MORE ABOUT INORGANIC COMPLEXES

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This article is a sequel to the one which appeared earlier in this Journal ("Inorganic Complexes: An Introduction" *Hyphen Vol. I,* Number 3, Spring 1978, pp. 31 — 39) and which dealt with certain aspects of the chemistry of complexes, notably: their definition, stereochemistry, nomenclature and some of their chemical properties. In this article we shall examine the stability of complexes and review some of the applications of coordination compounds in chemistry.

The Stability of Complexes

If a few crystals of copper (II) sulphate are dissolved in water, a sky-blue solution is obtained. On adding drops of concentrated hydrochloric acid to the solution, its colour changes to lime-green. If this green solution is diluted with water, its colour goes back to sky-blue; and this changes to indigo if excess aqueous ammonia is added. This indigo colour is not destroyed when the solution is diluted but if a few millilitres of a solution of sodium salicylate are added, then, the indigo colour is promptly replaced by a pale green one. Finally if this green solution is treated with a few drops of sodium ethylenediaminetetraacetate (EDTA), a blue colour is obtained which is not noticeably affected by the addition of reasonable amounts of water, hydrochloric acid, ammonia or salicylate ion.

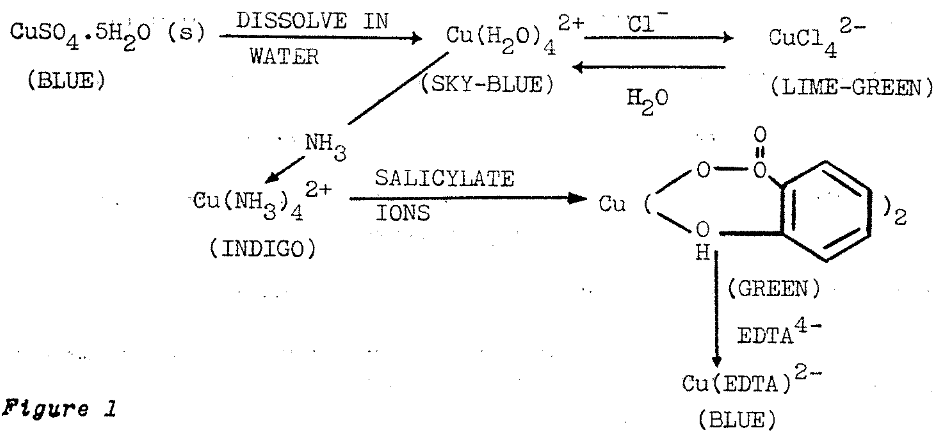

Figure 1

The colour changes occur as various copper complex ions get made and are destroyed giving rise to others in the process. The scheme above explains all.

From the above we can conclude that the chlorocuprate (II) ion is not particularly stable with respect to the aquo copper complex, the tetraamminecopper (II) is fairly stable but not with respect to replacement by the bidentate salicylate ion. And the stablest system is obtained when we use the sexidentate ethylenediaminetetraacetate ion, $EDTA^{4-}$.

If we consider reactions occurring in aqueous solution, the prospective ligand species (e.g. ammonia, chloride, cyanide etc) is involved in a competition with the water molecules for the metal ion. The formation of a complex ion ML_6 from the hexaquo complex can be represented by equations of the type

$$M(H_2O)_6 + L = M(H_2O)_5L + H_2O \quad \ldots \text{(I)}$$

$$M(H_2O)_5L + L = M(H_2O)_4L_2 + H_2O \quad \ldots \text{(II)}$$

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$$M(H_2O)L_5 + L = ML_6 + H_2O \quad \ldots \text{(VI)}$$

where we have ignored the charges on the metal ion and the ligands L. If, again for convenience, we also omit the water ligands, we can write expressions for the equilibrium constants for the above equations, termed *stepwise stability constants,* thus

For reaction I	K_1	=	$[ML]/[M][L]$
For reaction II	K_2	=	$[ML_2]/[ML][L]$
For reaction VI	K_6	=	$[ML_6]/[ML_5][L]$

If we combine the above steps into one *formal* overall reaction we get

$$M + 6L = ML_6$$

and for this hypothetical reaction, the equlibrium constant, K*f*, is given by

$$K_f = [ML_6]/[M][L]^6$$

K*f* is called the *overall stability constant* of the complex ion.

It is not difficult to show that the overall stability constant is related to the stepwise stability constants by the equation

$$K_f = K_1K_2K_3K_4K_5K_6$$

Kf is a measure of the energetic stability of the complex ion. Values for the stepwise stability constants of a few systems are given in the table below.

STABILITY CONSTANTS OF METAL COMPLEXES AT 25°C

Metal Ion	Ligand	Log K1	Log K2	log K3	log K4	log K5	log K6
Co^{2+}	NH_3	2.11	1.63	1.05	0.76	0.18	-0.62
Ni^{2+}	NH_3	2.67	2.12	1.61	1.07	0.62	-0.09
Cu^{2+}	NH_3	3.99	3.94	2.73	1.97	—	—
Cu^{2+}	Cl^-	0.00	-0.7	-1.5	-2.3	—	—
Fe^{3+}	F^-	5.21	3.95	2.70	—	—	—
Hg^{2+}	I^-	12.87	10.95	3.78	2.23	—	—
Cd^{2+}	CN^-	5.18	4.42	4.32	3.19	—	—
Cu^{2+}	$EDTA^{4-}$	18.8	—	—	—	—	—
Fe^{3+}	$EDTA^{4-}$	25.1	—	—	—	—	—
Hg^{2+}	$EDTA^{4-}$	21.8	—	—	—	—	—

Suppose we consider the equilibrium

$$[Cu(NH_3)_4]^{2+} \quad + \quad 4\,H^+(aq) \quad = \quad [Cu^{2+}(aq)] \quad 4\,NH_4^+(aq)$$

The equibrium constant is given by

$$Kc \quad = \quad [Cu^{2+}]\,[NH_4^+]^4 \;/\; [Cu(NH_3)_4^{2+}]\,[H^+]^4$$

Furthermore, one can easily show that

$$Kc \quad = \quad Kb^4/KfKw^4$$

where Kb is the base dissociation constant of ammonia, Kw is the ionic product of water and Kf is the overall stability constant of tetraamminocopper (II). Substitution of the values of the various constants in the last equation gives a numerical value for Kc of about 10^{24}. Thus, the reaction is energetically favoured. In fact, on adding acid to tetraamminocopper (II) ions, the ammino complex is rapidly destroyed and replaced by the aquocopper (II ion. A similar analysis of the reaction

$$[Co(NH_3)_6]^{3+}(aq) \quad + \quad 6\,H^+(aq) \quad = \quad Co^{3+}(aq) \quad + \quad 6\,NH_4^+(aq)$$

shows that its Kc value is also very large, but, in fact, the cobalt complex remains unaffected by the addition of acid. This situation is analogous with that of a mixture of carbon and oxygen which should be expected to react spontaneously at about room temperature since Kc for the conversion
$C + O_2 = CO_2$ is very large at this temperature. The cobalt complex, like the carbon/ oxygen mixture represents a kinetically stable system, the dissociation of the complex being prevented by the high activation energy of the reaction. We say that the tetraamminecopper (II) complex is *labile* whereas that of cobalt is not. Unless complexes are labile, any predictions made on the

basis of Kf values are, in fact, not realised in practise. This, of course, is a problem which bedevils any thermodynamic argument. concerning change in any chemical system.

Finally, it can be seen, on inspection of the Table above, that the values for Kf for the EDTA complexes are exceptionally high. This is true for all polydentate chelating complexes, which are known to form very stable complexes.

Complexes at Large

Coordination chemistry has many applications. The following examples serve to illustrate some of the more important of these applications.

(a) Qualitative Analysis

The colour of complexes is often used as a confirmatory test for the presence of a number of metals. Thus, copper (II) in solution is readily identified by the characteristic indigo colour of its amminocomplex, iron (III) is detected by the blood red colour formed with thiocyanate ions (SCN^-). Very small concentrations of metals are detected by the formation of colours in the so-called "spot tests" of analytical chemistry. Thus using the complexing agent ferroin, iron (II) ions show up by the red colour of the complex, $[Fe(ferroin)_2]^{2+}$ and the detection limit for iron by this method is very low indeed. Also certain mixtures of ions can be readily separted by employing complexation reactions. Thus when a solution containing zinc and aluminium ions is treated with ammonia, both ions are initially precipiated as the hydroxides, but on adding excess ammonia, the zinc hydroxide redissolves forming $[Zn(NH_3)_4]^{2+}$.

(b) Gravimetric Analysis

Certain ligands produce complexes with very low solubility. The formation of such complexes is used in determining the concentration of metal ions by precipitation techniques. Often the pH can be adjusted in such a way that if the metal ion is present in a mixture with other metals, it alone precipitates out when treated with the ligand. Thus at a pH of about 8, nickel (II) readily forms the insoluble complex $[Ni(DMG)_2]^{2+}$ where DMG stands for dimethylglyoxime, $CH_3.C(NOH).C(NOH).CH_3$; many other metals could be present in the same solution but all form very soluble complexes with DMG and hence their presence does not interfere with the nickel precipitate.

(c) Colorimetric Analysis

Many complex ions can interact strongly with electromagnetic radiation occurring in the ultraviolet and visible part of the spectrum. Since the absorption of radiation depends on the concentration of the absorber (complex) and on its electronic structure, the concentration of a particular metal in a solution can be found. The presence of other metals in the same solution will, generally, not interfere with this colormetric analysis. Moreover, since such analysis are fairly accurate and (most importantly) rapidly carried out, given the instrumentation, they are very popular with chemists working in industry.

(d) The Extraction and Purification of Metals

Gold occurs free in silica deposits and its separation from the earthy impurities depends on its ability to form a complex ion with cyanide. The ore is crushed and the powder is agitated with a solution of potassium cyanide. In the presence of air, and cyanide ions, the usually noble and unreactive gold is slowly oxidised to dicyanoaurate (1), which pass in solution,

4 Au + 8 CN- + 02 + 2 H20 = 4[Au(CN)2]- + 4 OH-

The gold is then recovered by reduction with zinc dust: any excess of zinc is removed by dissolution in acid.

The purification of several metals is achieved by electrodeposition. In such processes, the metal ions are often in complex form, e.g. silver as [Ag(CN)2] —; this technique gives better deposits of the pure metal than those obtained from the electrolysis of the simple aquo ions.

(e) Dyes and Pigments

The intense colours and insoluble nature of certain metal complexes (notably of iron, copper, cobalt and chromium) makes them very suitable as dyes and pigments in paints, printing inks and even plastics. An important class of such complexes are the metallo-organic pigments known as the phthalocyanines, one of the best known being Monastral Fast Blue B.S. This is copper (II) phthalocyanine (Figure 2), a bright blue pigment employed chiefly for colouring leather, printing inks and paints.

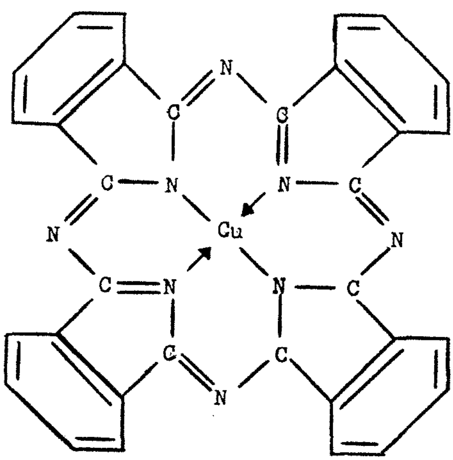

Figure 2

It can be prepared by heating phthalonitrile with copper or copper (II) salts; similar methods are employed in the preparation of other phthalocyanines, the colours obtained depending on the metals used. For example, lead phthalocyanine is a green pigment.

(f) Complexometric Analysis

The amount of calcium (and other polyvalent cations) in hard water can be determined by titrating with a standard solution of sodium EDTA,

$$Ca^{2+}(aq) \quad + \quad EDTA^{4-}(aq) \quad = \quad Ca(EDTA)^{2-}$$

Since EDTA is colourless, a dye is added (e.g. Eriochrome Black) which changes colour when a slight excess of EDTA is present — this marks the endpoint of the titration. Actually the indicator dye is itself a ligand and forms a coloured complex with the metal ion which is less stable than the metal-EDTA complex. At the endpoint all the dye molecules are expelled from their coordination with the metal ions and a colour change occurs.

(g) Biochemical Applications

Two key substances in biochemical systems are, indeed, complex compounds. These are haemoglobin and chlorophyll.

Haemoglobin consists of a protein, globin, with four haeme units attached to it. Haeme is a complex of iron (II) with protoporphyrin IX, which has the basic structure shown below. (Figure 3a). This iron porphyrin is then attached to the globin via three imidazole rings attached to the protein and acting as nitrogen donor ligands wih the iron (Figure 3b).

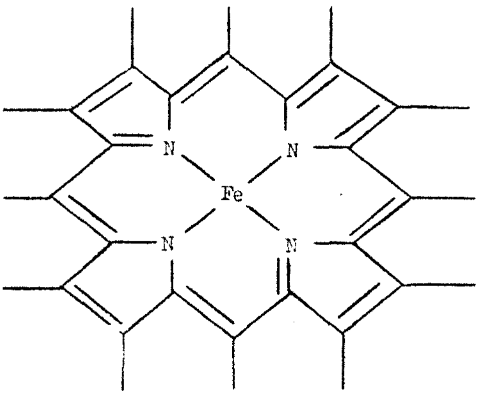

Figure 3a

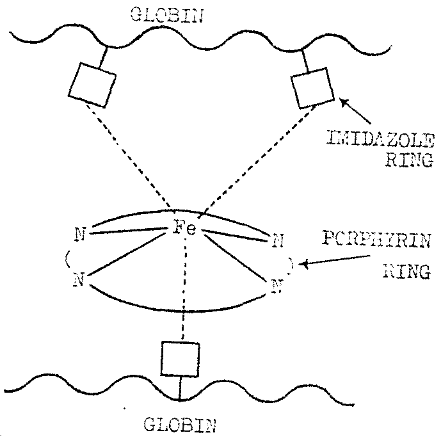

Figure 3b

The iron (II) is therefore seven-coordinate. In biological processes one iron-imidazole link is broken and an oxygen molecule gets bonded to the iron (II) instead. This oxyhaemoglobin then releases the trapped oxygen into the blood and the Fe-N link is re-established. The process is repeated, allowing the organism to extract vital oxygen from respired air. Other ligands, such as, carbon monoxide, or cyanide ions can combine with the iron in haeme to form very stable, non-labile complexes. These species destroy the function of the haemoglobin as an oxygen carrier and thus cause the eventual death of the organism.

Chlorophyll is a magnesium chelate. The structure of the porphyrin ring in chlorophyll is similar to that of the iron haeme except for variations in the side chains and groups attached to the pyrrole rings.

During the last decade, other "biological" iron complexes *not* containing haeme were discovered. These proteins contain iron linked to sulphur ligands and they have been implicated in a number of biological reactions in which they act as election transfer agents.

Recently, certain platinum complexes have been investigated for their possible use as anti-cancer agents, so that in the future, complex compounds could also become useful in chemotherapy.

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