Some Aspects of the Chemistry of Metal Complex Dyestuffs *

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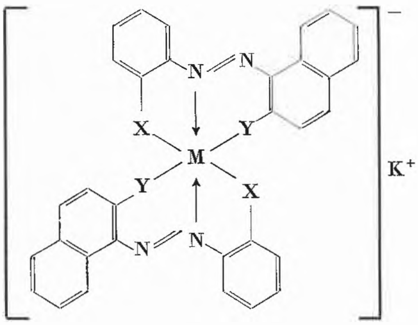
Summary

Metal complex formation by azo compounds is discussed in relation to the metal and the structure of the azo compound with particular regard to the effect of the electronic configuration of the former and the nature of the donor groups or atoms in the latter on the stability, stoicheiometry, geometry and oxidation state of the products obtained. The relevance of the various factors to the synthesis and practical application of 1:1 and symmetrical and unsymmetrical 2:1 chromium and cobalt complexes of tridentate azo compounds is considered in the light of current views regarding ligand replacement reactions and the influence of coordination on the reactivity of organic ligands.

Metal complexes of organic compounds enjoy an ever-increasing academic and commercial interest and their importance is well-known in many fields including catalysis biology, metal-winning and the technology of dyes and pigments where much progress has been made during the past few decades. Some indication of the importance of metal complexes in the latter field is afforded by the wide variety of metal complex dyes and pigments which have been employed commercially. These include chromium, cobalt and copper complexes of tridentate metallisable azo compounds such as *o,o'*-dihydroxy-diarylazo, *o*-hydroxyarylazopyrazolone, *o*-carboxy-*o'*-hydroxy-diarylazo and *o*-hydroxy-*o'*-amino-diarylazo types, copper complexes of arylazo-8-hydroxyquinolines and salicylaldoximes, chromium complexes of arylazosalicylic acids, copper, nickel and iron complexes of nitrosated arylazoresorcinols, copper chromium and cobalt complexes of formazans, iron complexes of nitrosonaphthols and nitrosohydroxyindazoles, and copper complexes of phthalocyanines.

The area is large and has been reviewed by many authors. It is not therefore the object of this paper further to review the subject; rather is it the intention to consider one area, medially metallised azo dyes (that is metal complex azo dyestuffs in which the azo group forms a part of the coordinating system), in relation to the metal and the structure of the azo compound with particular regard to the effect of the electronic configuration of the former and the number and nature of the donor groups in the latter on the stability, stoicheiometry, geometry, and oxidation state of the products obtained and the significance of these factors with regard to the synthesis and usefulness of these compounds as dyestuffs. Special reference is made to the effect of the azo ligand on the metal and the effect of the metal on the properties of the azo ligand.

Metal complexes of *o,o'*-dihydroxydiarylazo compounds were first prepared some 60 years ago and since that time a great deal of effort has been devoted to the study of this and related types and to their practical application as dyestuffs. Many notable advances have been made but probably the most important classes of dyes to emerge have been symmetrical and unsymmetrical 2:1 chromium and to a less extent cobalt complexes of tridentate metallisable azo compounds [I] which have been of major importance as dyestuffs for polyamide fibres for some 30 years. More recently, with the advent of fibre-reactive dyes, their use has been extended to cellulosic fibres.



X = —O—, —COO—
Y = —O—, —NH—
M = Cr^{III}, Co^{III}
K^+ = univalent cation

[I]

The term 'stability' will be used frequently and in order to avoid confusion the sense in which it is used will be clarified at this stage. The statement that a particular metal complex has inadequate 'stability' for it to be of value as a dyestuff in no way implies that the complex is thermodynamically unstable but simply that it undergoes demetallisation to some degree under dyebath conditions or during after-treatment processes. For example iron (III) complexes of *o,o'*-dihydroxydiarylazo compounds are thermodynamically stable

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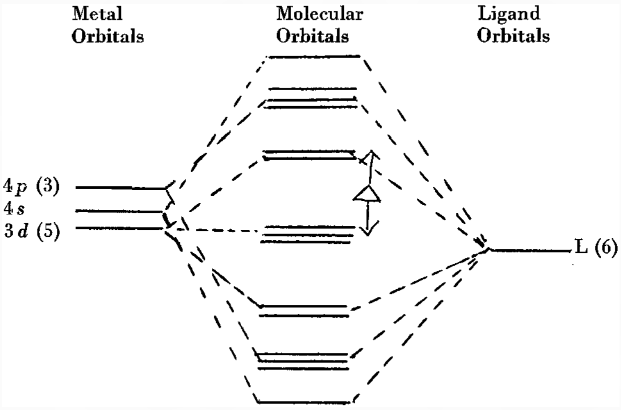
compounds and can be crystallised unchanged from a variety of solvents. They are however demetallised under relatively mildly acidic conditions and this 'instability' makes them of little or no value as dyestuffs. More precisely, to use TAUBE'S[3] classification, complexes of this type, although thermodynamically stable, are kinetically labile and readily undergo ligand exchange reactions, demetallisation involving replacement of the coordinated azo compound by different ligands, e.g. water. In contrast, chromium (III) and cobalt (III) complexes of *o,o'*-dihydroxydiarylazo compounds, which are 'stable' under corresponding acidic conditions, are kinetically inert and undergo ligand exchange reactions only slowly.

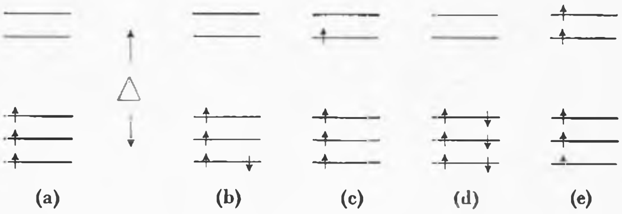
At this point it would be convenient very briefly and simply to consider octahedral complexes of first row transition metal ions from the point of view of molecular orbital theory in a purely qualitative fashion. If we consider only σ-bonding the molecular orbitals resulting from the combination of six atomic orbitals (s, px, py, pz, $dx^2{-}y^2$, dz^2) of the transition metal ion with six suitable ligand orbitals can be pictorially represented as [II].



[II]

Combination of the metal s orbital with a suitable ligand orbital produces two molecular orbitals a bonding orbital of lower energy and an anti-bonding orbital of higher energy. Similarly triply degenerate bonding and anti-bonding molecular orbitals are produced by combination of the metal p orbitals with ligand orbitals. Only two ($dx^2{-}y^2$, dz^2) of the metal d orbitals are involved in σ-bonding creating a situation in which the original fiive-fold degeneracy of the metal d orbitals disappears.

The six lower energy molecular orbitals are occupied by the twelve electrons contributed by the ligands and the metal d electrons are distributed between the next two sets of molecular orbitals. How the d electrons are distributed between these orbitals is determined by the energy gap $\triangle$ between them and this is dependent on the nature of the ligands involved in complex formation. In the case of trivalent chromium which has three d electrons the situation is simple and these occupy the lower energy orbitals [IIIa]. With an ion having four or more d electrons the orbitals occupied by the fourth and subsequent electrons is determined by the relationship between $\triangle$ and P, the energy required to cause electron pairing in an orbital. Thus, in a d^4 ion two situations are possible, one in which $\triangle$ is greater than P another in which P is greater than $\triangle$. In the former case electron pairing occurs to give a 'low spin' complex [IIIb] and in the latter a 'high-spin' complex [IIIc] is produced.

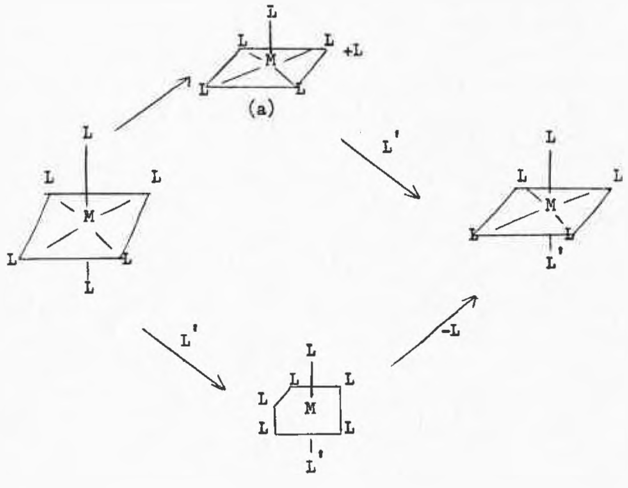


(a) (b) (c) (d) (e)

[III]

Octahedral d^6 cobalt (III) complexes derived from tridentate azo compounds invariably have low spin configurations [IIId] due to the high value of Δ in these complexes.

The stabilisation energy associated with the symmetrical d^3 and low-spin d^6 configurations is high. Complexes having these configurations are kinetically inert due to the considerable loss of stabilisation energy on forming a five-coordinate square-pyrimidal intermediate [IVa] by a dissociative mechanism (S_N1) or a seven-coordinate pentagonal bipyrimidal intermediate [IVb] by an associative mechanism (S_N2) in a ligand exchange reaction[4].



[IV]

Reverting to the iron complex example which was mentioned earlier, it might be asked why then does one not employ iron (II) complexes which would have d^6 configurations and could therefore be expected to be sufficiently 'stable' to be of value as dyestuffs? This introduces another factor—the oxidation state of the metal and how this is influenced by the dyestuff ligand.

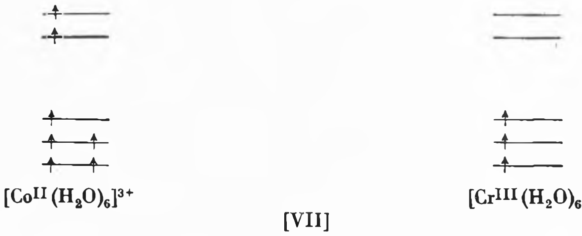
In general terms it is true to state that the relative stability of the oxidation states of a metal having two readily accessible oxidation states is determined by the nature of the ligands attached to the metal ion. This is illustrated in the case of cobalt and a number of simple ligands by the oxidation potentials [V].

$$
\begin{array}{lll}
[\mathrm{Co^{II}(H_2O)_6}]^{2+} \rightleftharpoons [\mathrm{Co^{III}(H_2O)_6}]^{3+} + \mathrm{e} & E_0 = -1{\cdot}84\,\mathrm{V} \\
[\mathrm{Co^{II}(NH_3)_6}]^{2+} \rightleftharpoons [\mathrm{Co^{III}(NH_3)_6}]^{3+} + \mathrm{e} & E_0 = -0{\cdot}1\,\mathrm{V} \\
[\mathrm{Co^{II}(CN)_6}]^{4-} \rightleftharpoons [\mathrm{Co^{III}(CN)_6}]^{3-} + \mathrm{e} & E_0 = +0{\cdot}83\,\mathrm{V}
\end{array}
$$

[V]

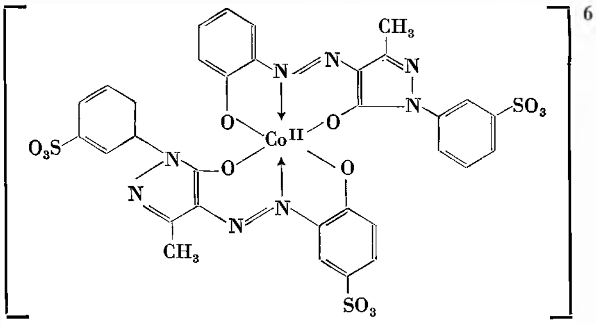
Thus in the case of the hexa-aquo cobalt ion the divalent oxidation state is preferred while the trivalent oxidation state is preferred in the hexacyano cobalt ion. It so happens that the favoured oxidation state of iron to which two molecules of an *o,o'*-dihydroxydiarylazo compound are coordinately bound is 3 and any attempt to from an iron (II) complex by the interaction of an iron (II) salt and an *o,o'*-dihydroxydiarylazo compound invariably gives the iron (III) complex with a labile d^5 configuration [IV]. These two factors which relate to the metal ion i.e. its oxidation state and electronic configuration, then, at least partially account for the restriction of the use of 2:1 metal complexes of tridentate azo compounds as dyestuffs to those of chromium (III) and cobalt (III) ions. They are also very relevant to the actual synthesis of the dyestuff complexes themselves. This becomes very apparent when one considers the very obvious differences which exist in practice in the synthesis of 2:1 cobalt and chromium complexes of tridentate azo dyestuffs. In the former case it is usual simply to treat an aqueous solution of the azo compound at about 60°C, with a solution of slightly more than the stoicheiometric amount of a cobalt (II) salt. Under these conditions formation of the 2:1 cobalt (III) complex of the tridentate azo compound is rapid. In contrast, formation of the 2:1 chromium complex of a tridentate azo compound by the interaction of the azo compound and a chromium (III) salt in aqueous solution is slow and the reaction normally goes to completion only after many hours at the boil.

This is a kinetic effect and arises from the fact that the soucre of cobalt is an aquated cobalt (II) salt having the 'labile' d^7 configuration which readily undergoes ligand exchange reactions, whereas the source of chromium is an aquated chromium (III) salt having the 'inert' d^3 configuration [VII].

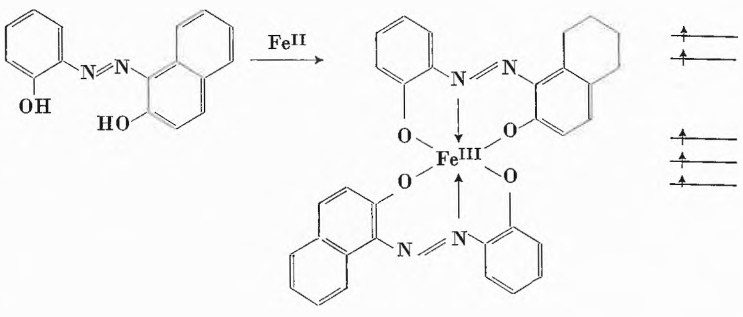

$[\mathrm{Co^{II}(H_2O)_6}]^{3+}$ $[\mathrm{Cr^{III}(H_2O)_6}]^{3+}$

[VII]

Thus the coordinated water molecules of the aquated cobalt (II) ion are readily replaced by the azo dyestuff molecules to give the 2:1 cobalt (II) complex of the latter which, because of its oxidation potential is rapidly oxidised to the cobalt (III) state. Cobalt (II) complexes of tridentate azo compounds e.g. 1-(3-sulphophenyl)-3-methyl-4-(2-hydroxy-4-sulphophenylazo)-5-pyrazolone [VIII] have been isolated[5] in the absence of oxygen and at very high *p*H and their very facile conversion to cobalt (III) complexes has been demonstrated.



[VIII]



[VI]

The use of cobalt (II) salts in the preparation of cobalt (III) complex azo dyestuffs does incur a penalty in that, although the change in oxidation state of the metal ion occurs partly as a result of aerial oxidation, some of the azo compound itself is reduced[5, 6, 7]. Various methods have been recommended[8] to avoid this, e.g. the use of sacrificial nitro compounds which are themselves reduced.

Chromium (II) salts having the labile d^4 configuration cannot be used to prepare chromium complexes of azo dyestuffs since their oxidation potential is such that oxidation to the chromium (III) state at the expense of the azo compound occurs more rapidly than the ligand exchange reaction.

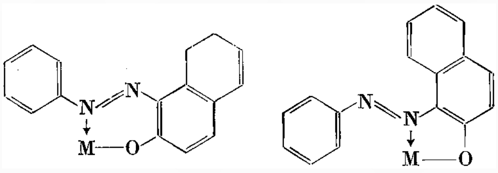
Having established that the formation of 2:1 chromium complexes of tridentate azo compounds by the interaction of hexa aquo chromium (III) salts and the azo compounds is a relatively slow reaction, it is worth considering in rather more detail. The overall reaction may be represented simple as [IXa]. In fact many reactions are involved and, simplifying the reaction scheme only slightly [IXb], one must invoke the intermediacy of the 1:1 chromium complex. When the reaction between a chromium salt and a tridentate azo dyestuff is carried out under conditions under which the 2:1 complex is stable, i.e. at relatively high pH, no 1:1 complex is detected in the reaction mixture. One must therefore conclude that the second part of the overall reaction proceeds very much more rapidly than the first and that the rate-determining step is involved in the formation of the intermediate 1:1 complex. Unfortunately, although several authors[9] have studied the kinetics of the overall reaction, no conclusive results have been obtained since the system is not really suitable for study by the usual methods because of the very slow rate of reaction[10]. However, one can consider the reactions involved and draw certain conclusions. As coordination of a tridentate azo compound to a metal ion must proceed by three distinct steps in which successive coordinated water molecules are displaced from the aquated metal ion, it is reasonable first to consider the formation of metal complexes of bidentate azo compounds since the complex of a bidentate type may be regarded as comparable to one of the intermediates in the formation of a complex of a tridentate type.

$$2\,DH_2 + [Cr(H_2O)_6]^{3+}\,3X^- \rightleftharpoons [D_2Cr]^-\,H^+ + 3HX + 6H_2O \quad (a)$$

$$\left.\begin{array}{l} DH_2 + [Cr(H_2O)_6]^{3+}\,3X^- \rightleftharpoons [DCr(H_2O)_3]^+ + 2HX + 3H_2O \\ DH_2 + [DCr(H_2O)_3]^+X^- \rightleftharpoons [D_2Cr]^-\,H^+ + HX + 3H_2O \end{array}\right\} (b)$$

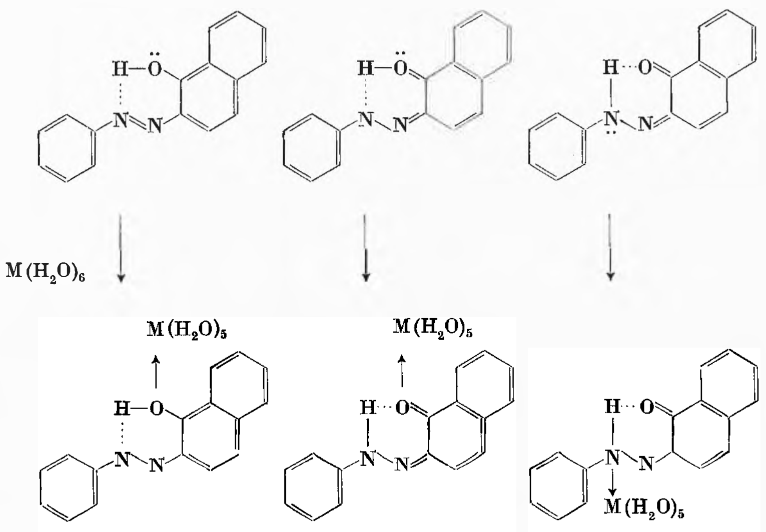
[IX]

The first step in the formation of a metal complex of an o-hydroxydiarylazo compound must involve replacement of a coordinated water molecule on the metal ion by one of the donor atoms in the azo compound by either an associative or a dissociative mechanism. This may of course occur through an ionised form of the ligand but this appears very unlikely since o-hydroxydiarylazo compounds are very weak acids and metal complex formation occurs under conditions under which



(a) (b)

[X]



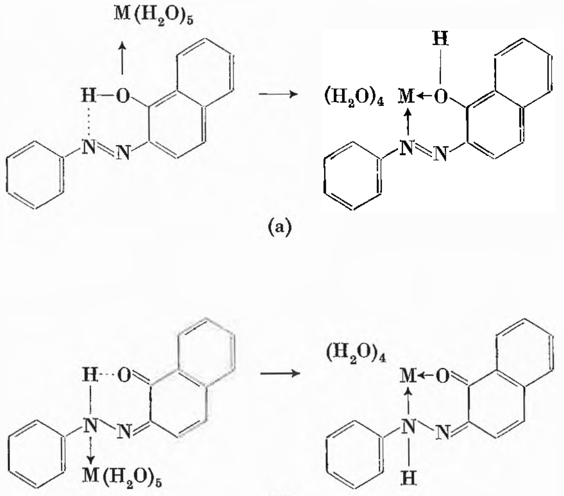
(a) (b) (c)

[XI]

the ligand is unlikely to be ionised. It has been established[11] that the β-nitrogen atom of the azo group relative to the *o*-hydroxy substituent is involved in coordination, the metal ion being a member of a 6-membered chelate ring [X a rather than X b].

It is also known[12] that ligands of this type exist in solution as equilibrium mixtures of the *o*-hydroxyazo and hydrazone forms. The first step in coordination may therefore occur through either the oxygen atom or the nitrogen atom of the ligand in a variety of ways [XI; a, b, c] to give a complex in which the ligand functions in a monodentate fashion.

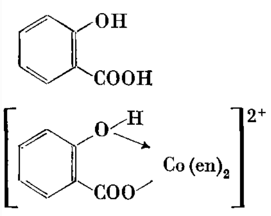
Of these possibilities (a) and (c) appear more likely than (b) since the next probable step is formation of a chelate complex by replacement of a further molecule of coordinated water [XII; a, b].



[XII]

Proton loss from the ligand may occur when it is bound to the metal atom by a single coordinate bond as a result of the enhancement of the acidity of the ligand by the polarisation associated with coordination. It is more probable, however, that proton loss follows the formation of the chelate complex when this effect is much more marked (cf. XIII).

$[Cr^{III}(H_2O)_4Cl_2]^-$ $pK_A = 5.7$



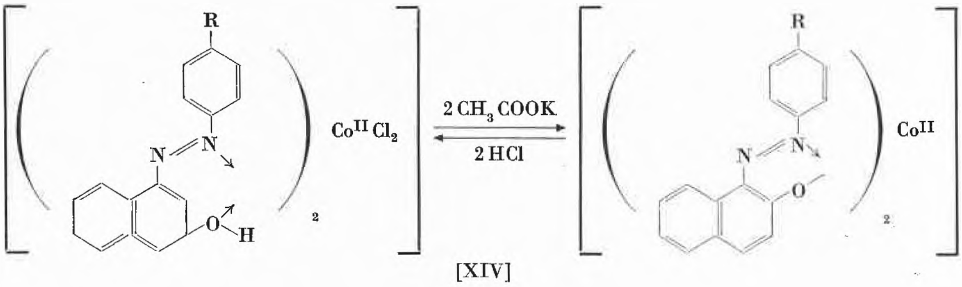
$pK_A(OH) = 13.2$

$pK_A(OH) = 1.8$

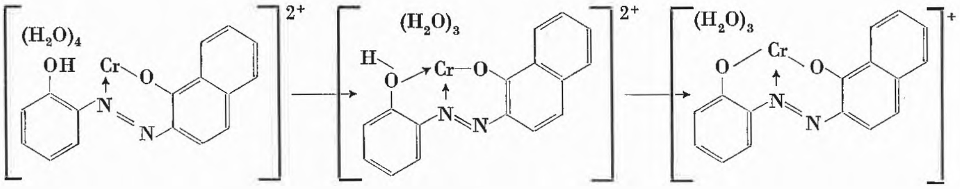
[XIII]

In support of this, cobalt complexes of *o*-hydroxydiarylazo compounds have been isolated[13] in which no proton loss from the azo compound has occurred. These compounds [XIV] are nonconducting in nitroethane solution and have magnetic susceptibilities (5.2 BM) consistent with their formulation as octahedral cobalt (II) complexes. They readily lose the elements of HCl on treatement with potassium acetate to give the tetrahedral 2:1 cobalt (II) complex of the deprotonated ligand. This reaction is reversible.

In the case of an *o,o'*-dihydroxydiarylazo compound, the next step in the reaction sequence is replacement of a further coordinated water molecule by the remaining phenolic oxygen atom to give a complex in which the metal atom is a member of two annelated chelate rings. Proton loss from the chelated azo compounds is then promoted by the polarisation associated with coordination [XV].

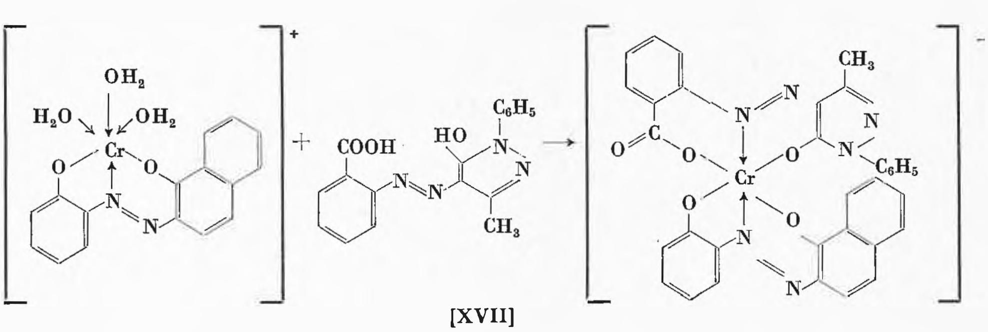


[XIV]



[XV]

Thus five steps are involved in the overall reaction between a hexa-aquo chromium (III) salt and a tridentate metallisable azo compound to form the 1:1 chromium complex dyestuff: three ligand replacement reactions and two ionisation stages. Studies with other ligands lead to the conclusion that the probable rate-determining step is replacement of the first of the six coordinated water molecules in the highly symmetrical hexa-aquo chromium (III) ion by one of the donor functions of the ligand. For example, it has been shown[14] that the rate of reaction between the hexa-aquo chromium (III) ion and the bidentate oxalate or malonate ions was to form monochelate complexes, although slow, is effectively the same as that between the hexa-aquo chromium (III) ion and acetate ion to form the monoacetate complex [XVI], i.e. the second, chelation step is relatively rapid. Similarly it has been demonstrated[15] that the first step in the reaction between the hexa-aquo chromium (III) ion and glycine to form a chelate complex is slow and determines the overall rate.



[XVII]

$$[Cr(H_2O)_6]^{3+} + CH_3COO^- \xrightarrow{\text{slow}} [(H_2O)_5CrOOCCH_3]^{2+} + H_2O$$

$$[Cr(H_2O)_6]^{3+} + \bar{O}OC{-}CO\bar{O} \xrightarrow{\text{slow}} [(H_2O)_5CrOOC{-}COO]^+$$

$$\xrightarrow{\text{rapid}} \left[(H_2O)_4Cr\begin{array}{l} OOC \\ \quad\ | \\ OOC \end{array}\right]^+$$

[XVI]

In considering improved methods for the preparation of chromium complexes of tridentate metallisable azo dyestuffs one must therefore examine means by which the first step can be accelerated. It is known[16] that the conjugate base of the highly symmetrical hexa-aquo chromium (III) ion undergoes ligand exchange reactions more readily than the latter as a result of the labilising effect of the hydroxo group. Since the hexa-aquo chromium (III) ion is a relatively strong acid,[17] pK_A 3.8, the reaction between chromium salts and tridentate azo compounds would be expected to proceed more rapidly at high than at low pH values. This is borne out in practice but the reaction is complicated by the formation of hydroxo-bridged or 'olated' and oxo-bridge or 'oxolated' chromium species under these conditions and invariably gives the 2:1 complex.

In an alternative approach one may consider the use of less stable species than the hexa-aquo chromium (III) ion as a source of the metal in the chroming reaction. The chromium (III) ion has 'class a' character, to use CHATT's[18] classification, or is a 'hard' acid using PEARSON's[19] notation and forms its most stable complexes with 'hard' or unpolarisable ligands such as water. It is not surprising, therefore, that chromium complexes derived from 'softer' or more polarisable ligands than water, e.g. hexa-urea chromium (III) chloride[7] and potassium tris-(oxalato) chromium (III)[20], react much more rapidly with tridentate metallisable azo compounds than does hexa-aquo chromium (III) chloride. However, the usual product in these cases is again the 2:1 complex of the azo compound and the method is not suitable for the preparation of complexes having 1:1 stoicheiometry. The latter, which are the principal products when tridentate azo compounds react with aquated chromium salts at low pH (about 1.9 or below), are key intermediates in the preparation of the commercially important unsymmetrical 2:1 chromium complex dyestuffs. These are prepared by the interaction of the 1:1 chromium complex of a tridentate azo compound with an equimolecular amount of a different tridentate azo compound at relatively high pH [XVII], the sequence of reactions presumably being similar to those discussed earlier.

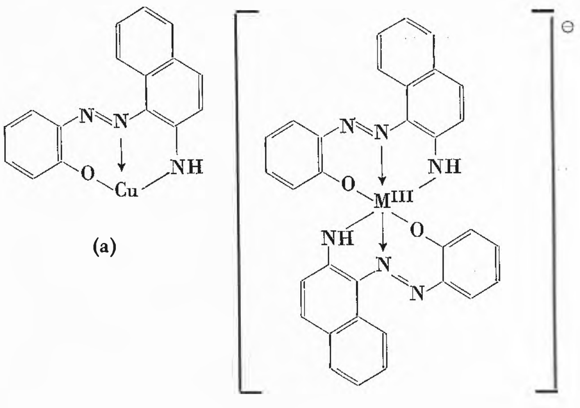
In sharp contrast to chromium complexes it has proved impossible to prepare 1:1 cobalt complexes of tridentate metallisable azo dyestuffs in which the coordination sphere of the metal is completed by three molecules of water. When a tridentate azo compound is treated with a hydrated cobalt (II) salt, little reaction occurs at very low pH values and at higher pH values the product is invariably the 2:1 cobalt complex. However, 1:1 cobalt (III) complexes of tridentate metallisable azo compounds have been prepared in which the coordination sphere of the metal is completed by three molecules of coordinated ammonia. Complexes of this type are prepared under an inert atmosphere by the interaction of a tridentate azo compound and a cobalt (II) salt in the presence of a large excess of ammonia. In every case the product is the kinetically inert, diamagnetic cobalt (III) complex, oxidation occurring at the expense of the azo compound[7].

It may therefore be inferred that the nature of the product in these reactions is governed by the oxidation potential of the intermediate 1:1 complex. In the former case this is such that oxidation to the kinetically inert cobalt (III) state does not occur under the conditions of the reaction and the kinetically labile 1:1 cobalt (II) complex undergoes further ligand exchange reactions to give the 2:1 cobalt (II) complex which it then oxidised to the cobalt (III) state [XVIIIa]. Support for this view is provided by the isolation by Wittwer[5] of 2:1 cobalt (II) complexes of tridentate azo compounds. In the latter case the oxidation potential of the 1:1 cobalt (II) complex, in which the coordination sphere of the cobalt ion is completed by three molecules of ammonia, is such that oxidation to the kinetically inert cobalt (III) state occurs rapidly [XVIIIb]. Like 1:1 chromium complexes of tridentate azo compounds, such complexes will react with an equimolecular amount of the same or a different tridentate azo compound to give a symmetrical or an unsymmetrical 2:1 cobalt (III) complex dyestuff.

$$\begin{tikzcd}
DH_2 + [Co^{II}(H_2O)_6]^{2+} \arrow[r] & \substack{[D\,Co^{II}(H_2O)_3] \\ \text{(labile)}} \arrow[r, "DH_2"] \arrow[d, "\times" marking] & {[D_2Co^{II}]^{2-}} \arrow[r] & D_2Co^{III}]^- \\
 & {[DCo^{III}(H_2O)_3]^+} & & \\
DH_2 + [Co^{II}(NH_3)_6]^{2+} \arrow[r] & {[D\,Co^{II}NH_3)_3]} \arrow[r, "DH_2", "\times" marking] \arrow[d] & {[D_2Co^{II}]^{2-}} \arrow[r] & {[D_2Co^{III}]^-} \\
 & \substack{[DCo^{III}(NH_3)_3]^+ \\ \text{(inert)}} & &
\end{tikzcd}$$

[XVIII]

When a ligand becomes coordinated to a metal ion its properties are markedly modified and coordination may help, hinder or even completely change the reactions which the ligand can undergo. An example of this has already been encountered in the enhancement of the acidity of the phenolic hydroxyl groups in *o,o'*-diarylazo compounds when these become coordinated to a metal ion. *o*-Hydroxy-*o'*-aminodiarylazo compounds offer an even more dramatic example of this effect. The ability of *o*-amino-*o'*-hydroxydiarylazo compounds to react with transition metal salts to form complexes in which two protons are lost from the azo compound was first observed[22] with the formation of the copper complex of 1-(2-hydroxyphenylazo)-2-naphthylamine [XIX a]. Subsequently 2:1 chromium and cobalt complexes were prepared and formulated[23] as [XIXb].

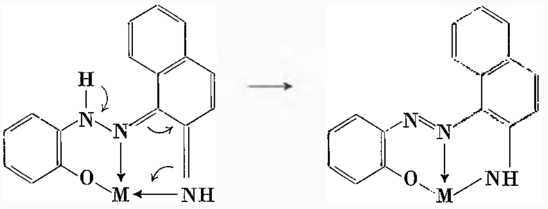


(b) $M = Cr^{III}, Co^{III}$

[XIX]

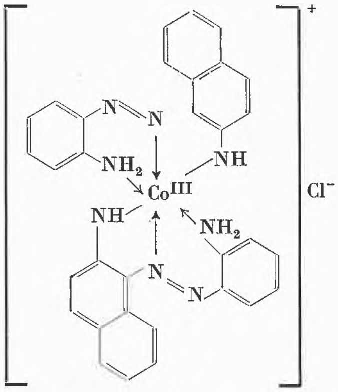
At first, sight loss of a proton from the amino group in such a compound is rather surprising since aromatic amines such as aniline form metal complexes with no loss of proton. However, proton loss from the hydrazone form of the ligand appears considerably less surprising since hydrazones are, in general, acidic in character. The acidity of the hydrazone is markedly enhanced in a complex such as [XX] as a result of the polarisation associated with coordination. This may be compared with the enhanced acidity of 2,4-dinitrophenyl hydrazones over that of the corresponding phenyl hydrazones.

Strong support for the view that proton loss from coordinated *o*-hydroxy-*o'*-aminodiarylazo compounds does in fact occur through the hydrazone form of the



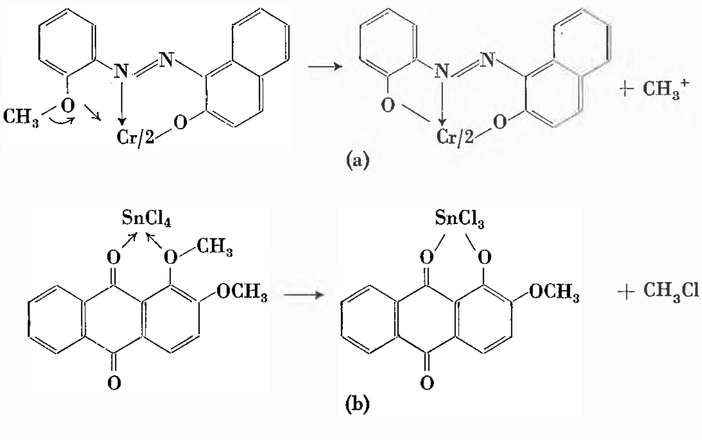
[XX]

ligand is provided by the observation[24] that only one proton is lost from an *o,o′*-diaminoazo compound when the latter forms a metal complex, e.g. [XXI].



[XXI]

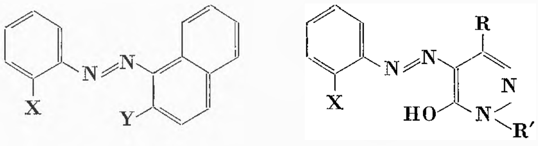
The effect on the properties of ligands of the polarisation associated with coordination is utilised in the synthesis of chromium complexes of certain *o,o′*-dihydroxydiarylazo compounds which are themselves difficult to prepare. In certain cases, diazo oxides derived from *o*-aminophenols react only slowly with naphthol coupling components giving low yields of impure products. This problem can be overcome by using a diazotised *o*-alkoxyaniline in place of the diazo to obtain an *o*-methoxy-*o′*-hydroxydiarylazo compound. Dealkylation of compounds of this type normally requires very severe conditions but in the presence of a chromium salt, this proceeds under relatively mild conditions[25] to give the 2:1 chromium complex of the corresponding *o,o′*-dihydroxyazo compound. In this reaction [XXII a] dealkylation is promoted by coordination of the methoxy group. A direct analogy is to be found[26] in the selective dealkylation of 1,2-dimethoxyanthraquinone in the presence of $SnCl_4$ [XXIIb].



[XXII]

Other examples of the effects of coordination on the properties of dyestuff ligands are to be found in the oxidative coppering[27] of *o*-hydroxydiarylazo compounds to obtain the copper complex of the corresponding *o,o′*-dihydroxydiarylazo compound and the hydrolytic coppering[28] of *o*-chloro-*o′*-hydroxydiarylazo compounds again to obtain the copper complex of the corresponding *o,o′*-dihydroxydiarylazo compound. The template effect of the metal ion in the synthesis of copper phthalocyanine is also noteworthy.

2:1 Chromium and cobalt complexes of a wide variety of tridentate metallisable azo compounds [XXIII] have been examined as potential dyestuffs but only those derived from the *o,o′*-dihydroxydiarylazo pyrazolone, *o*-carboxy-*o′*-hydroxydiarylazo, *o*-carboxyarylazo pyrazolone and *o*-hydroxy-*o′*-aminodiarylazo systems find practical application.

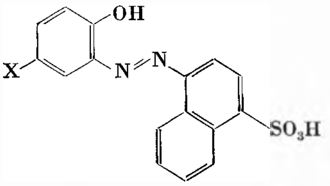


X	Y	
OH	OH	(a)
OH	NH_2	(b)
COOH	OH	(c)
$AsO(OH)_2$	OH	(d)
SO_3H	OH	(e)
etc.		

X = OH, COOH

[XXIII]

The principal reason for this is the relative instability of the other systems. The main factors which influence the thermodynamic stabilities of chelate complexes are chelate ring size, the number of chelate rings per ligand molecule, the basicity of the ligand and the nature of the metal. The latter has been discussed at length and here we are concerned only with those ligands which form two annelated chelate rings with the metal. The main factors under consideration are therefore chelate ring size and ligand basicity. In this context basicity refers to that of the anion which is actually involved in coordination rather that of the unionised ligand molecule. Basicity may be regarded in simple terms as a measure of the ability of a compound to bind a proton and therefore as a measure of the availability of a lone pair of electrons for coordinate bond formation. If no steric factors are involved it follws then that in a series of related ligands coordinately bound to the same metal the most basic will usually form the most stable complex. Alternatively the most strongly ionised, or acidic, free ligand will form the least stable complex. This has been amply demonstrated[29] in the copper complexes of a series of related *o*-hydroxydiarylazo dyestuffs [XXIV].

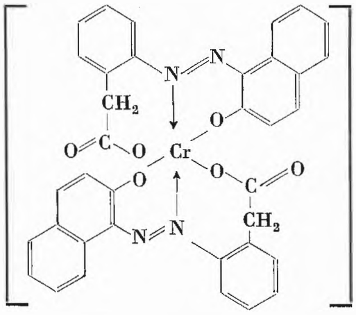


X	pK_A(OH)	log K
$-NO_2$	8.1	17.2
$-Cl$	8.15	17.6
$-COCH_3$	8.2	17.8
$-CH_3$	8.35	18.2
$-NH_2$	8.45	18.9
$-OCH_3$	8.5	19.2

[XXIV]

It is to be expected, therefore, that complexes of *o,o'*-dihydroxy-diarylazo compounds will be more stable in the thermodynamic sense than those of the more acidic *o*-carboxy-*o'*-hydroxy-diarylazo compounds and this has been shown[30] to be true. Similarly the stability of the chromium complexes of the related series of ligands [XXIII c, d, and e] falls with increasing acidity of the parent ligand. Thus 2:1 chromium complexes of *o*-carboxy-*o'*-hydroxydiarylazo compounds find wide technical application as dyestuffs. Similar complexes derived from azo compounds in which the carboxyl group is replaced by the more acidic arsonic acid group give dyeings having much inferior fastness properties[31] due to their lower stability and 2:1 chromium complexes of azo compounds in which the carboxylic acid group is replaced by the highly acidic sulphonic acid group are very unstable and readily undergo demetallisation[32].

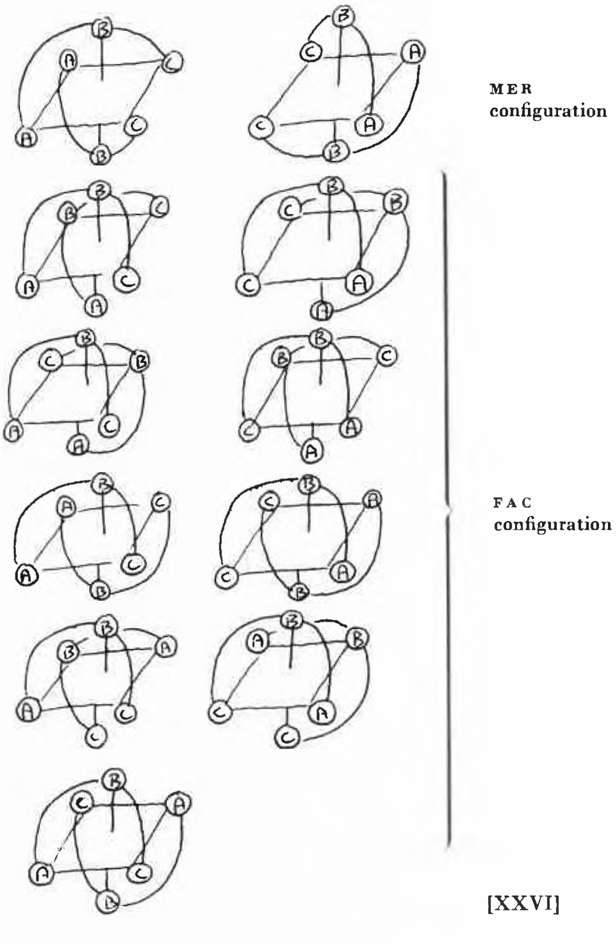
With regard to the influence of the sizes of the annelated chelate rings on the stability of metal complexes of tridentate metallisable azo compounds it has long been known[33] that complexes derived from ligands which form annelated 5,6 and 6,6 membered chelate rings are stable and it was not until relatively recently that a 2:1 chromium complex [XXV] which contained annelated 6,7 membered chelate rings was synthesised[34]. However, none of the latter finds commercial application.



[XXV]

The most marked effect of the formation of a 5,6 [XXIII a, b] or a 6,6 [XXIII c] annelated chelate ring system relates to the stereochemistry of the derived 2:1 chromium and cobalt complexes. Isomerism in 2:1 metal complex dyestuffs is of considerable interest because of its implications regarding the stability of such complexes. Various types of isomerism have been demonstrated in metal complexes of tridentate azo dyestuffs and these arise in a variety of ways.

1. In 2:1 chromium and cobalt complexes of tridentate azo compounds the ligand molecules can adopt meridial or facial positions on the valency octahedron of the metal ion [XXVI]. It can be seen that the meridial configuration permits only an enantiomorphic pair of isomers while four enantiomorphic pairs and one centrosymmetric isomer are possible in the case of the facial configuration.

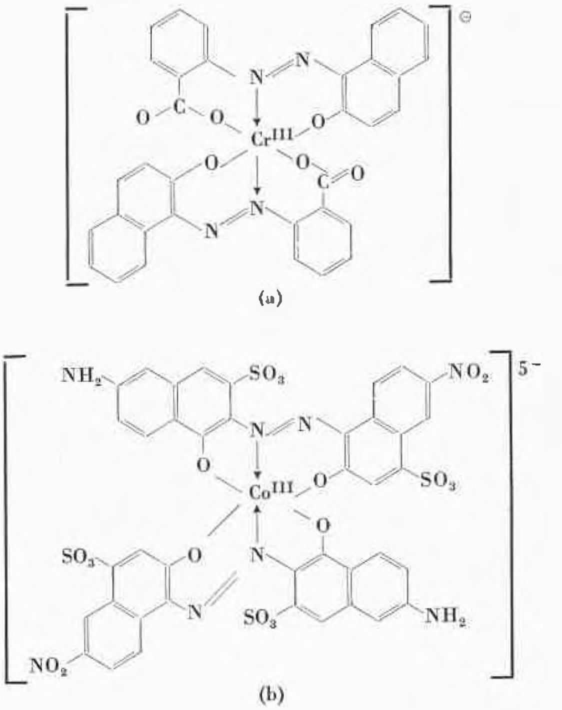


[XXVI]

Although Peiffer[35] succeeded in resolving the 2:1 chromium complex of an *o*-carboxyarylazopyrazolone dyestuff into 2 isomers as long ago as 1941, this provided little conclusive information regarding the geometry of the complex. A further 20 years elapsed before any further information became available when SCHETTY[36] published the first of a series[37] of papers on this subject in which he described the chromatographic separation of the 2:1 chromium complex of an *o*-carboxy-*o'*-hydroxy-diarylazo compound, 1-(2-carboxyphenylazo)-2-naphthol [XXVIIa] into four components. The four components each had the same empirical formula but different electronic spectra and solubility properties. Of prime importance was the observation that each isomerised readily in solution to give an equilibrium mixture of the four components which were considered to be geometrical isomers and therefore to have facial configurations.

Chromatographic separation of the 2:1 cobalt complex of the *o,o'*-dihydroxydiarylazo compound, 2-amino-6-(2-hydroxy-6-nitro-4-sulphonaphth-1-ylazo)-5-naphthol-7-sulphonic acid, [XXVII b] into two isomers has been achived by MORRIS[38]. These may well be a pair of enantiomers with meridial configurations but they possess markedly different degrees of cellulose substantivity. Like the various isomeric 2:1 chromium complexes examined by SCHETTY, the individual isomers are each rapidly converted into an equilibrium mixture in hot aqueous solution.

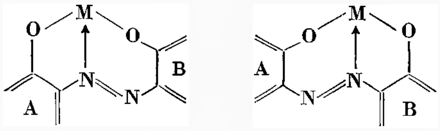
2. In metal complexes derived from unsymmetrical *o,o'*-dihydroxy-diarylazo dyestuffs the possibility exists of isomerism as a result of different nitrogen atoms of the azo group being involved in coordination to the metal [XXVIII]. Recently PFITZNER[39] has demonstrated isomerism of this type in a number of copper, nickel, and 2:1 chromium and cobalt complexes of unsymmetrical *o,o'*-dihydroxy-diarylazo compounds. Again the individual isomers are readily interconverted as shown by the facility with which equilibrium mixtures are obtained in solution.



(a)

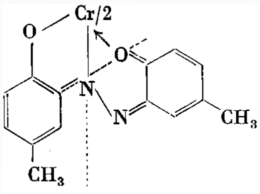
(b)

[XXVII]



[XXVIII]

3. The third type of isomerism in 2:1 chromium and cobalt complexes depends upon sp^3 hybridisation of the nitrogen donor atom in the hydrazone form of the ligand. This creates a situation in which the ligand can adopt two non-planar configurations [XXIX] giving rise to 3 possible conformers (+ 3 mirror images) in meridial complexes.

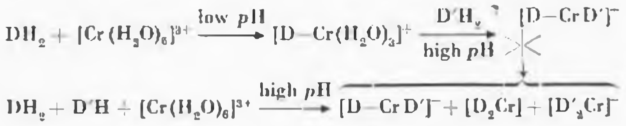


sp^3, tetrahedral nitrogen

[XXIX]

Isomerism of this type has recently been demonstrated by SCHETTY[40] who also showed that the various isomers were mutually inter-convertible in ethanolic solution.

One of the most important facts to emerge from studies on isomerism in 2:1 chromium and cobalt complexes of tridentate azo compounds is the facile interconversion of isomers which must proceed through a process of breaking and reforming bonds between the metal and the various donor atoms in the ligands.



[XXX]

Presumably similar processes must operate with unsymmetrical 2:1 chromium and cobalt complexes but it is very significant that such complexes do not undergo ligand redistribution in solution to give equilibrium mixtures comparable to those obtained by metallising mixtures of tridentate dyestuffs [XXX]. It must be concluded therefore that the ligands do not become completely detached from the metal in isomerisation reactions. Comparable results have been observed in the isomerisation[41] of potassium diaquo-dioxalato chromium (III) and the racemisation[42] of optically active potassium trisoxalato chromium (III) when no exchange with free ligand in solution occurs. Thus, while it is not practicable to take advantage of desirable technical properties of particular isomers of 2:1 chromium and cobalt complexes of tridentate azo compounds, e.g. the high cellulose substantivity of one the isomers of [XXb], because of the facility with which such compounds isomerise in solution, the technically important unsymmetrical 2:1 complexes are capable of practical application because they show little tendency to disproportionate in solution.

The synthesis and properties of 1:1 and symmetrical and unsymmetrical 2:1 chromium and cobalt complexes of tridentate metallisable azo compounds serve to illustrate within one series of related, commercially important compounds a number of the interesting facets of coordination chemistry, in particular the significance of the electronic configuration of the metal, the influence of coordination on the properties of the organic ligands and the effect of the latter on the properties of the metal. Work carried out in this area has made a considerable contribution to fundamental knowledge on coordination compounds in general and the application of knowledge gained in other areas of coordination chemistry has resulted in a number of important advances in the field of metal complex dyestuffs. There can be little doubt that this mutually beneficial interaction will be a continuing process.

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