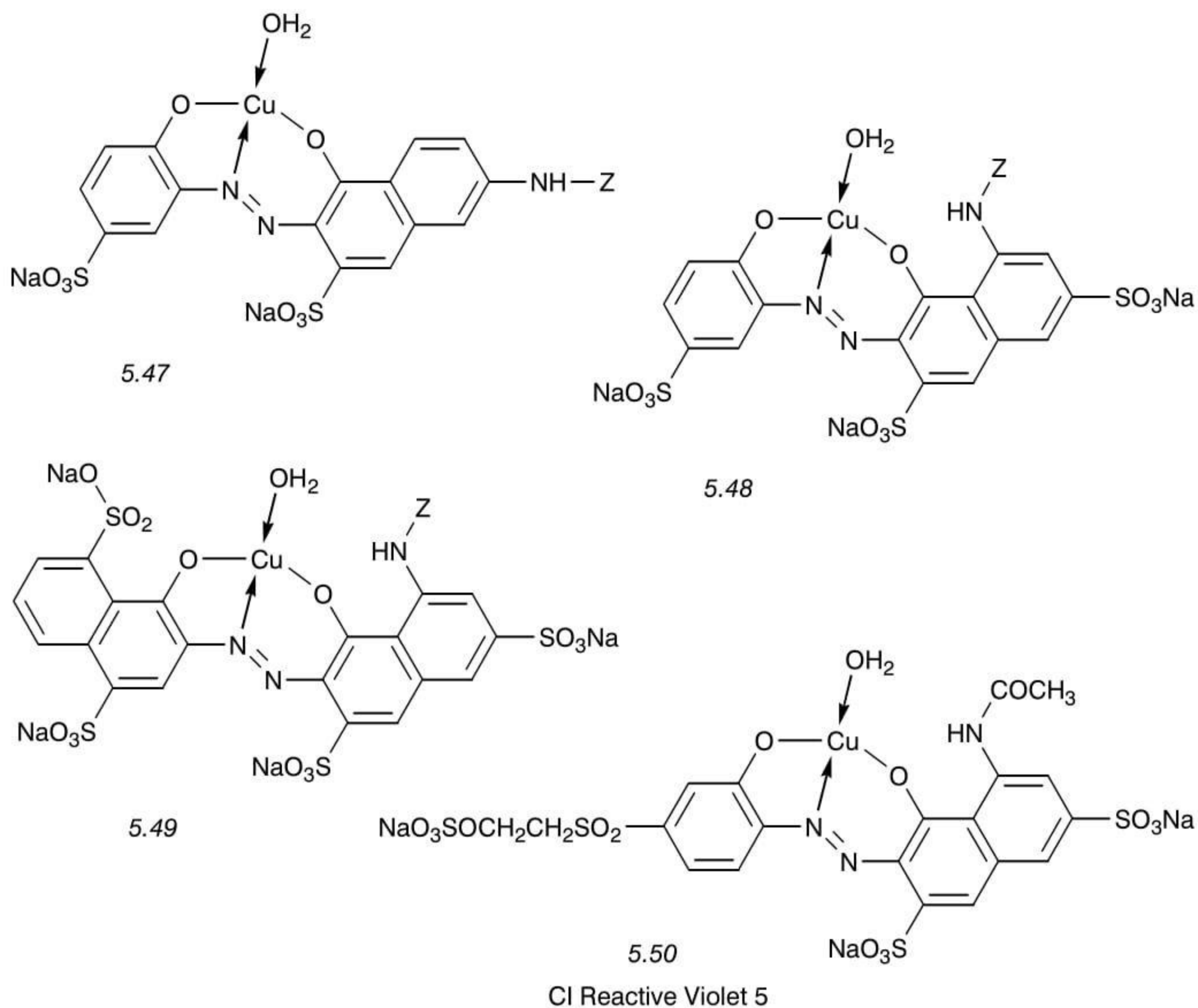
In contrast to direct dyes, metal-complex azo reactive dyes are almost always monoazo chromogens coordinated to one copper(II) ion per molecule. The important structural types include phenylazo J acid reds (5.47), phenylazo H acid violets (5.48) and naphthylazo H acid blues (5.49), where Z represents the reactive system attached through the imino group in the coupling component. Less often the reactive system is located on the diazo component, as in CI Reactive Violet 5 (5.50) and analogous red to blue members of various ranges.





Scheme 5.12



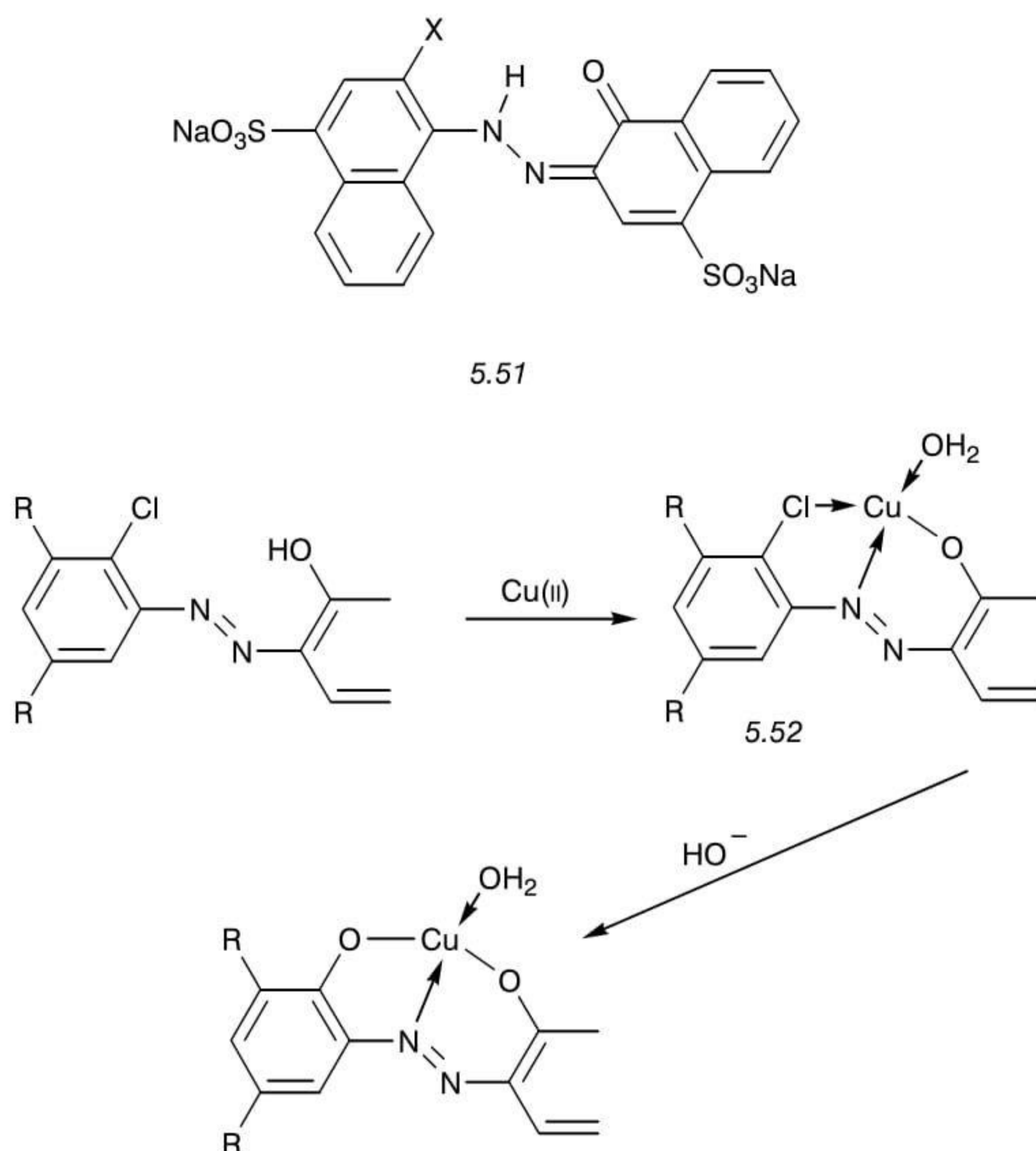


#### Oxidative coppering of monohydroxyazo ligands

This is an alternative method of introducing copper into an *o*-hydroxyazo dye structure. The azo compound is treated with a copper(II) salt and an oxidant in an aqueous medium at 40–70 °C and pH 4.5–7.0. Sodium peroxide, sodium perborate, hydrogen peroxide or other salts of peroxy acids may be used as oxidants, the function of which is to introduce a second hydroxy group in the *o*'-position [25]. This process is reminiscent of earlier work on CI Acid Red 14 (5.51; X = H), an *o*-hydroxyazo dye that will not react with a chromium(III) salt to form a 1:1 complex but will do so by oxidation with an acidified dichromate solution. This oxidation product was later found to be identical with that obtained by conventional reaction of CI Mordant Black 3 (5.51; X = OH) with a chromium(III) salt [7].

#### Replacement of labile *o*-halogeno substituents

The halogen atom in an *o*-halogeno-*o*'-hydroxyazo compound may be replaced by a hydroxy group under mildly alkaline conditions, provided that the halogeno substituent is activated by the presence of electron-withdrawing groups (acetyl, cyano, nitro) in the *o*- and/or *p*-positions [26]. The mechanism is believed to involve formation of an intermediate complex (5.52; R = electron-withdrawing substituent) of low stability in which chlorine is coordinated with the copper atom [27]. This facilitates attack by hydroxide ion at the



Scheme 5.13

carbon atom to which the chlorine is attached, leading to the formation of a conventional bicyclic 1:1 complex, as in Scheme 5.13.

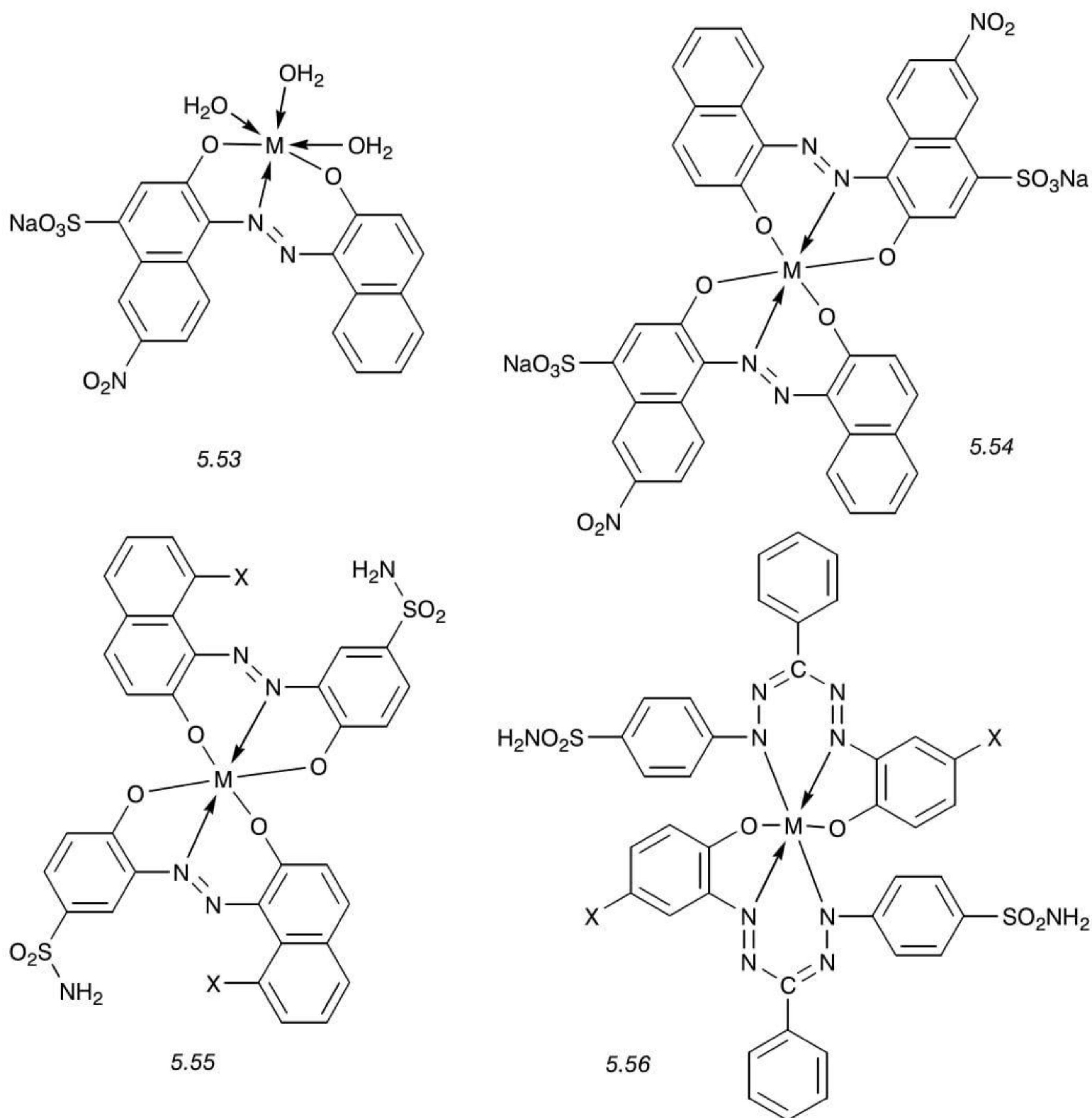
#### 5.5.4 Iron complexes

With the exception of the 1:3 iron complexes of bidentate ligand systems, for example the *o*-nitrosonaphthols (such as 5.8 in section 5.2.1), there has been little interest shown in iron(III) complexes of azo dye ligands as textile dyes until quite recently. Difficulties arising from the presence of chromium residues in effluents from factories involved in the manufacture or use of premetallised dyes have stimulated research on complexes of other transition metals, notably iron(III) which is unlikely to give rise to significant effluent problems because of a much higher permitted level in effluent than that for chromium. Certain black iron-complex dyes are already claimed to be strong candidates for use on wool or nylon in carpets, furnishings and automotive fabrics where high fastness to light is essential [28].

The same naphthylazo-2-naphthol ligand grouping is present in the 1:1 complex CI Acid Black 52 (5.53;  $\text{M} = \text{Cr}$ ) and its symmetrical 1:2 analogue Black 172 (5.54;  $\text{M} = \text{Cr}$ ), which are both widely used in the dyeing of wool. The corresponding 1:1 and 1:2 complexes of trivalent iron ( $\text{M} = \text{Fe}$ ) have been synthesised and their properties compared with the

existing chromium blacks. Excellent light fastness was found but shade differences were observed that would prevent direct replacement in existing recipe formulations [29]. In a further evaluation of this kind, the symmetrical 1:2 iron complexes (5.55;  $M = \text{Fe}$ ) analogous to CI Acid Violet 83 (5.55;  $M = \text{Cr}$ ,  $X = \text{H}$ ) and Black 99 (5.55;  $M = \text{Cr}$ ,  $X = \text{NHCOCH}_3$ ) were synthesised by reacting the metal-free ligands with iron(III) sulphate. Black dyeings on wool and nylon based on these iron complexes exhibited ratings of fastness to light and washing that were similar to those of control dyeings using the conventional chromium-complex dyes [30].

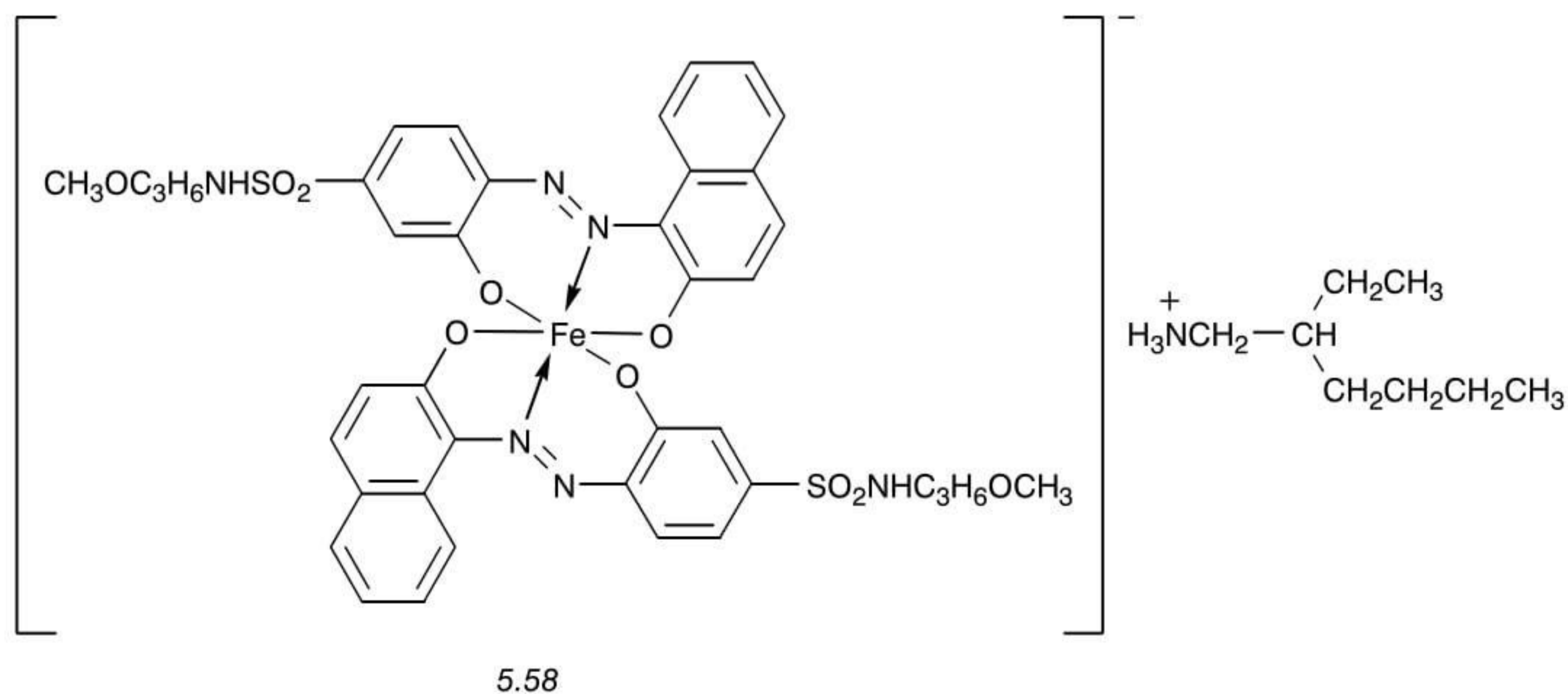
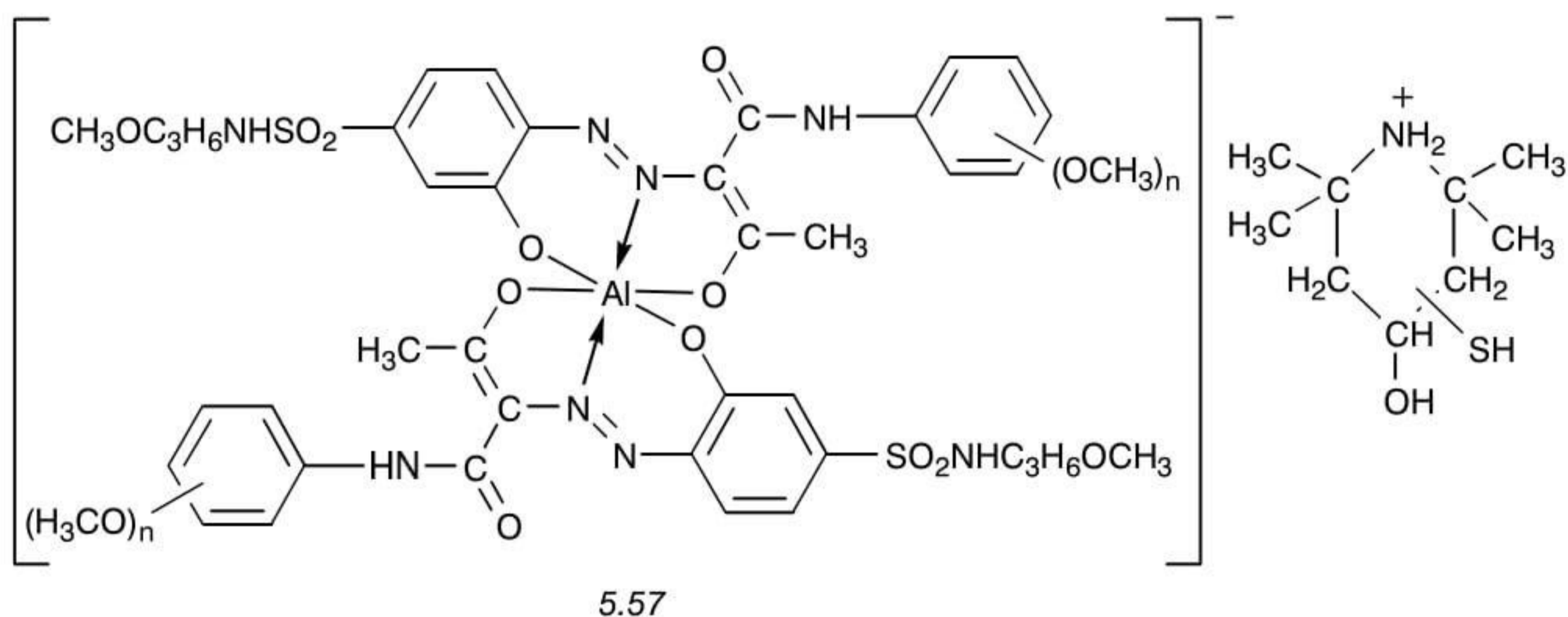
This work has been extended to the synthesis and evaluation [31,32] of various 1:2 iron(III) complexes of tridentate formazan ligands containing two bicyclic ring systems (as 5.29 in section 5.4.2). In an interesting study of the photodegradation of dyes of this kind, their light fastness ratings on nylon and their rates of photofading in dimethylformamide solution were determined. The light fastness of the three unmetallised formazans ( $X = \text{H}$ ,  $\text{Cl}$  or  $\text{NO}_2$ ) was improved by metallisation, the 1:2 cobalt(III) complexes (5.56;  $M = \text{Co}$ )



giving consistently higher ratings than the 1:2 iron(III) analogues (5.56;  $M = \text{Fe}$ ). These cobalt formazans, unlike their iron counterparts, were found to be effective quenchers of singlet oxygen. The presence of an electron-withdrawing substituent in the *o*-hydroxyphenylazo grouping also enhanced photostability ( $\text{H} < \text{Cl} < \text{NO}_2$ ), the highest light fastness being shown by the nitro-substituted cobalt complex [33].

More recently, attention has turned to the aftertreatment of commercially available mordant dyes on wool with iron(II) and iron(III) salts as a potential source reduction approach to eliminating chromium ions from dyebath effluent [34]. The anticipated improvements in fastness performance were achieved. The structures of the conventional 1:2 iron-dye complexes formed on the wool fibres were characterised by negative-ion fast-atom bombardment spectroscopy and HPLC analysis [35].

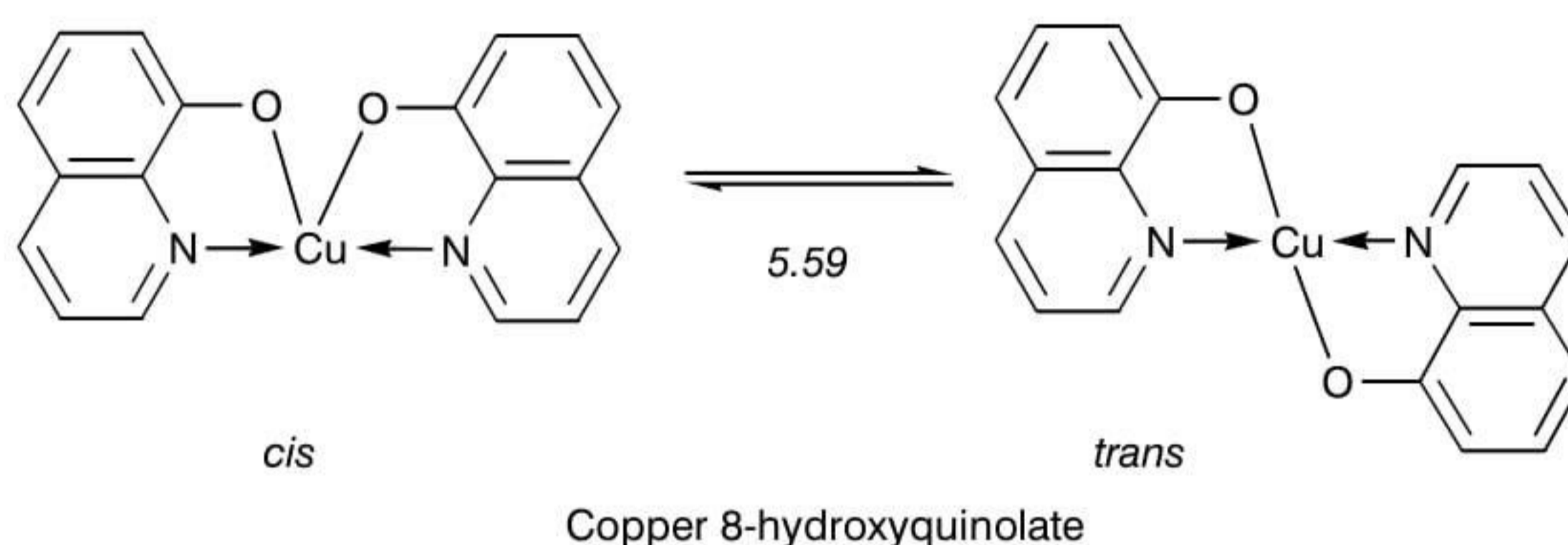
Symmetrical premetallised 1:2 metal-dye complexes of unsulphonated monoazo structures with aluminium (5.57) or trivalent iron (5.58) have been patented recently for use as solvent dyes [36]. They contain a polar methoxypropylaminosulphone grouping in each diazo component and are marketed as alkylamine salts. It remains to be seen, however, whether a full colour gamut of bright aluminium and iron complex dyes can be discovered with light fastness performance equivalent to that of currently available chromium and cobalt complex dyes.



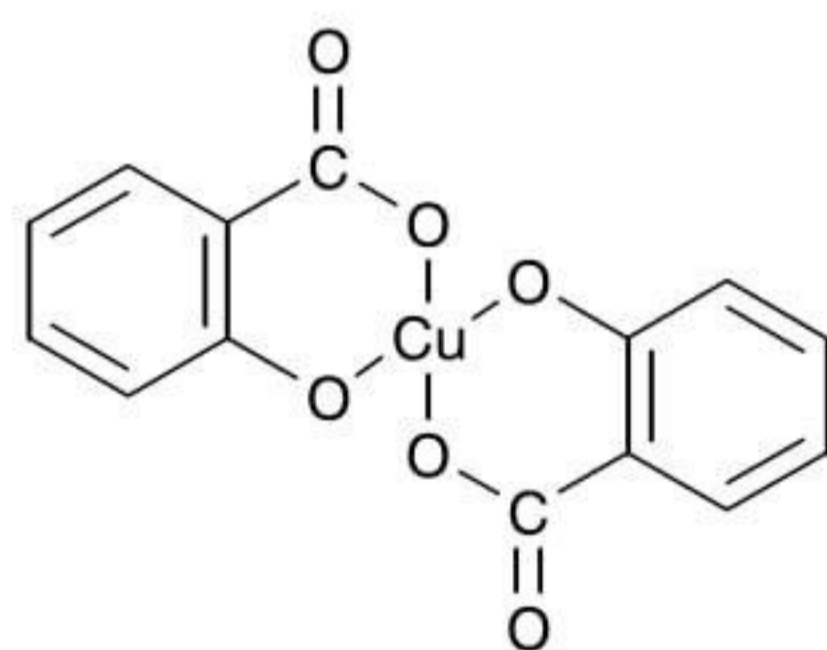
## 5.6 ISOMERISM IN METAL-COMPLEX DYES

### 5.6.1 Stereoisomerism

The three-dimensional character of metal-complex structures allows the possibility that they can form stereoisomers. Thus all structures represented in this chapter should be regarded as a convenient simplification. As already noted, metals of CN<sub>4</sub> can participate in either tetrahedral or planar arrangements (section 5.3). Two symmetrical and identical bidentate ligands surrounding a metal atom in a tetrahedral configuration is an entirely unambiguous structure. A pair of unsymmetrical bidentate systems, however, can exist as enantiomers possessing non-superimposable mirror images and exhibiting optical isomerism. Likewise, equatorial planar arrangements of unsymmetrical bidentate entities, such as copper 8-hydroxyquinolate (5.59), exist in *cis* and *trans* forms (Scheme 5.14). Copper salicylate 1:2 complexes (5.60) exhibit only the *trans* planar configuration. Apparently the *cis* isomer is too unstable to be isolated in this instance.



**Scheme 5.14**



5.60

Copper salicylate

In those 1:2 complexes of major commercial importance as premetallised dyes containing two unsymmetrical tridentate ligands coordinated to a trivalent metal of CN<sub>6</sub> such as chromium(III) or cobalt(III), the possible number of stereoisomers becomes much greater. The requirement that the tridentate dye molecules retain a high degree of coplanarity in forming the complex, however, does restrict this number. As early as 1939 it was concluded [12] that in symmetrical 1:2 complexes of *o,o'*-dihydroxyazo dyes with chromium(III) the major planes of the two dye molecules are arranged about the central atom in a mutually perpendicular fashion. This spatial structure later became known as the Drew–Pfitzner model or a meridial complex [6]. Such an arrangement is unambiguous and these complexes do not exhibit isomerism.

In 1941 two different isomers of the 1:2 chromium complex of an *o*-carboxy-*o'*-hydroxyazo dye were isolated. It was concluded that the three donor ligand atoms of each

dye molecule were situated at the apices of an equilateral triangle forming the face of a regular octahedron [37]. During the early 1960s the existence of such isomers was elegantly confirmed in an extensive series of papers [38,39]. In meridial complexes derived from *o,o'*-dihydroxyazo dyes the angle subtended by the three coordinating groups is a right angle and is best fitted by the Drew–Pfitzner model. On metallisation such dye ligands form a 5,6'-membered bicyclic ring system (5.24 in section 5.4.2). In contrast, *o*-carboxy-*o'*-hydroxyazo ligands form a 6,6'-membered ring system (5.22), with an angle of 60 degrees between the three coordinating groups. Such a configuration can be accommodated more fittingly at the corners of the equilateral faces of the octahedron. This so-called Pfeiffer–Schetty 'sandwich' model or facial complex exhibits a minimum of three isomeric forms, each existing as an enantiomeric mirror-image pair.

Further studies were extended to *o*-amino-*o'*-hydroxyazo ligands and their azomethine analogues, as well as *o*-carboxy- and *o*-hydroxyformazan complexes [40], fully confirming that all diarylazo chromogens yielding 5,6'-membered annelated rings adopt the meridial configuration, whereas those forming a 6,6'-membered ring system give isomers of the facial type. An elegant confirmation of the latter arrangement has been obtained by X-ray crystallography [41]. Facial stereoisomers may differ in solubility or absorption spectra and can be separated by chromatographic techniques. The activation energy of conversion from one form to another is low, however, so that a solution of one isomer rapidly transforms into an equilibrium mixture containing several components. Attempts to demonstrate differences in dyeing properties between facial isomers are difficult to assess. Nevertheless, facial chromium isomers of *o*-carboxyazopyrazolone dyes have been claimed to show significantly inferior wet fastness but marginally higher light fastness on wool than analogous meridial structures [42].

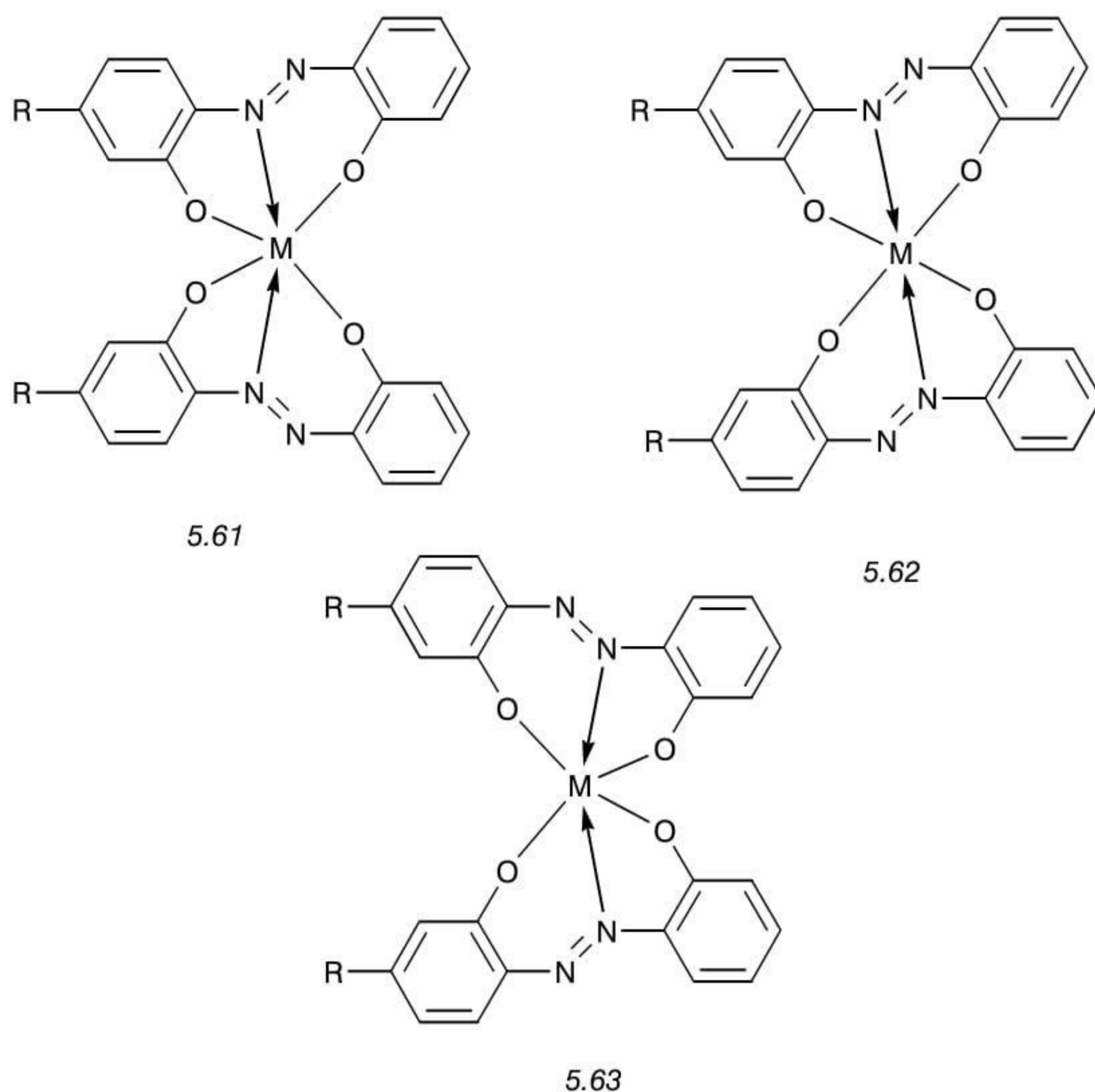
### 5.6.2 $N_{\alpha}/N_{\beta}$ isomerism

A different type of isomerism in metal-complex azo dyes, originally defined by Zollinger [43], has become known as  $N_{\alpha}/N_{\beta}$  isomerism. It is found in 1:1 complexes of copper(II) or nickel(II), as well as 1:2 complexes of chromium(III) and cobalt(III) ions, provided that the *o,o'*-dihydroxyazo ligands are unsymmetrical. There are two isomers ( $\alpha$  and  $\beta$ ) of the bicyclic 1:1 complexes but the doubly bicyclic 1:2 complex structures can form three, namely the  $\alpha,\alpha$  (5.61),  $\alpha,\beta$  (5.62) and  $\beta,\beta$  (5.63) configurations. If group R is alkyl, differences between the proton magnetic resonance signals associated with the alkyl group protons are dependent on the relative positions of the R groups and the N atoms that coordinate with the central metal atom M. From these data and corresponding results for azomethine analogues in which the coordinating N atoms can be identified unambiguously, the proportions of the three isomers present in a mixture can be calculated [44].

## 5.7 STABILITY OF METAL-COMPLEX DYES

### 5.7.1 Factors governing the stability of metal complexes

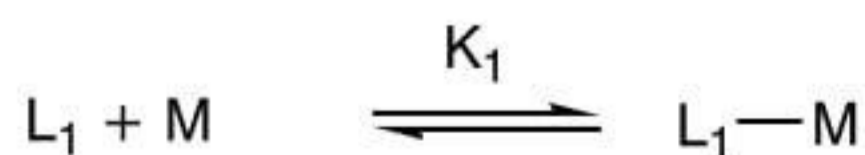
The formation of any metal complex is a reversible reaction and at equilibrium the complex is always partially dissociated into its ligand (L) and metal ion (M) components (Scheme 5.15). The thermodynamic stability constant (K) is a measure of the extent of this



dissociation. The simplest general definition of  $K$  is as the ratio of the factor of the concentrations of the end-products to that of the starting materials, as in Equation 5.1 where the square brackets denote concentration terms such as mol/l. In dilute solution dissolved solutes show an approximation to ideal behaviour, but at higher concentrations activity coefficients should also be included. If the complex  $L-M$  is thermodynamically stable, only traces of the components  $L$  and  $M$  remain at equilibrium and  $K_{1:1}$  has a high value.

$$K_{1:1} = \frac{[L_1 - M]}{[L_1][M]} \quad (5.1)$$

**Scheme 5.15**

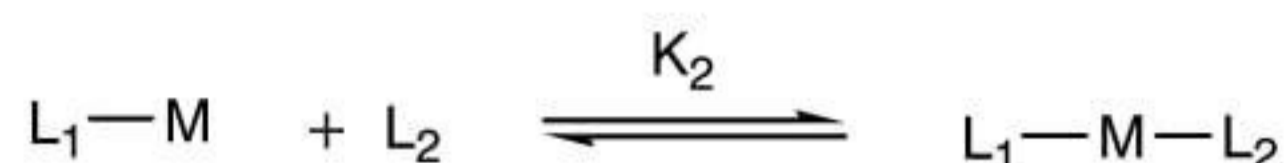


Formation of a 1:1 dye–ligand complex, as in Scheme 5.15, is the simplest case. Further reaction to give a 1:2 complex  $L-M-L$  (Scheme 5.16) involves a second equilibrium constant  $K_2$  related to the concentrations of the 1:1 and 1:2 complexes present at equilibrium (Equation 5.2). If the two ligands are different, the stability constant of the 1:2 complex ( $K_{1:2}$ ) is the product of  $K_1$  and  $K_2$  (Equation 5.3). In the special but widely



prevalent case of a symmetrical 1:2 complex, the  $K_{1:2}$  value is related to the product of the metal ion concentration and the square of the ligand concentration (Equation 5.4). In practice, premetallised 1:2 dyes have  $K$  values of  $10^{15}$  or greater.

$$K_2 = \frac{[L_1 - M - L_2]}{[L_1 - M][L_2]} \quad (5.2)$$



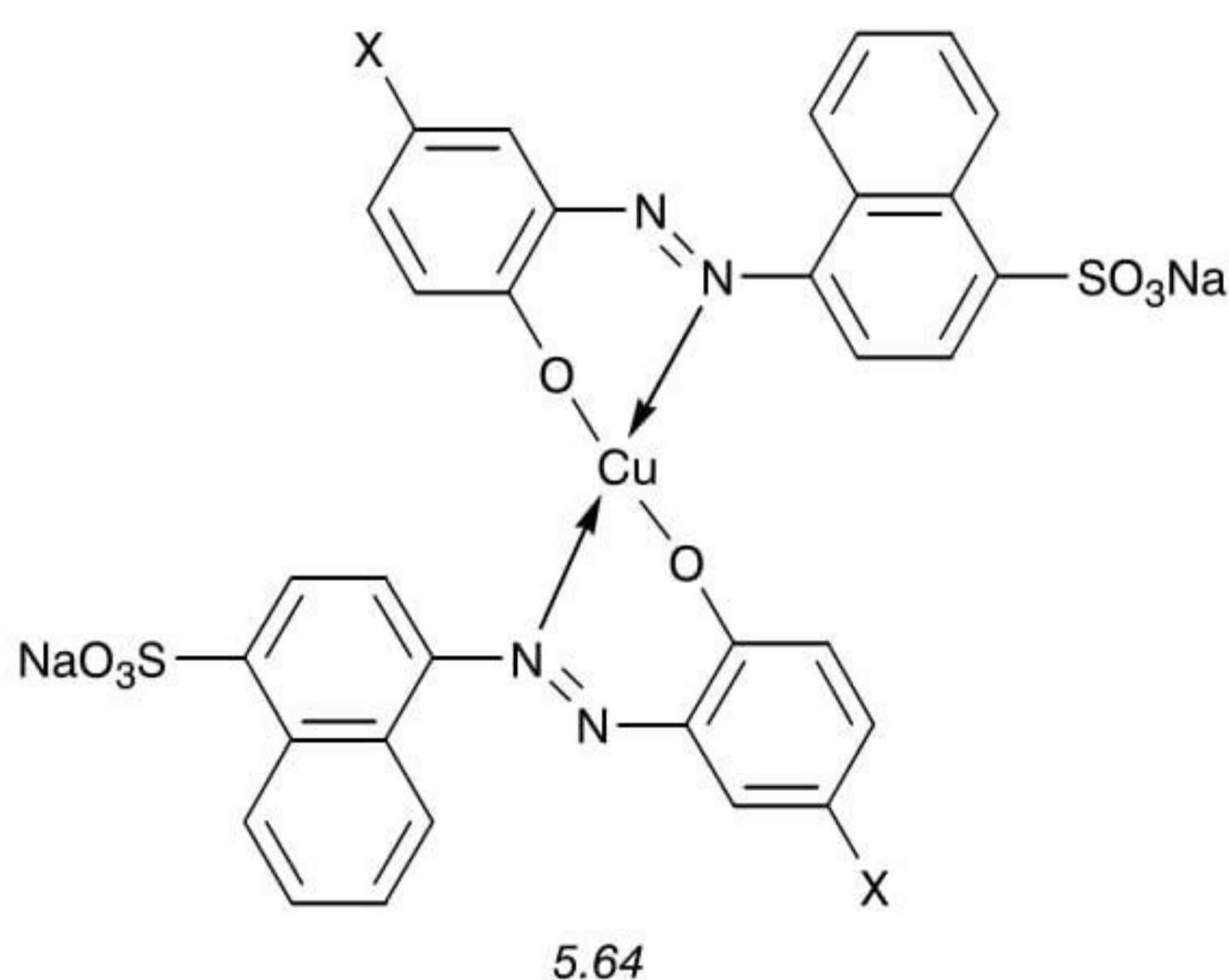
**Scheme 5.16**

$$K_{1:2} = K_1 K_2 = \frac{[L_1 - M - L_2]}{[L_1][L_2][M]} \quad (5.3)$$

$$\text{symm. } K_{1:2} = \frac{[L - M - L]}{[L]^2[M]} \quad (5.4)$$

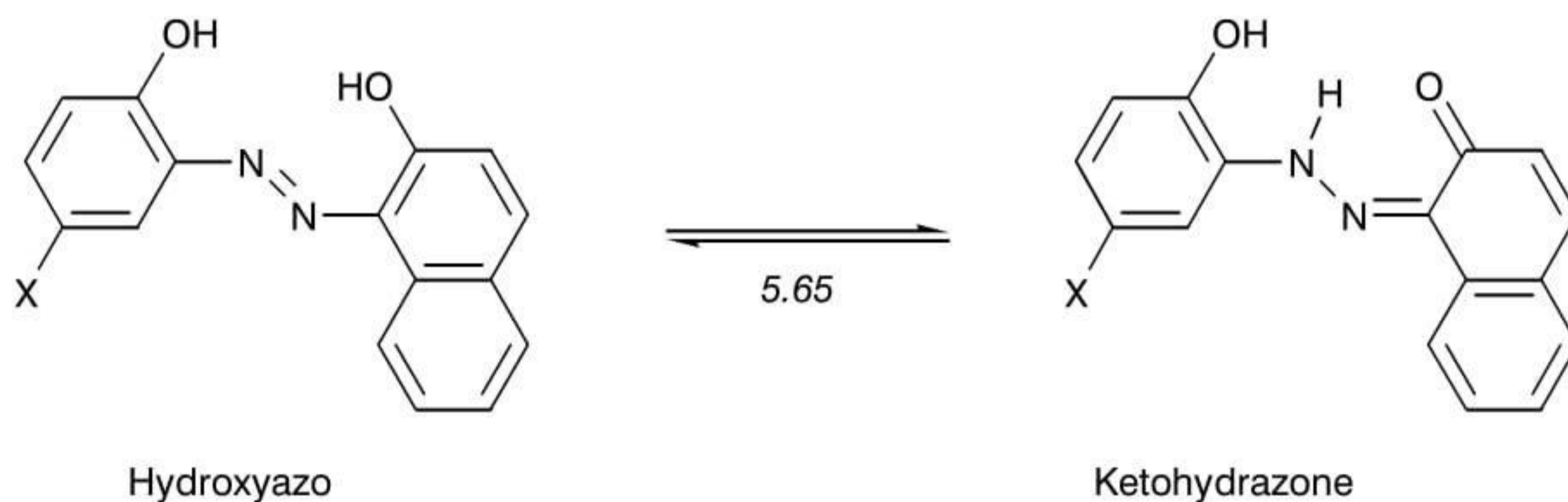
As already discussed (section 5.4.2), factors influencing the stability of metal-complex structures include the size and number of annelated ring systems formed on metallisation. Chelates with five- and six-membered rings are more stable than complexes formed from terminal salicylic acid residues that contain only a single coordinated ring. Tridentate ligands yielding 6,7-annelated ring systems, such as those formed by *o,o'*-dicarboxyazo groupings, show stabilities closer to those of bidentate ligand systems.

Metal-complex stability is also related to the basic strength of the ligand entity. For a series of 1:2 complexes of the bidentate naphthylazophenol ligand (5.64) with copper(II) ion, the acidic dissociation constants ( $pK_a$ ) are linearly related to the stability constants ( $\log K_{1:2}$ ), the more acidic groups forming the less stable complexes. Thus where  $X = \text{NO}_2$  in structure 5.64 then  $pK_a = 8.1$  and  $\log K_{1:2} = 17.2$ , and where  $X = \text{OCH}_3$  then  $pK_a = 8.5$



and  $\log K_{1:2} = 19.2$ . This relationship is only valid, however, for a series of strictly related ligand groups and is dependent on the nature of the solvent [45].

In a similar investigation of the tautomeric tridentate ligand 2'-hydroxyphenylazo-2-naphthol (5.65 in Scheme 5.17), the first and second acidic dissociation constants ( $pK_a$ ) related to the two hydroxy groups in the parent structure ( $X = H$ ) were found to be 11.0 and 13.75 respectively. On introduction of an electron-withdrawing substituent ( $X$ ) the first dissociation constant decreased from 11.0 to 10.55 ( $X = Cl$ ) or 7.67 ( $X = NO_2$ ). The stability constants ( $\log K_{1:1}$ ) of the derived 1:1 complexes were dependent on the metal ion introduced [46], being particularly high for nickel(II) at 19.6 and copper(II) at 23.3.



**Scheme 5.17**

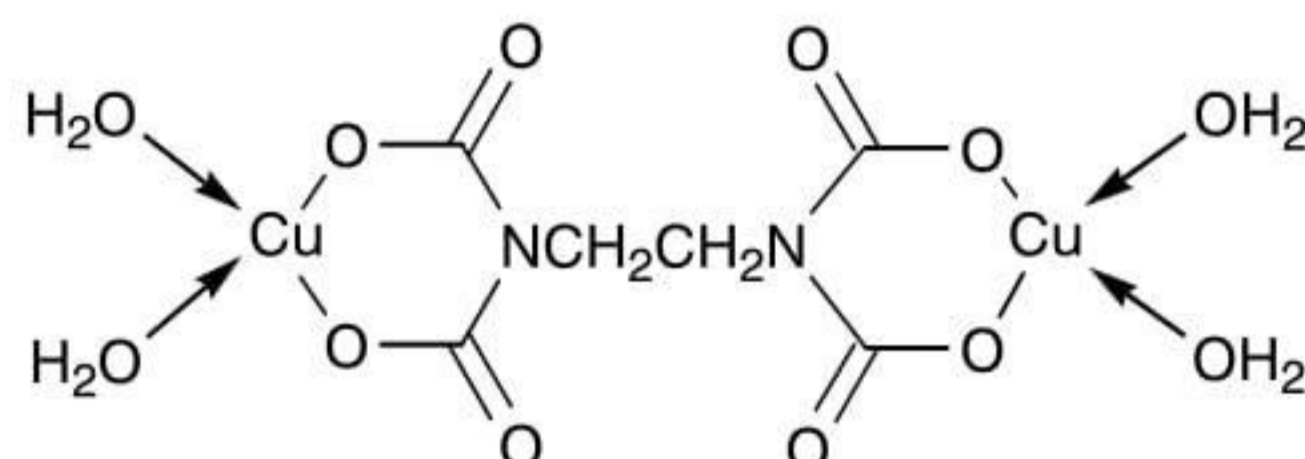
The nature of the donor atom in a coordinating group plays a significant part in the resultant stability of the metal complex. As already mentioned (section 5.5.2), stable 1:1 cobalt(III) complexes can be obtained when the coordination sphere is completed by three nitrogen atoms. Iron(III) atoms tend to form more stable complexes with oxygen donor atoms, as in the 1:3 *o*-nitrosonaphthol structures. Chromium(III) complexes, on the other hand, show equal stability with either nitrogen or oxygen donors, which helps to explain their ubiquitous versatility. A series of *o*-substituted-*o'*-hydroxyazo ligands was derived from the same pyrazolone coupling component, where the *o*-substituent was methoxy, methylthio or dimethylamino. It was shown that even though the acidic dissociation constants of the methoxy- and methylthio-substituted ligands were practically identical, those metal complexes containing sulphur donors exhibited greater stability constants than those containing oxygen donors [47].

### 5.7.2 Instability of metal-complex dyes during textile processing

The sensitivity of premetallised acid dyes to the presence of traces of other metal ions during dyeing and finishing is attributable to demetallisation of the complex, leading to marked changes in colour, dyeing properties and fastness to light or other agencies. The chromium-complex CI Acid Brown 360, of interest specifically for the dyeing of leather, is sensitive to the presence of copper(II) and nickel(II) ions even at ambient temperature [48]. Ultrafiltration can be applied to distinguish between the chelated metal colorants and free copper, chromium or nickel ions in textile effluents. Chromium transfer through the membrane is the least efficient [49]. Proposed ecological criteria for the EU ecolabel with respect to metal-complex dye effluents are  $\leq 50$  mg/kg Cr and  $\leq 75$  mg/kg Cu or Ni [50].

It is well known that transition-metal ions such as copper(II) or iron(III) will catalyse the

decomposition of hydrogen peroxide in solution to form excessive concentrations of perhydroxide ( $\text{HOO}^-$ ) anions. If colour-woven cotton fabrics containing undyed yarns as well as yarns dyed with copper-complex reactive dyes, for example, are subjected to a post-bleaching treatment with alkaline peroxide, copper ions desorbed from the dyed material may catalyse oxidative degradation of the cotton. Addition of salts of ethylenediaminetetraacetic acid (EDTA) to the bleach liquor is an effective means of sequestering these released ions (5.66) and hence suppressing the damage and discoloration of the substrate [51].

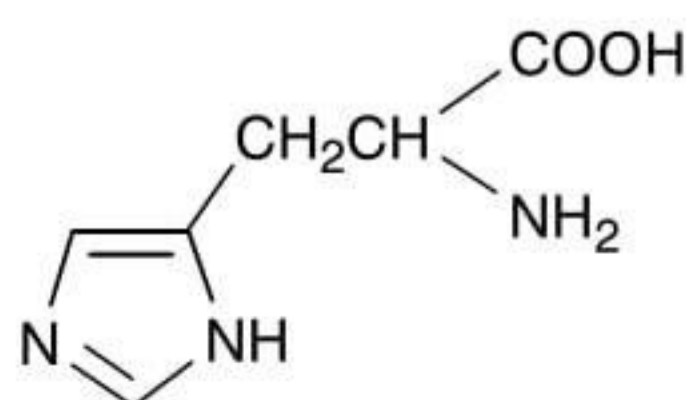


5.66

An appropriate ion-specific electrode was found to provide a convenient, precise and relatively inexpensive method for potentiometry of copper(II) ion in copper-complex azo or formazan dyes. Copper(II) ion in copper phthalocyanine dyes can be quantified after anion exchange. Twelve commercial premetallised dyes evaluated using this technique contained copper(II) ion concentrations in the range 0.007 to 0.2%. Thus many copper-complex direct or reactive dyes are likely to contribute low but possibly significant amounts of ionic copper to textile dyeing effluents [52].

The presence of residual unbound transition-metal ions on a dyed substrate is a potential health hazard. Various eco standards quote maximum permissible residual metal levels. These values are a measure of the amount of free metal ions extracted by a perspiration solution [53]. Histidine (5.67) is an essential amino acid that is naturally present as a component of perspiration. It is recognised to play a part in the desorption of metal-complex dyes in perspiration fastness problems and in the fading of such chromogens by the combined effects of perspiration and sunlight. The absorption of histidine by cellophane film from aqueous solution was measured as a function of time of immersion at various pH values. On addition of histidine to an aqueous solution of a copper-complex azo reactive dye, copper-histidine coordination bonds were formed and the stability constants of the species present were determined [54]. Variations of absorption spectra with pH that accompanied coordination of histidine with copper-complex azo dyes in solution were attributable to replacement of the dihydroxyazo dye molecule by the histidine ligand [55].

On immersion of cellophane films dyed with four copper-complex azo reactive dyes in aqueous histidine, the absorption spectra of the dyeings changed as a result of abstraction of



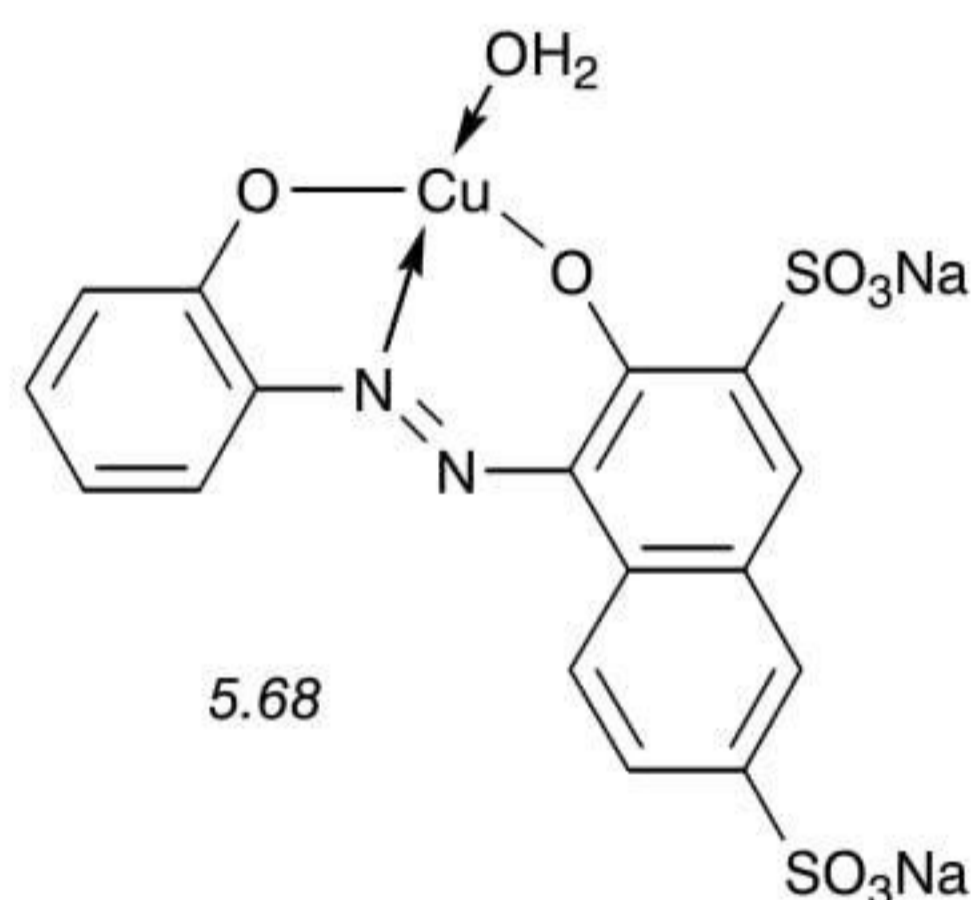
5.67

Histidine

copper ions by the amino acid. The coordination of histidine to a copper-complex dye appears to be promoted by hydrogen bonding of the amino acid to cellulose hydroxy groups. Shade variations and lowering of light fastness were observed following the immersion of cotton fabrics dyed with various premetallised reactive dyes in a histidine solution [56,57].

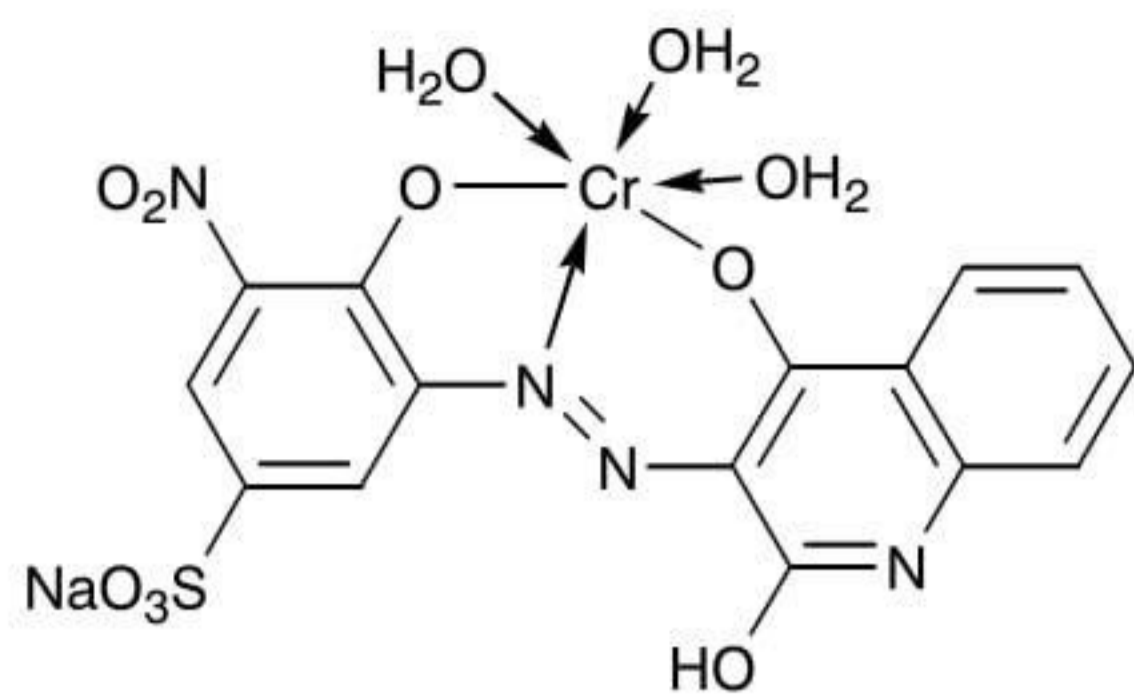
### 5.7.3 Decolorisation of waste liquors containing metal-complex dyes

The problem of residual colorants in waste-waters is a subject of increasing concern (section 1.7.3) and various techniques are exploited to treat coloured effluents. Destructive decolorisation using powerful oxidising agents such as ozone is one important approach. The reactivities with this reagent of disodium 1-(2'-hydroxyphenylazo)-2-naphthol-3,6-disulphonate and its 1:1 complex (5.68) with copper(II) were compared with those of several classical dye structures: Alizarin (CI Mordant Red 11), Chrysophenine (CI Direct Yellow 12), Indigo carmine (CI Acid Blue 74), Malachite green (CI Basic Green 4) and Orange II (CI Acid Orange 7). The relative ease of oxidation increased in the order: Malachite green < Alizarin < Cu-complex 5.68 < Orange II < Chrysophenine < Unmetallised 5.68 < Indigo carmine. Ozonation of the unsulphonated analogue of the copper-complex 5.68 yielded phenol, 2-naphthol and phthalic anhydride [58].



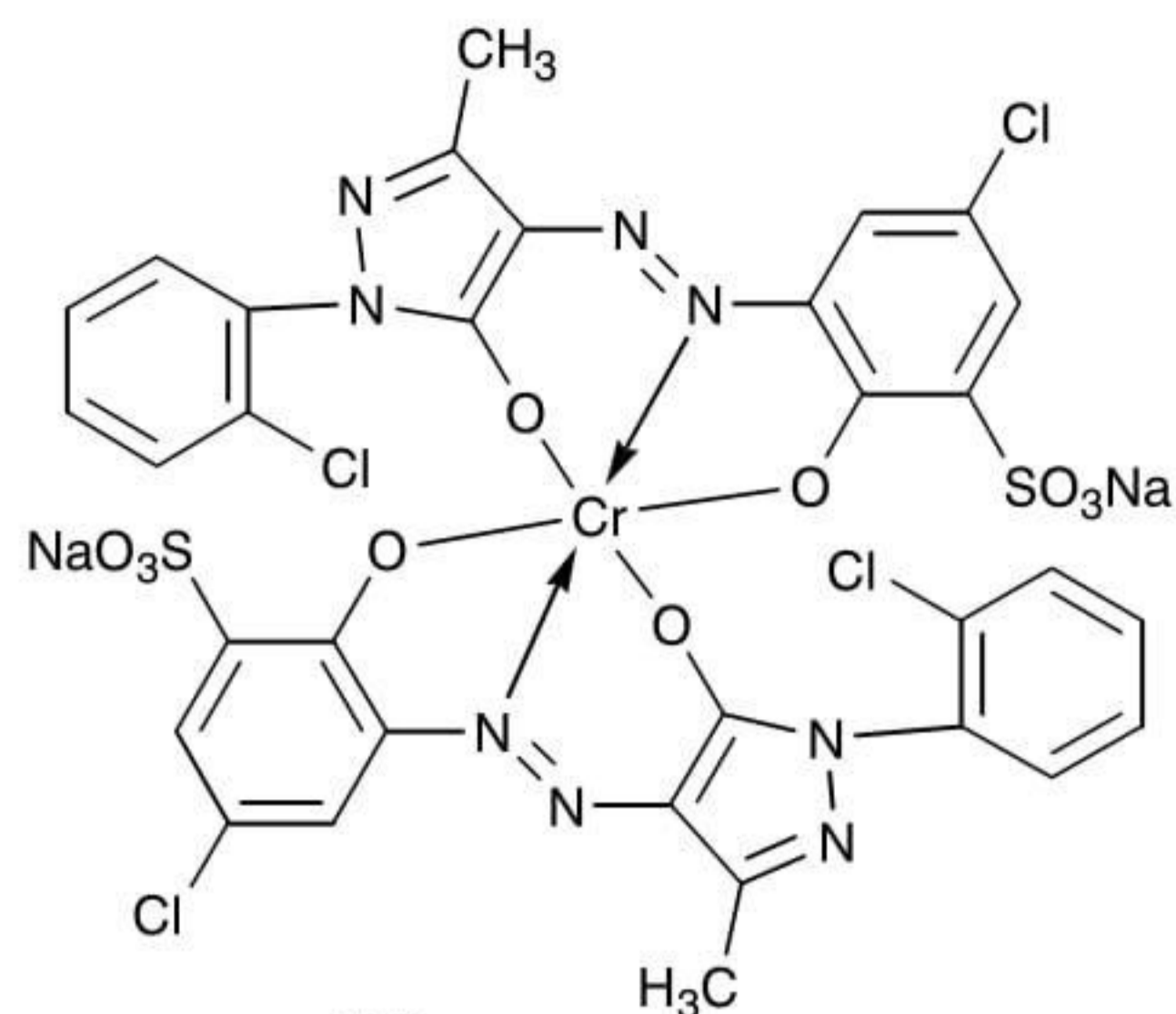
An alternative approach to decolorising waste dyebaths of particular relevance to anionic metal-complex dyes is by means of ion-pair extraction using long-chain amines. The metal-complex dyes can be recovered from the organic phase by extraction with caustic soda and then reused in dyeing. The amines that result after dye recovery are practically colourless and may be recycled. Waste water from a cotton dyeing containing the hydrolysed form of the copper phthalocyanine CI Reactive Blue 41 was shaken at pH 3 with a secondary alkylamine and a mixture of aliphatic hydrocarbons. The dye was almost totally removed and the copper content of the liquor reduced from 30 mg/l to 0.1 mg/l. In similar experiments [59] on wool dyeing effluents (a) the concentration of CI Acid Red 214 (5.69) was lowered from 204 to 10 mg/l and the chromium content from 5.0 to 0.1 mg/l, and (b) a solution of 25 mg/l CI Acid Red 362 (5.70) became practically colourless and the AOX from this halogenated dye fell from 1.6 to 0.5 mg/l.

An evaluation of the macrocyclic ligand cucurbituril in powder form as a precipitant for direct dyes varying in molecular size, including CI Direct Red 79 (disazo), Blue 71 (trisazo) and Red 80 (tetrakisazo), established the influence of pH and ligand concentration on adsorption [60]. The cucurbituril molecule contains six acetylenediurein units linked in



5.69

CI Acid Red 214

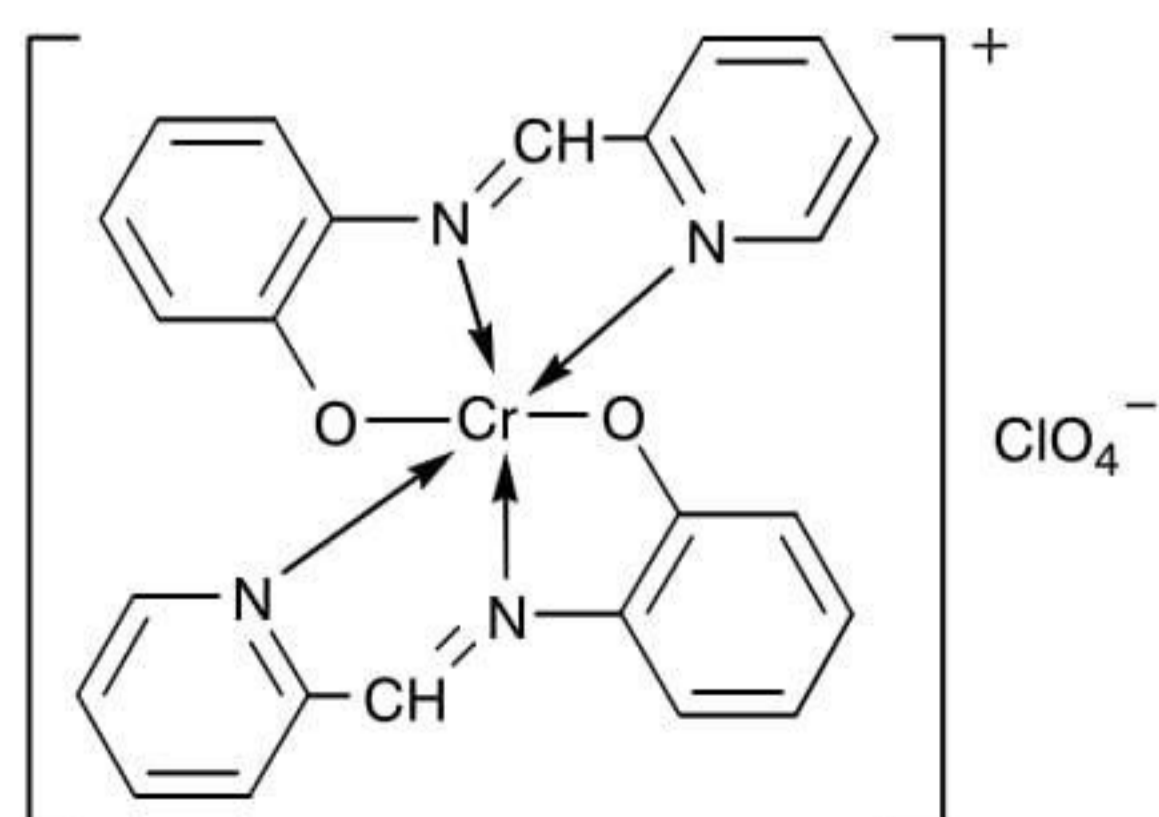


5.70

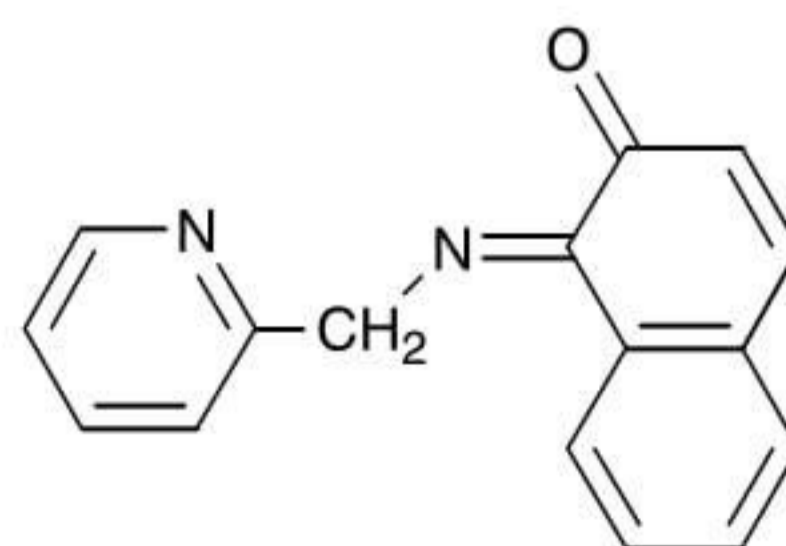
CI Acid Red 362

annular form via methylene groups between pairs of nitrogen atoms in adjacent units. Most of the copper in effluents from direct dyeing is in the form of copper-complex dyes. Thus selective removal of the dye from the waste liquor by treatment with cucurbituril simultaneously reduces the heavy metal content present. An investigation of this complexing agent to remove the copper phthalocyanines CI Reactive Blues 41 and 116, the copper-complex disazo Blue 120 and the chromium-complexes CI Acid Yellow 120, Reds 214 (5.69), 296 and 362 (5.70), Violet 58 and Black 194 from dyehouse effluents gave highly promising results [61].

Quite recently, the removal of the symmetrical 1:2 chromium complex of an azomethine ligand (5.71) from waste-water using a chromium-tolerant bacterial culture was investigated. At low dye concentration initial biosorption was insignificant but about 50% of dye was subsequently decolorised by bacterial degradative activity. At high dye concentration, however, an initial biosorption of about 20% led to only 27% decolorisation overall. The concentration of chromium in the solution followed a similar pattern [62]. The properties of the corresponding manganese(II) complex for dyeing wool and nylon 6.6 have been assessed [63]. Interest has also been shown in the analogous azomethine-2-naphthol ligand (5.72) and its complexes with copper(II), nickel(II) and cobalt(III) ions, which have been evaluated for the dyeing of wool under controlled conditions [64].



5.71



5.72

## 5.8 CHROMIUM-RELATED PROBLEMS IN THE MORDANT DYEING OF WOOL

There are problems of definition with the term 'mordant dye' (section 1.6.8) and it is often more precise to refer to those chelatable dyes, mostly *o,o'*-dihydroxyazo ligands, that are applied to wool at low pH and fixed by dichromate aftertreatment as chrome dyes. Nevertheless, mordant dyeing is a convenient way to describe this two-stage process that has become the focus of substantial development work in recent years because of increasing concern about the environmental hazards associated with residual chromium in dyehouse effluent.

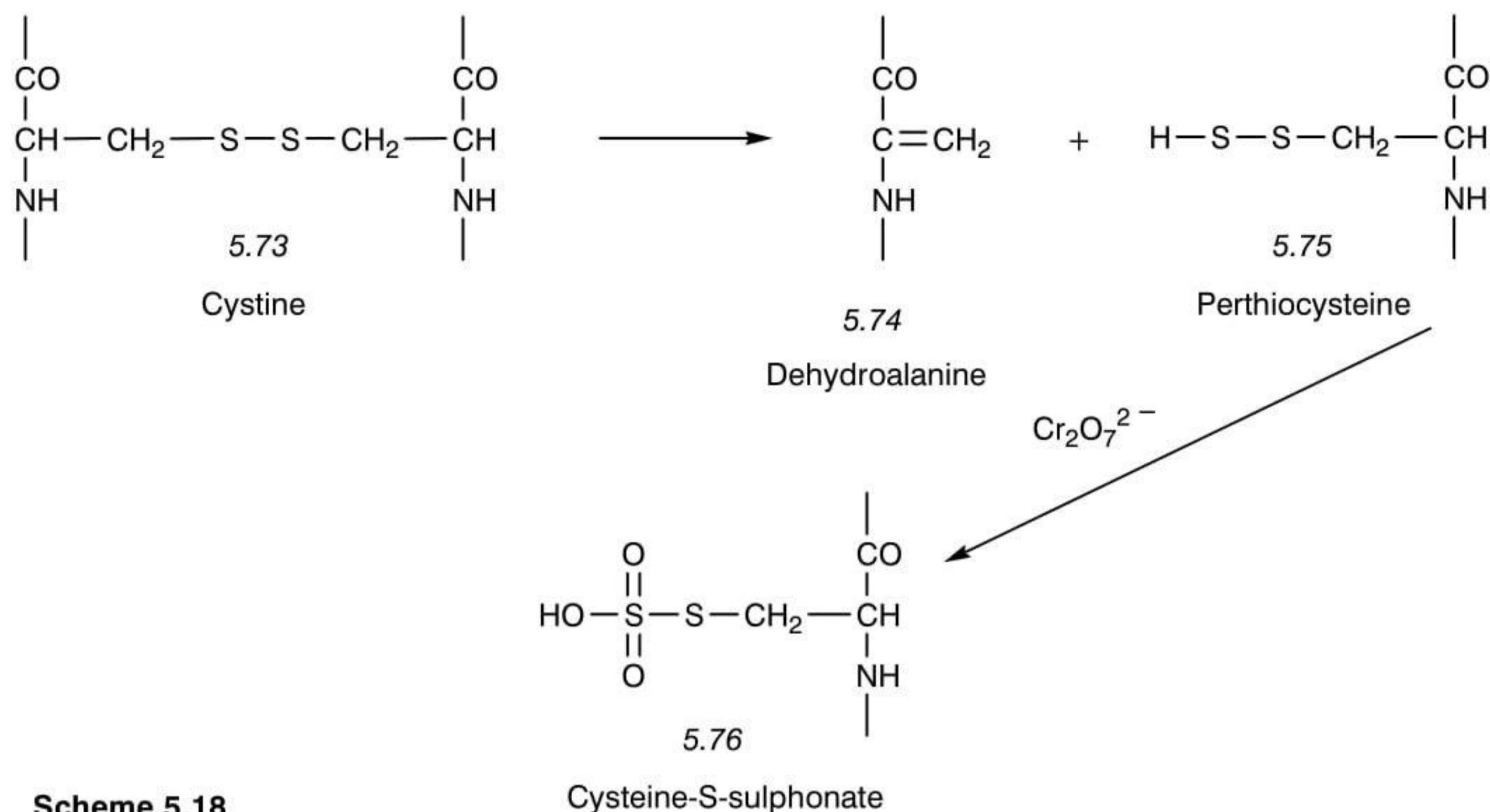
Virtually all of the chrome dyes that remain of major commercial importance are simple monoazo structures, such as CI Mordant Violet 5 (5.65; X = SO<sub>3</sub>Na). These products are easy to manufacture from low-cost intermediates, readily soluble and build up well to heavy depths. Owing to their relatively small molecular size ( $M_r$  300–600), they show good level-dyeing properties when applied to wool at pH 4 and the boil. Glauber's salt is an effective levelling agent for chrome dyes but it impairs the efficiency of the afterchroming stage. The unique combination of level dyeing behaviour and outstanding wet fastness offered by chrome dyes made them increasingly important in the 1970s, when shrink-resist wool knitwear suitable for treatment in household washing machines was launched [65].

Levelling agents of the weakly cationic type, often based on ethoxylated alkylamines, are satisfactory for use with chrome dyes. The effect of cationic surfactants with and without phenyl rings on the spectral properties of chrome dyes of the *o,o'*-dihydroxyazo series has been investigated recently. There was evidence of dye-agent interaction by means of a combination of electrostatic forces and hydrophobic bonding. The specific orientation of the associated molecules was strongly influenced by opportunities for stacking of the planar aryl rings in dye and agent structures. Stacking interactions were promoted by low electron density in the aryl rings [66].

The growing reliance of the dyeing industry on rapid instrumental colour matching has tended to be a handicap for users of chrome dyes. A marked change in hue normally accompanies conversion of the mordant dye to its chromium complex during aftertreatment, although matching difficulties can be overcome by careful control of conditions [67]. More serious problems include the prolonged dyeing procedure, oxidative damage to the wool by dichromate treatment, as well as growing awareness of the environmental hazards associated with chromium compounds, especially the hexavalent chromium form [68]. Although 10 mg per day of chromium(III) in food is normal for good health, it is important to concede that chromium(VI) is highly toxic to mankind and aquatic life [69]. Typical limiting values in the UK regarding permissible amounts of chromium for discharge to effluent are 0.2–0.5 mg/l as the more potent chromium(VI) dichromate anion and 2–4 mg/l as the chromium(III) cation. Proposed ecological criteria for the EU ecolabel with respect to chroming baths are 0.5 mg/l for chromium(VI) and 5 mg/l for chromium(III) ions [50]. Legislation covering the release of chromium-containing effluents is becoming increasingly strict, especially in Germany, the UK and the USA [70]. Draft regulations indicate that no more than 0.1 mg/l total chromium will be tolerated in future [69].

Dichromate anions are readily absorbed under acidic conditions by wool that has been dyed with chrome dyes. The chromium(VI) on the fibre is then gradually reduced by the cystine residues in wool keratin to chromium(III) cations, which react with the dye ligands to form a stable complex. In this way the cystine disulphide bonds are destroyed, resulting in oxidative degradation of the wool fibres [71].

It has been demonstrated recently that the dichromate oxidation of wool cystine proceeds as shown in Scheme 5.18. The cystine crosslinks (5.73) are cleaved to give dehydroalanine (5.74) and perthiocysteine (5.75) residues, the latter being readily oxidised by the dichromate ions to yield cysteine-S-sulphonate (Bunte salt) residues (5.76).



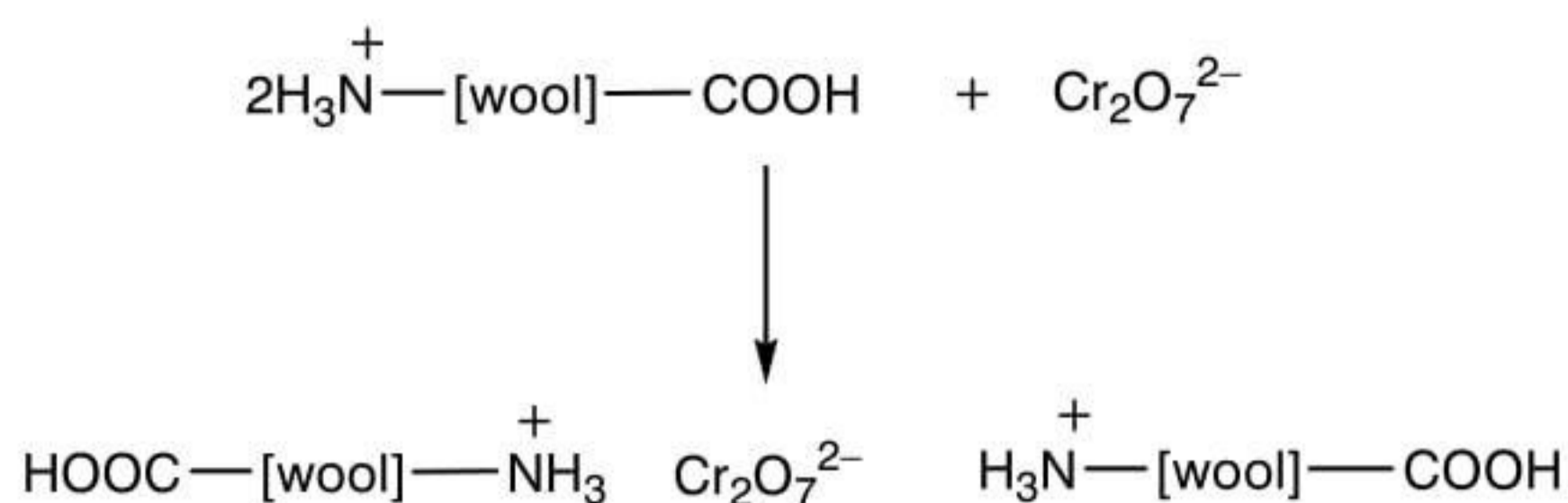
**Scheme 5.18**

### 5.8.1 Controlling factors in the afterchroming process

By far the most widely used chroming agent is sodium dichromate, although the potassium salt has occasionally been preferred. The dichromate may be applied before the dye (mordant method), simultaneously with the dyeing process (metachrome method) or as an aftertreatment (afterchrome method), but only the afterchrome process remains of practical significance. The theoretical aspects of chroming have been reviewed [72,73] and the mechanism of the reactions may be represented as follows:

- (1) Dichromate anions are absorbed and interact with protonated amino groups in wool (Scheme 5.19), the sorption proceeding most rapidly below pH 3.5.
- (2) The absorbed chromium(VI) is gradually reduced to chromium(III) as a result of participation in the oxidative decomposition of cystine crosslinks as represented by Scheme 5.18.
- (3) The chromium(III) cations then combine with the carboxylate groups in the wool fibre (Scheme 5.20).
- (4) The dye ligand interacts with free or complexed chromium(III) to form 1:1 and 1:2 chromium-dye complexes (Scheme 5.21), mainly the more stable 1:2 complex. These coloured complexes are bound to the wool primarily through van der Waals and electrostatic forces. Any excess chromium(III) will remain linked to carboxylate sites in the wool.

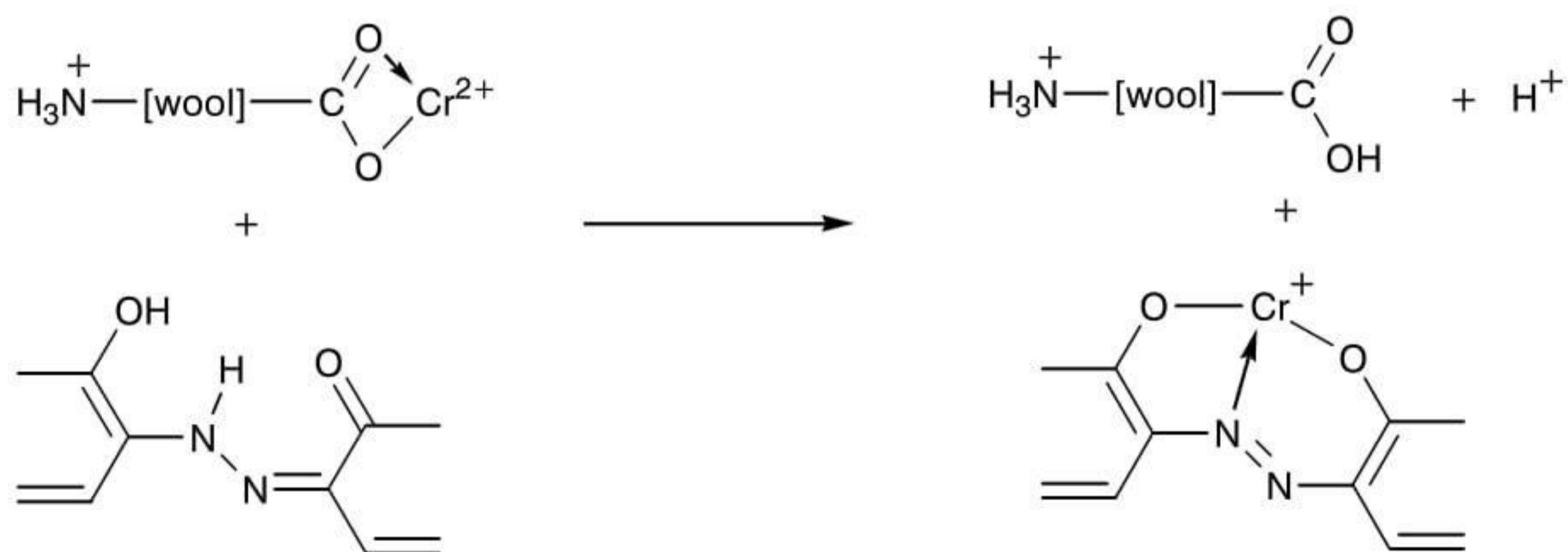
Originally the amounts of dichromate used in the traditional afterchrome process varied between about 25 and 50% of the total amount of chrome dyes present, with the lower and upper limits set at 0.25% and 2.5% of the mass of wool. These quantities were well in excess



Scheme 5.19



Scheme 5.20



Scheme 5.21

of the stoichiometric amount required even for formation of the 1:1 complex. This approach resulted in excess dichromate remaining in the aftertreatment bath for discharge to effluent, as well as on the wool fibre where it contributed to further oxidative degradation. Users of chrome dyes are increasingly concerned with dyeing under mild conditions at pH 4–5 and 85 °C, followed by chroming at pH 3.5–3.8 and 90 °C to minimise wool damage [73,74]. Chroming in a fresh bath tends to give lower residual chromium content but does increase the processing costs. Hercosett-treated wool generally requires more dichromate than does untreated wool, since some of the dichromate is absorbed by the cationic polymer layer [75].

Every effort should be made to exhaust the dyebath as much as possible, because any residual mordant dye will complex with chromium(III) ions in the dye liquor. Apart from complicating effluent treatment, this raises the possibility of lower fastness resulting from deposition on the surface of the wool. Methods that give lower residual chromium tend to produce unlevel chroming, but this can be effectively countered using appropriate levelling agents. The amphoteric agents originally developed for the reactive dyeing of wool are particularly effective but nonionic alkylarylethoxylates can also be used. Water free from



traces of iron or copper is essential, since sequestering agents such as EDTA (5.66) or polyphosphates must be avoided. An aftertreatment in ammonia solution (pH 8.5) for 20 minutes at 80 °C, followed by acidification to pH 5, helps the development of optimum fastness, especially on shrink-resist wool.

Concern regarding exposure to chromium is not just related to effluent discharge. It is obvious that residual unbound chromium present on the fibre is also a potential hazard. The Oeko-Tex ecolabel specifies 1 ppm total chromium or cobalt on babywear and 2 ppm chromium or 4 ppm cobalt on other garments [76]. These figures represent the amount of free metal extracted by a standard perspiration solution. In general, typical 1:2 metal-complex dyeings will satisfy these requirements in full depths, chrome dyeings only to medium depths and premetallised 1:1 complexes only in pale-depth dyeings [65].

### 5.8.2 Improved mordant dyeing methods to minimise residual chromium

In one low-chrome method the wool is initially dyed at the boil to facilitate maximum penetration and levelling. The temperature is then lowered to 75 °C, since maximum exhaustion of chrome dyes takes place below the boil. After adjusting to pH 3.5–3.8 by addition of formic acid, the near-stoichiometric quantity of dichromate as recommended by the dye supplier is added and the temperature again raised to the boil. About 7.5% o.w.f. sodium sulphate is added after chroming for 10–15 minutes and boiling is continued for a further 30 minutes. Sodium sulphate gradually displaces chromium from the wool carboxylate sites, making the chromium(III) cations more readily available for interaction with the dye ligands so that less dichromate is needed [73].

An alternative method relies on a constant temperature of 92 °C for dyeing and chroming, thus minimising damage to the wool and dispensing with the need to lower the dyebath temperature before commencing the chroming stage [68]. After dyeing at 92 °C and exhausting the dyebath with a small amount of formic acid, an addition of dichromate is made according to Equation 5.5, where C% is the amount of dichromate required for a dyeing at D% depth.

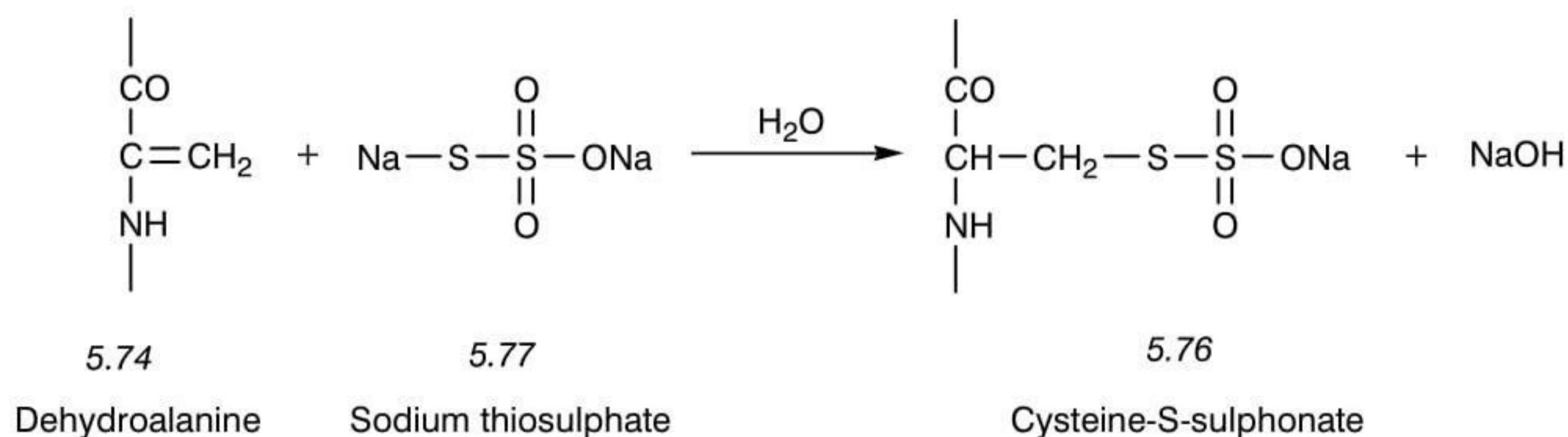
$$C = 0.2 + 0.15D \quad (5.5)$$

Chroming is allowed to continue at a relatively mildly acidic pH for about 10 minutes to improve the uniformity of chroming with this reduced quantity of dichromate. The pH is then lowered to 3.5–3.8 to ensure maximum utilisation of the chromium and treatment is continued at 92 °C for 45 minutes.

There are several redox methods of chroming that depend on the addition of a reducing agent to the chroming bath after about 10 minutes at or near the boil. The precise mechanism is not fully understood, but clearly the increased rate and extent of reduction of hexavalent to trivalent chromium plays a crucial part. The first technique of this type used 1–3% o.w.f. lactic acid, which was found to be the most effective of the  $\alpha$ -hydroxymonocarboxylic acids evaluated to assist the rapid conversion of chromium(VI) anions to chromium(III) cations [77]. The method should be used in conjunction with reduced amounts of dichromate if the advantages to be gained from a lack of residual chromium fixed in the fibre are to be attained. Lactic acid is only effective at high concentrations, resulting in higher processing costs and an increased total oxygen demand in the effluent.

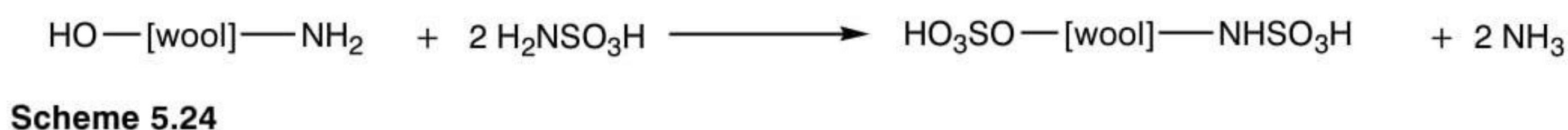
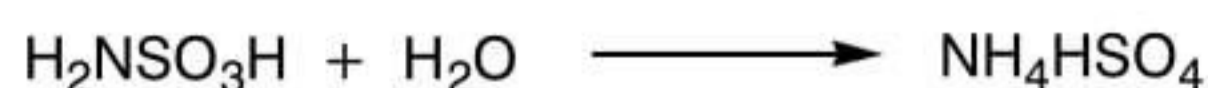
Sodium thiosulphate was later proposed [78] instead of lactic acid. This enabled many chrome dyes to be effectively aftertreated at a temperature as low as 80 °C with consequent advantages in respect of improved levelling and decreased fibre damage. Some dyes are inadequately chromed at 80 °C, however, so a minimum temperature of 90 °C was later recommended [75]. When sodium thiosulphate is present in the chroming bath, the concentration of Bunte salt residues (5.76 in Scheme 5.18) is considerably increased. The thiosulphate nucleophile (5.77) will readily add to the activated double bond in dehydroalanine (5.74), as shown in Scheme 5.22. The protective effect of thiosulphate ions in preventing some of the wool damage is attributable to their reducing properties, so that they compete with perthiocysteine (5.75) in the overall reduction of chromium(VI) to chromium(III) ions [72]. In a modification of this redox approach, a glucose-based proprietary product Lyocol CR (Clariant) is recommended instead of sodium thiosulphate. This agent also accelerates the conversion of Cr(VI) to Cr(III) and forms a complex with the chromium(III) cations that is then absorbed by the wool [79].

Sulphamic acid has been evaluated as a replacement for formic acid in controlling the optimum pH of chroming. If the process is initiated at a pH lower than 3.5 before the dichromate is added and then allowed to gradually become less acidic when reduction of most of the dichromate has taken place, the optimum result for both Cr(VI) and Cr(III) in the effluent should be achieved. Sulphamic acid slowly hydrolyses under these conditions (Scheme 5.23) to give ammonium hydrogen sulphate. It is also able to react [80] with primary amino and hydroxy groups in wool keratin, releasing ammonia (Scheme 5.24). All these reactions will contribute to an increase in pH of the chroming bath. There are no significant differences in wet fastness of chrome dyeings or in the damage caused to the wool by the sulphamic acid process compared with the conventional afterchrome method using formic acid [81].

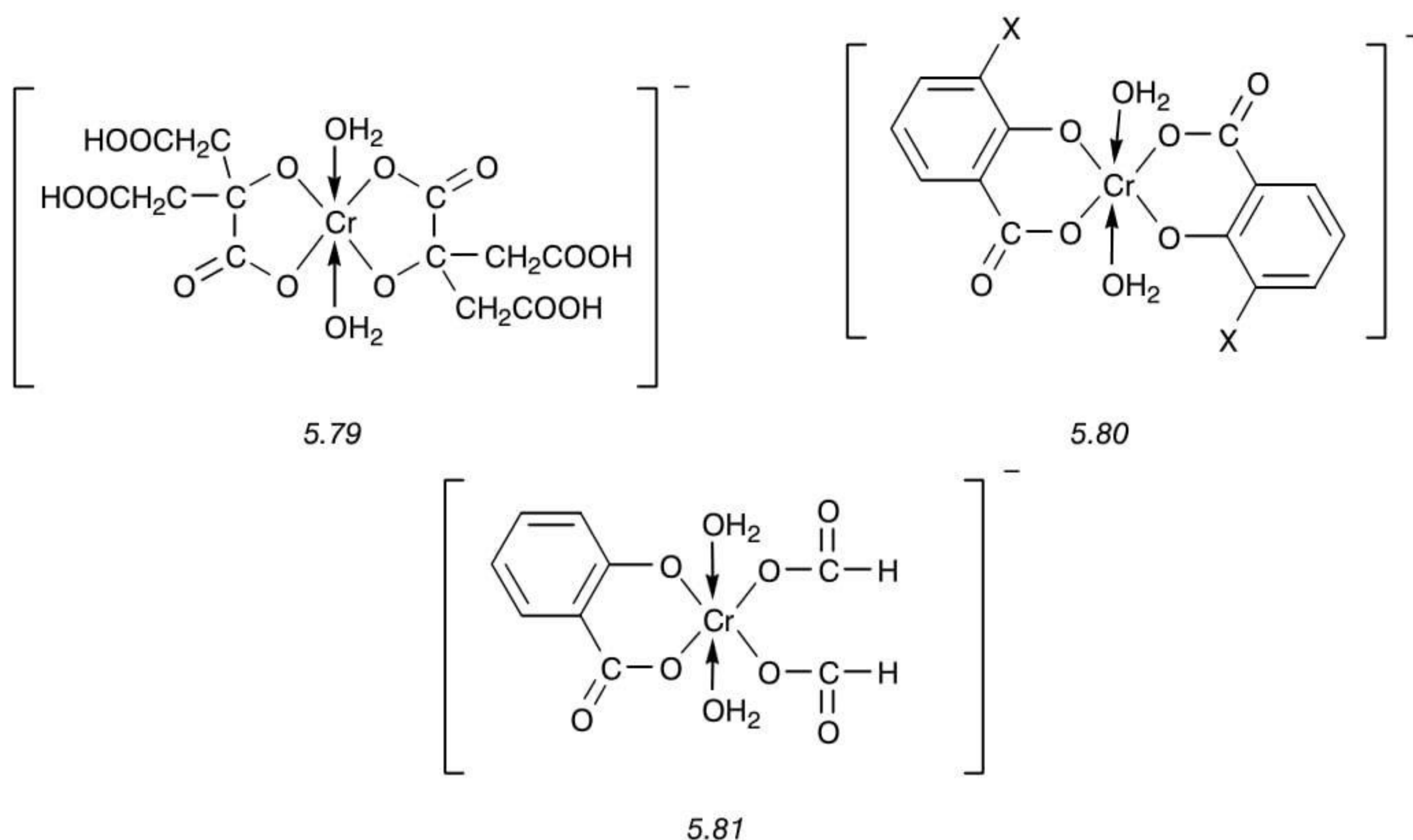


Scheme 5.22

Scheme 5.23







improving the performance of these ranges, which have their own characteristic limitations. There has been considerable activity in the selection of compatible members from different but related classes of wool dyes, such novel selections often being given a distinctive brand name [67].

Carbonised wool can be dyed uniformly with 1:1 metal-complex dyes in 8% sulphuric acid solution without prior neutralisation. These dyes show excellent penetration of tightly woven fabrics and better wet fastness than levelling acid dyes in full depths [86]. Their major disadvantage is the need to apply them at pH 2, causing damage to the wool and requiring a subsequent neutralisation step. The Neolan Plus system was introduced in 1988, consisting of eight Neolan P (Ciba) modified 1:1 metal-complex dyes containing fluorosilicate anions. They are applied with formic acid at pH 3.5–4 using AlbeGal Plus (Ciba), a synergistic mixture of quaternary and esterified alkylamine ethoxylates and fluorosilicates [87]. High dyebath exhaustion ensures shade reproducibility not attainable hitherto, as well as low residual chromium in the dyebath. Wool quality is preserved by the above-normal dyebath pH and post-neutralisation is not necessary. An improved BASF process for conventional 1:1 metal-complex dyes utilises sulphamic acid, commencing at pH 2–2.5 and gradually increasing to pH 3–3.5 (Schemes 5.23 and 5.24). Together with a novel levelling agent, these conditions promote good exhaustion and dye migration, improved wool quality and low values for residual chromium [70].

The Lanaset (Ciba) system introduced in 1983 is based on a compatible range of fifteen milling acid and 1:2 metal-complex dyes. For minimum damage to the wool, they are applied in the isoelectric region (pH 4.5–5) in the presence of AlbeGal SET (Ciba), an amphoteric levelling agent [88]. The required pH is maintained with formic acid for loose stock and tops. A dyebath accelerant, Miralan T (Ciba), is mainly of interest on these goods. Full exhaustion is attained in 10–20 minutes at the boil, resulting in increased reproducibility and improved wool quality. Dye liquors can be reused where a full-volume reserve tank is available, giving energy savings and lower volumes of effluent [74]. Glauber's salt is

recommended for yarn and piece dyeing, with an acetate/acetic acid buffer system for improved control of pH. Although adopted primarily for the dyeing of loose stock, slubbing and yarn, the Lanaset system can be applied with care to the winch dyeing of woollens and the jet or overflow dyeing of worsteds.

The versatility of this system is reflected in its suitability for blends of wool with other fibres [89]. The ideal conditions for the dyeing of wool/acrylic blends are at pH 4-5 and Albeal SET inhibits the risk of co-precipitation between Lanaset anionic dyes and basic dyes. Lanaset dyes are quite stable when dyeing polyester/wool at pH 4-5 and 115-120°C using Irgasol HTW (Ciba) as wool protectant. These dyes are also suitable for dyeing wool in its blends with silk, nylon or cellulosic fibres.

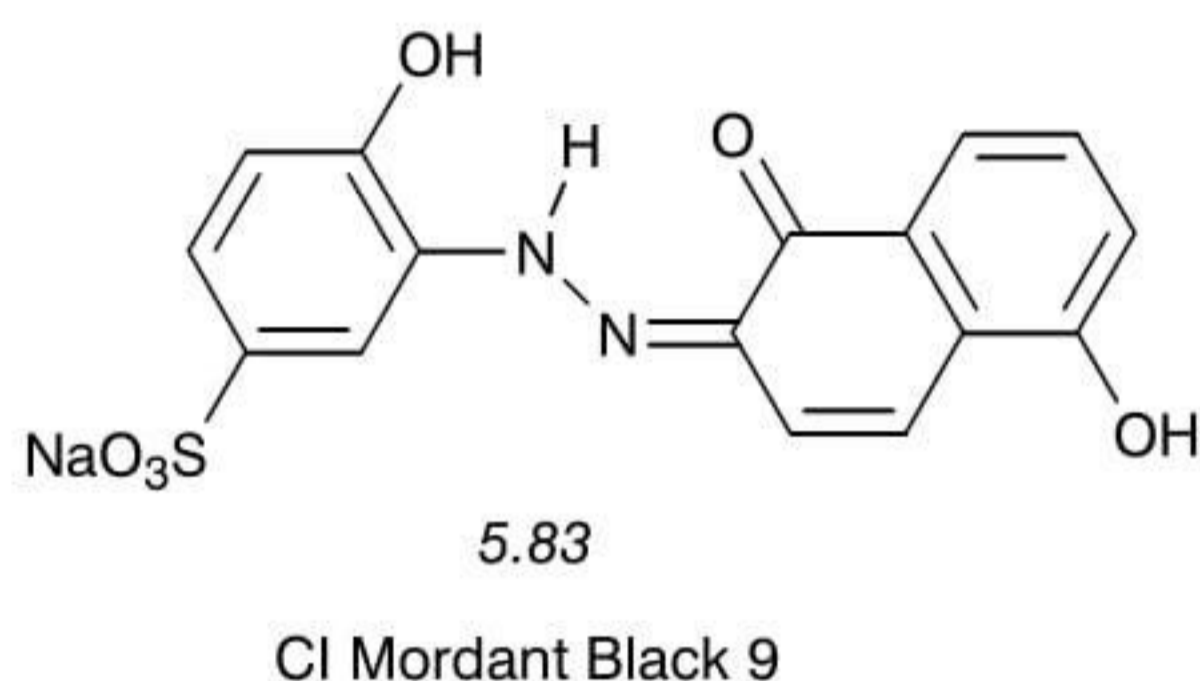
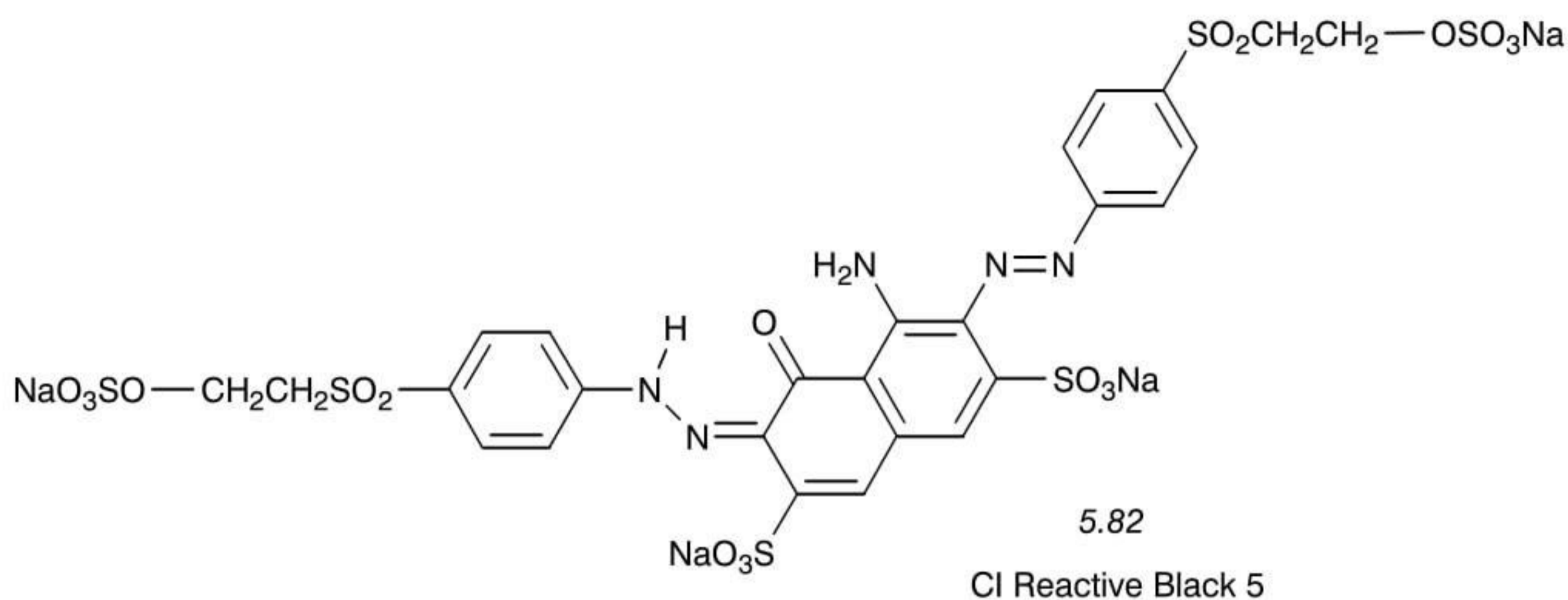
The new Neolan A (Ciba) range of eight optimised combinations of metal-free acid dyes has been developed specially for the dyeing of wool and wool/nylon blends. Five members of the range can be further combined in trichromatic recipes, enabling wool dyers to achieve 80-90% of fashion shades [90]. Brilliant hues and excellent migration properties are obtained in hank and piece dyeing. Selected products can be used in dyeing wool yarns for carpets. Neolan A dyes are applied at pH 5-6 to give exhaustion values exceeding 95% and a uniform migration rate of about 30%. Albeal NA (Ciba) is a levelling agent developed specially for use with these dyes [91].

Although reactive dyes account for only about 5% of total dye usage on wool, no other class can achieve such brilliant hues of high fastness to light and wet treatments. Chrome dyes are mainly used for navy blue and black dyeings, where reactive dyes in general are particularly costly by comparison. Mill trials have been carried out to compare the fastness of a reactive black dyeing based on CI Reactive Black 5 (5.82) with a dyeing of the chrome black CI Mordant Black 9 (5.83) that gives the highest wet fastness. In the most demanding route of dyeing loose wool and assembling into knitted garments that are given an oxidative shrink-resist treatment followed by resin application, the reactive dyeing met all processing and end-use fastness requirements [65]. Chrome-dyed wool is brittle and has a characteristically harsh handle. This is attributed to oxidative damage and the excessive crosslinking imparted during afterchroming. Reactive dyes, however, offer fibre-protective effects during dyeing by:

- (1) inhibiting thiol-disulphide interchanging and thus restricting the degree of permanent set during dyeing
- (2) minimising the hydrolytic peptide bond breakdown that is responsible for impairing the dry tensile strength of wool fibres.

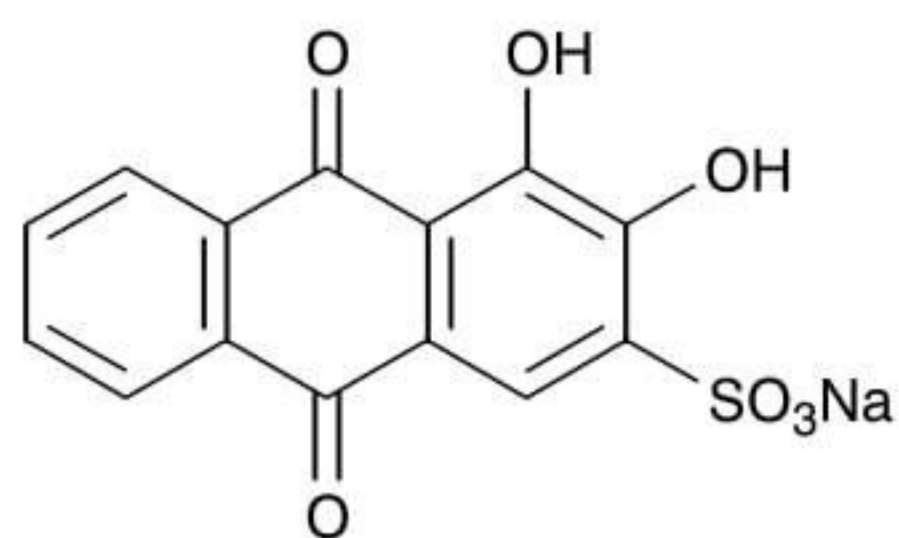
In 1996 Ciba introduced a new reactive black, Lanazol Black PV, that is an attractive alternative to established chrome blacks, even as regards price. It has been designed to give tinctorial strength, shade metamerism and light fastness that are close to those of the afterchromed complex of Eriochrome Black PV (5.83). Only in the case of fastness to extreme processes such as potting and cross-dyeing with acetic acid is the target standard not entirely achieved. To attain optimum exhaustion and good level dyeing behaviour, 2% o.w.f. Albeal B (Ciba) must be used and aftertreatment with ammonia is necessary to ensure the highest wet fastness ratings [92].

The new range of Lanazol CE (Ciba) metal-free reactive dyes for wool has been developed to offer the option of replacing chrome dyes in full depths by cost-effective alternatives. These five dyes (yellow, red, blue, navy and black) are based on the  $\alpha$ -

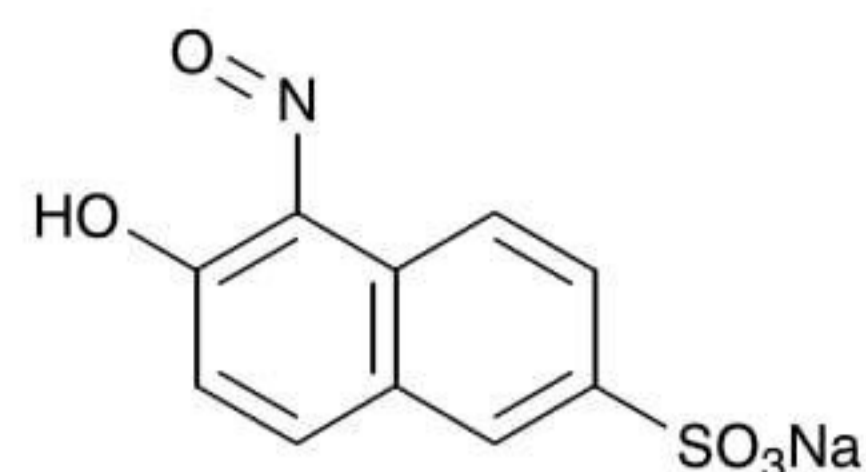


bromoacrylamide reactive system and can be shaded with existing Lanazol brands using the standard application methods for these dyes [93]. Lanazol Navy CE is particularly versatile, being suitable for the exhaust dyeing of untreated, chlorinated or machine-washable wool, as well as continuous dyeing, vigoureux printing and coloured discharge styles and in silk dyeing [90]. Excellent fastness to light and wet treatments with outstanding fixation, levelling and reproducibility are claimed for Lanazol CE dyes, which fulfil the requirements of the Oeko-Tex 100 ecolabel [76].

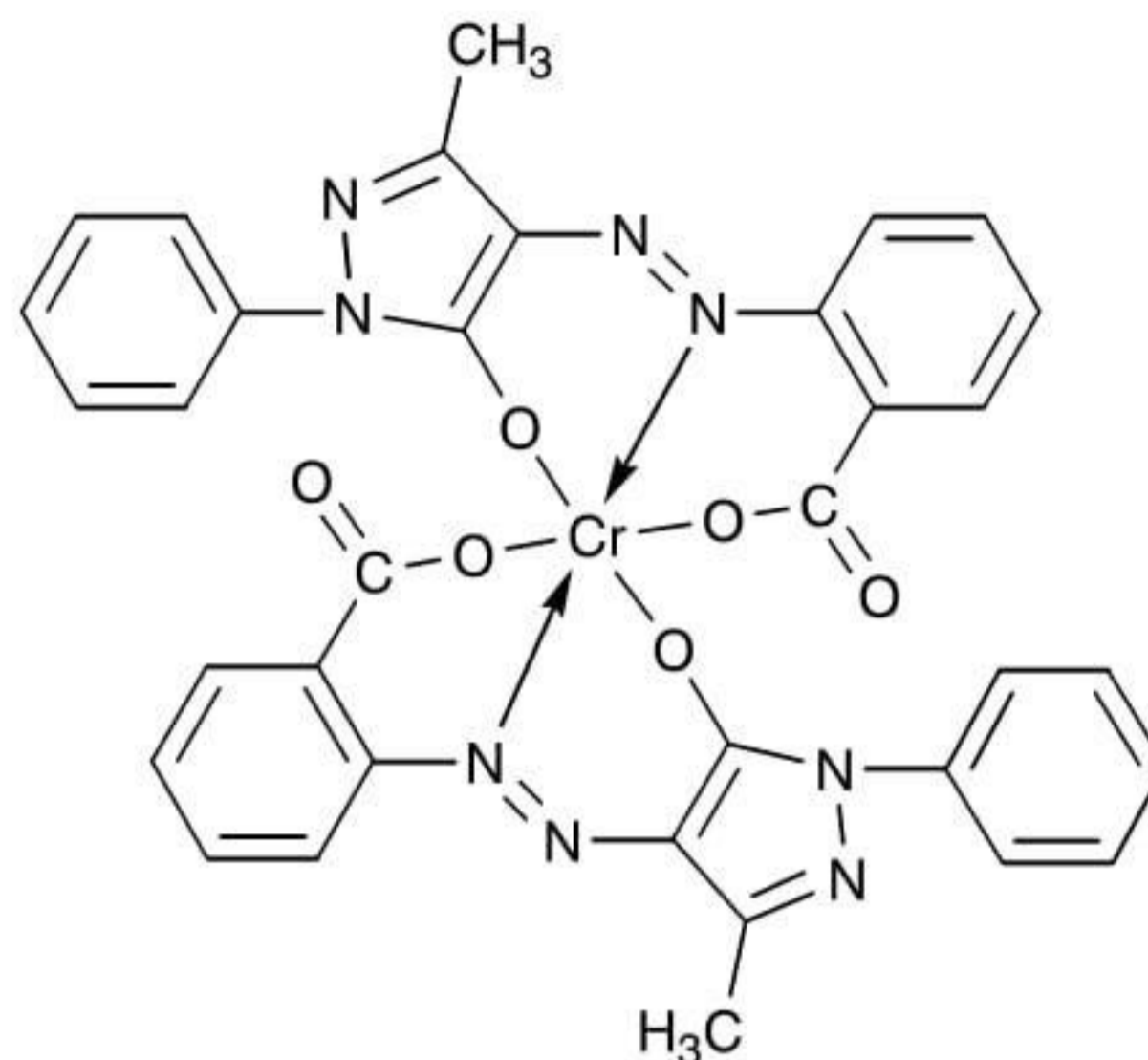
The influence of transition-metal salts, mordant dyes and premetallised acid dyes on the photodegradation of wool has been investigated [94]. Certain yellow dyes that absorb UV radiation in the 320–400 nm region will inhibit phototendering but most other dyes accelerate the process. The uranyl(II) ion ( $\text{UO}_2$ ) also absorbs in this region and was found to be an effective UV screen. Treatment with aluminium or iron(III) hydroxide brought about a light-induced strengthening of wool fabric, but a harsher handle developed on prolonged exposure. Treatment of wool with alizarin-3-sulphonate (5.84; CI Mordant Red 3) resulted in some light-induced increase of breaking strength but on aluminium-treated wool it was considerably more effective and durable for at least 6000 h irradiation. Wool pretreated with a uranyl salt followed by alizarin-3-sulphonate dyeing was phototendered extremely rapidly, in contrast to the protective effects when either component was applied separately. The mordant dye 1-nitroso-2-naphthol-6-sulphonate (5.85) on aluminium-mordanted wool imparted protection from strength loss for 3000 h but accelerated photodegradation on untreated wool. The 1:2 chromium-complex dyes CI Acid Yellow 59 (5.86) and Black 58 (5.4) did not significantly modify the rate of phototendering of wool, with or without an aluminium mordant.



5.84  
CI Mordant Red 3



5.85



5.86  
CI Acid Yellow 59

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