
INORGANIC COMPLEXES:

AN INTRODUCTION

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DEFINING COMPLEXES

A **complex** or **coordination compound** consists of a central metal atom which is associated with a number of molecules or ions called the **ligands**. The complex may or may not be charged and generally its properties are distinct from those of the free metal ion and ligands that constitute it.

Complexes are, in fact, more ubiquitous than is generally imagined. When a soluble ionic compound is dissolved in water, its ions are hydrated, i.e. become associated with the solvent molecules by an ion-dipole interaction (fig. 1). In general, cationic radii are smaller than anionic ones and the

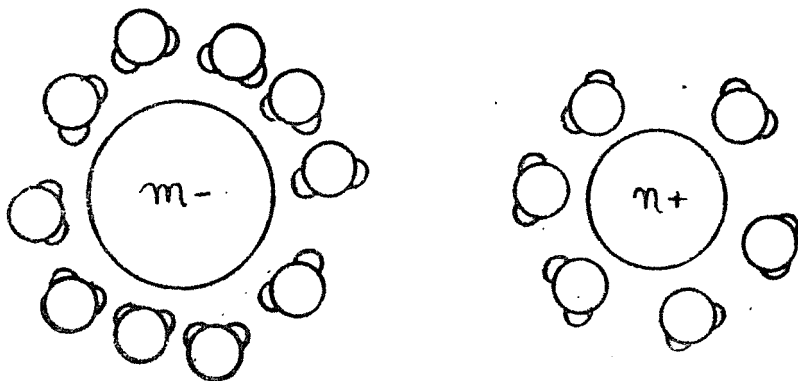


fig. 1.

cation-water interaction is therefore greater and more important than that between anions and water. In fact we can consider the cations to form new distinct species in aqueous medium, namely, **aquo complex ions**. The greater the charge density of the cation (i.e. the charge/radius ratio), the stronger will be the force of attraction of the ion for the water ligands. Thus species like Fe^{2+} , Mn^{2+} , Cr^{3+} etc. exist, at low pH, mainly as discrete hexaquo complex ions $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ and direct evidence for the existence of these species comes from ultraviolet spectroscopy and other sources. Non-transition metal ions, e.g., Mg^{2+} , Sn^{2+} , Al^{3+} , Zn^{2+} , are also composed of aquo complexes and physical methods of investigation (e.g. Raman spectroscopy and $\text{O}^{17}\text{n.m.r.}$ studies) support formulations such as $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. Corroborative evidence for the existence of aquo complexes stems from the fact that many salts containing these cations crystallise with

a number of water molecules equal to the coordination number of the presumed aquo complex, e.g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ or better $[\text{Mg}(\text{H}_2\text{O})_6]\text{Cl}_2$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ or better $[\text{Al}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3$. However, not all crystal water need be ligand water in the sense that it has little or no association with the anions. Thus in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, the water is largely bound to the sulphate (VI), in $\text{CuSO}_4 \cdot 5(\text{H}_2\text{O})$ the water is partly bound to the metal (4 moles) and partly shared between the metal and the sulphate (VI) (1 mole), i.e., $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$.

For large, weakly charged ions like Na^+ , K^+ , Cs^+ , the metal ion — water association will be weak (Coulomb's law) and thus the aquo complexes will be of a rather fragile nature.

MORE ABOUT AQUO COMPLEXES

With few exceptions, metal aquo complexes have the general formula $[\text{M}(\text{H}_2\text{O})_6]^{n+}$. Since the water ligands are neutral, $n+$ is the charge present on the metal ion M. The six waters surround the central ion in an octahedral fashion, as would be anticipated from the Sidgwick-Powell repulsion theory. We say that we have an **octahedral** complex and fig. 2 illustrates the shape of such a species.

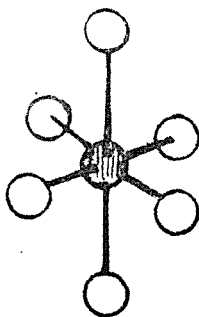
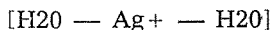


fig. 2.

This octahedral shape is the most common structure of all complex ions. Octahedral hexaquo complexes are found in blue-green solutions of chromium (III) salts, in pink solutions of manganese (II) sulphate (VI) and in the sky-blue solutions of copper (II) compounds.

A notable exception to this octahedral geometry is afforded by the silver aquo complex; for some obscure reason, this complex exists as $[\text{Ag}(\text{H}_2\text{O})_2]^+$, i.e. it is a bi-coordinate **linear** species with structure

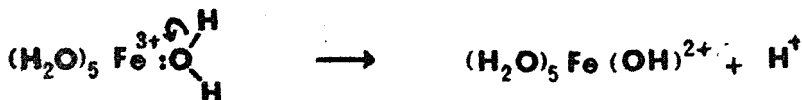


All solutions of hexaquo ions have a pH lower than 7 — the higher the charge on the central atom, the higher will be the acidity (and the lower the pH) of these solutions. This acidity must be due to the ionisation of one or more of the ligand waters of the aquo complex. For $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, for example, we have



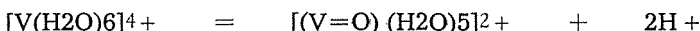
For which, $\text{PKa}, 1 = 2.2^*$, i.e. the iron complex ion is as strong an acid as orthophosphoric (v) acid with a $\text{pka}, 1$ equal to 2.1.

Presumably, the attraction of the electrons of the O-H bonds by the highly polarizing Fe^{3+} ion induces the observed ionisation, a process which we can depict as follows:



For large, unipositively charged ions, e.g. Na^+ , K^+ , this attraction for the electrons of the water molecule is small, and these ions do not function as acids.

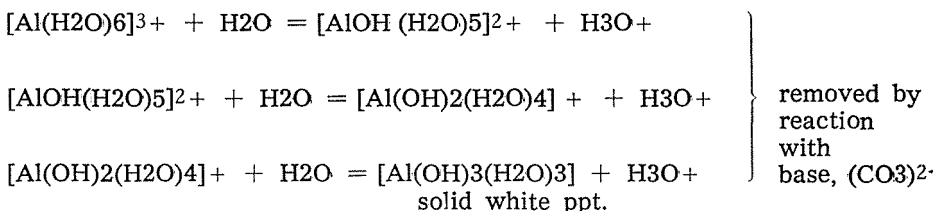
For small, highly charged ions like V^{4+} , this attraction is actually so intense that species like $[\text{V}(\text{H}_2\text{O})_6]^{4+}$ do not even exist. Instead, the aquo vanadium ion is in the form $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$, a species that can be thought of as arising from the complete deprotonation of one of the six ligand waters in the hypothetical hexaaquovanadium (IV),



All ionic vanadium (IV) compounds contain this oxo ion; thus, the so-called vanadyl sulphate pentahydrate, a blue crystalline material, is, in fact, pentaquooxovanadium (IV) sulphate: $[\text{VO}(\text{H}_2\text{O})_5]\text{SO}_4$.

Other similar oxo ions are known, e.g., the uranium (VI) species $(\text{UO}_2)^{2+}$, which occurs in the aquo complex $[\text{UO}_2(\text{H}_2\text{O})_4]^{2+}$ and in other uranium complexes.

The acidic properties of aquo ions also explains why carbonates of Cr(III), Fe(III), Al(III) etc. are unknown. When solutions containing these metal ions are treated with aqueous sodium carbonate, carbon dioxide is evolved and a precipitate of the metal hydroxide is thrown down. Thus, for aluminium (III), we may represent the process by the following diagram:



Similarly, certain sulphides cannot be prepared by 'wet' reactions, i.e. by the interaction of metallic aquo ions and solutions containing sulphide. Thus, no Fe_2S_3 is formed when iron (III) solutions are treated with aqueous

* $\text{pKa}, 1$ stands for $-\log$ (acid ionisation equilibrium constant). The subscript 1 refers to the first ionisation of the six that are theoretically possible.

sodium sulphide. Instead, hydrogen sulphide is given off and hydrated iron (III) hydroxide precipitates. That this is not due to the instability of the sulphide itself is shown by the fact that the compound Fe_2S_3 can readily be prepared by dry methods.

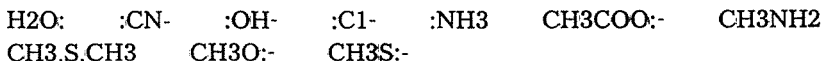
In all the above reactions, the hydroxide of the metal is formed when the complete ionisation of three water molecules occurs. This ionisation is induced by the presence of basic species (e.g. $(\text{CO}_3)^{2-}$ or S^{2-}) which react with H_3O^+ and remove it from the equilibrium system (see above). When the base is very strong, as in the case of OH^- , and with highly acidic complexes, e.g. hydrated aluminium (III), beryllium(II) or titanium(IV), the solid metal hydroxides may dissolve in excess base to form anionic hydroxo complexes. e.g.



Such complexes, therefore, show amphoteric behaviour.

OTHER LIGANDS

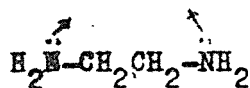
A species can act as a ligand if it can be strongly attracted by a positively charged metallic nucleus. This rules out all positively charged ion, e.g. H_3O^+ , NH_4^+ , $(\text{CH}_3.\text{NH}_3)^+$ and also neutral, non-polarizable molecules which are devoid of any readily available lone pair electrons, e.g. CH_4 , SiH_4 , CF_4 . Preferably, the ligand should possess a lone pair of electrons sited on an electronegative atom, and be negatively charged. A few examples of commonly encountered ligands are:



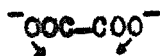
Hydrogen sulphide does not generally function as a ligand. Although the sulphur atom has two lone pairs of electrons, these are not easily accessible since sulphur is not a very electronegative atom and therefore the C-S bond is not sufficiently polarized. If we substitute the hydrogens in H_2S with methyl groups, as in dimethyl sulphide, $\text{CH}_3\text{-S-CH}_3$, the inductive effect of the alkyls renders the S atom slightly negatively charged, and thus 'activates' the lone pairs towards ligation with a metal ion.

Ligands may be classified on the basis of the number of bonds that they can form with the metal atom. Thus, if they can form one bond with the metal, they are said to be **unidentate**. All the ligands mentioned so far in this article normally act as unidentate species. Ligands that have two donor sites per molecule are said to be **bidentate**, i.e. having two 'teeth' with which to hold on to the metal. Examples of bidentates are

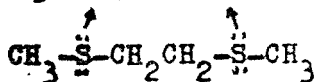
1,2-diaminoethane



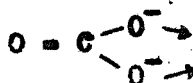
ethandioate ion



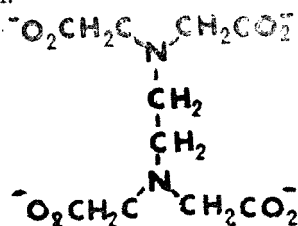
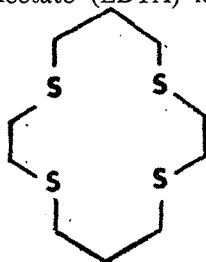
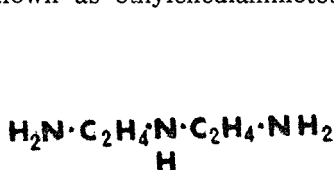
2,5-dithiahexane



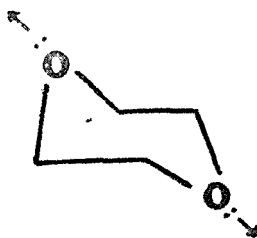
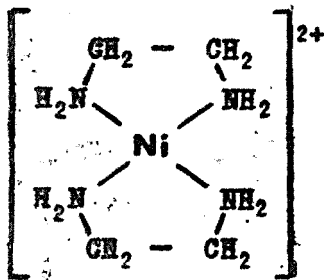
carbonate ion



Ligands with higher denticity are known, thus the tridentate 1,4,7-triazaheptane (I), the quadridentate 1,4,8,11-tetrathiacycloctetradecane (II) and the sexidentate bis(di(carboxymethyl)amino)ethane, (III), more commonly known as ethylenediaminetetraacetate (EDTA) ion.



When a polydentate ligand forms a ring structure by bonding with the metal, then it is said to be a **chelate** ligand. Thus bidentate 1,2-diaminoethane is acting as chelate ligand when forming the complex $[\text{Ni}(\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2)_2]^{2+}$; two 5-membered rings are formed each composed of a nickel atom, two nitrogens and two carbon atoms (fig. 3a):



On the other hand, dioxan (fig. 3b), although a bidentate ligand, is not a chelate. In dioxan, the two oxygen atoms have their lone pair electron lobes directed away from each other and cannot, as it were, bend over backwards to bond to the same metal atom and form a ring.

A few years ago, a formidable ligand was synthesised containing eight donor atoms. Labelled OTO (for 1,4,8,11,15,18,22,25-octathiacyclooctacosane), it acts as a sort of double quadridentate ligand with Ni^{2+} when it forms the complex compound $[\text{Ni}_2(\text{OTO})](\text{BF}_4)_4$. The structure is shown in fig. 4. The four sulphur atoms bonded to each nickel atom are in one plane: the plane of the nickel atom.

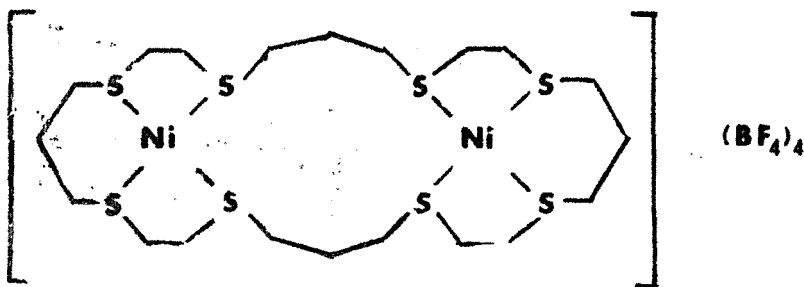


fig. 4

NAMING COMPLEXES

As is usual in naming simple salts, the cation is mentioned first and then the anion. The ligands are named before the metal ion, negatively charged ligands preceding neutral molecule ligands. If more than one type of neutral (or negatively charged) ligand is present, they are named in alphabetical order. Thus, for example, ammine before aquo, bromide before chloride. The prefixes di-, tri-, tetra-, etc.* are used for multiple ligands of the same kind and the central ion's oxidation number is shown with a Roman numeral. When the complex ion is overall negatively charged, then the metal ion's name takes on an -ate ending. The names of some common ligands are given in the Table below.

* The prefixes mono-, bis-, tris-, tetrakis, etc. are used for the more complex-named ligands.

H ₂ O	aquo	F-	fluoro
NH ₃	ammine	Cl-	chloro
CO	carbonyl	Br-	bromo
NO	nitrosyl	I-	iodo
CH ₃ NH ₂	methylamine	CN-	cyano
(C ₆ H ₅) ₃ P	triphenylphosphine	OH-	hydroxo
		(CO ₃) ²⁻	carbonato
		(NO ₂)-	nitro
		(NO ₃)-	nitrate

The following list of names shows how the above rules are applied in practise.

[Co(NH ₃) ₆]Cl ₃	hexamminecobalt(III) chloride
[CoCO ₃ (NH ₃) ₅]NO ₃	carbonatopentamminecobalt(III) nitrate(V)
K ₃ [Mn(CN) ₆]	potassium hexacyanomanganate(III)
[NiCl ₂ (P.Ph ₃) ₂]	dichlorobis(triphenylphosphine)nickel(II) (Ph=phenyl)
(NH ₄) ₂ [NiCl ₄]	ammonium tetrachloronickelate(II)
K ₃ [Fe(C ₂ O ₄) ₃]	potassium tris(ethanedioate)ferrate(III)
[Fe(NO)(H ₂ O) ₅]SO ₄	pentaquonitrosyliron(II) sulphate(VI)

SHAPES OF COMPLEXES

We have already mentioned the octahedral shape of six-coordinate complexes. Coordination compounds of the type ML₆, where L is a unidentate ligand would possess this shape, e.g. [CrCl₂(H₂O)₄]⁺, [Fe(NO)(H₂O)₅]²⁺, [Cu(NH₃)₄(H₂O)₂]²⁺, [Fe(CN)₆]⁴⁻. When chelating ligands are present in octahedral complexes, the chelate always straddles two *cis* positions of the octahedron, e.g. in [CoCl₂(NH₂.C₂H₄.NH₂)₂]⁺, fig. 6 where en stands for the 1,2-diaminoethane molecules.

It is not difficult to see that when more than one type of ligand is present, isomerism will be possible. Indeed the multitude of possible isomers (and sometimes the ease with which they can interconvert) has perplexed early workers in the field of complex chemistry — and perhaps even earned it its name! Thus from aqueous solutions of chromium(III) chloride, three different complexes can be isolated:

a violet compound with structure [Cr(H₂O)₆]³⁺ (Cl⁻)₃
 a pale-green compound with structure [Cr(H₂O)₅Cl]²⁺ + (Cl⁻)₂. H₂O
 and a deep-green compound with structure [Cr(H₂O)₄Cl₂]⁺ + (Cl⁻). 2H₂O

A fourth isomer, the neutral complex Cr(H₂O)₃Cl₃. 3H₂O, has been prepared from ether solutions. This last isomer can in fact, exist in two possible forms: the *facial* isomer (fig. 5a) and the *meridional* isomer (fig. 5b). The deep green isomer, dichlorotetraaquo chromium(III) chloride can also exist in two forms: the *cis* isomer (fig. 5c) and the *trans* (fig. 5d).

Optical isomerism is also possible, especially when chelating ligands are involved. Thus the cation in dichloro-bis(1,2-diaminoethane)cobalt(III) can

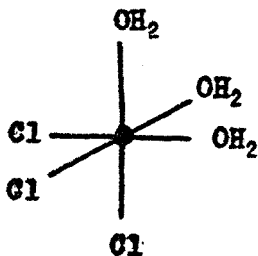


fig. 5a

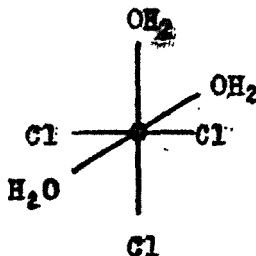


fig. 5b

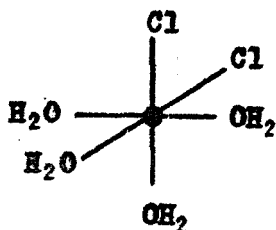


fig. 5c

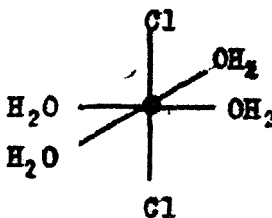


fig. 5d

exist in three forms: the **trans**, optically inactive form (fig. 6a) and two **cis** forms, one being the mirror image of the other (figs. 6b, 6c). These two **different** compounds are both optically active*.

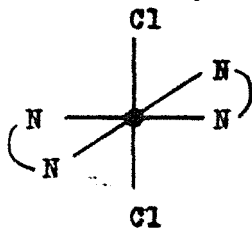


fig. 6a

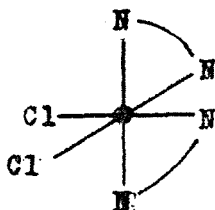


fig. 6b

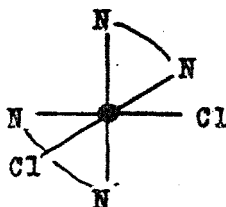


fig. 6c

Four coordinate complexes ML_4 , can either be tetrahedral, as in $[ZnCl_4]^{2-}$, $[Hg(CN)_4]^{2-}$, $[FeCl_4]^{2-}$, $[CoBr_4]^{2-}$ or flat planar. The only important flat planar complexes are those of nickel(II) and copper(II) and a few other second and third row transition metals. Perhaps the best known of these flat complexes

* To ascertain whether a complex or (any molecular species) is optically active or not, look for the presence of a plane of symmetry. If *absent*, the molecule will exist in two different mirror image forms and both forms will be optically active, i.e. will be able to rotate the plane of polarization of plane polarized light.

is the tetramminecopper(II) ion, $[\text{Cu}(\text{NH}_3)_4]^{2+}$. However, such an ion, when present in aqueous solution, will certainly be approached very closely by the water molecules, especially above and below the plane of the ion. It is probably best to regard such 'flat' complexes as being tetragonally distorted octahedral ones, at least when present in solution (fig. 7).

Moreover, even when they crystallise into solids, planar complexes are known to arrange themselves in such a way that each metal ion is still octahedrally surrounded by ligand atoms (fig. 8).

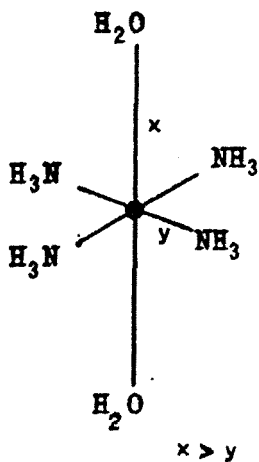


Fig. 7

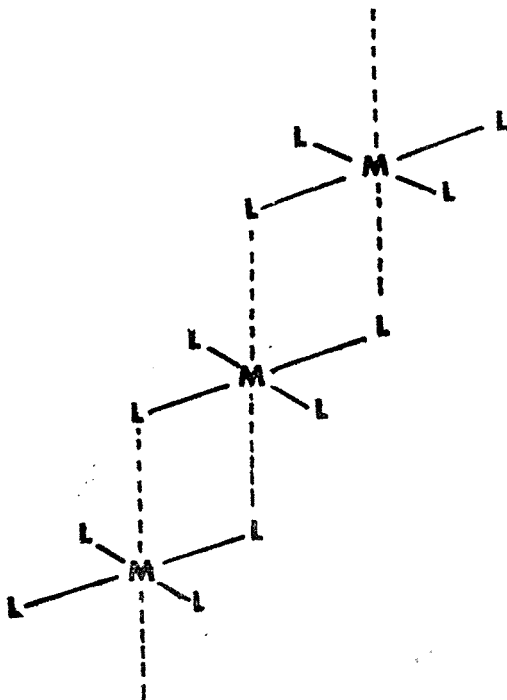


fig. 8