

Chapter 2

RELATIVE AFFINITIES OF LIGAND ATOMS,

CLASSIFICATION OF ACCEPTORS AND

ANALYTICAL PROPERTIES OF BERYLLIUM, URANIUM AND MERCURY

The most common ligand atoms consist of nitrogen, oxygen and sulphur, although an extension may be made to include other non-metallic or metalloid elements of the groups Vb, VIb and VIIb of the periodic table. In an attempt to correlate the relative affinities of different ligand atoms for various acceptors, Ahrlund, Chatt and Davis¹ observed two regular features in spite of a non-uniformity in the general trend.

1. There is, in general, a great difference between the coordinating affinities of the first and second elements of the three groups (Vb, VIb and VIIb) of ligand atoms, i.e., between N and P, O and S as well as F and Cl.

2. There are two distinct classes of acceptors, (a) which form most stable complexes with the first ligand atom of each group (N, O and F) and (b) which form their most stable complexes with the second or subsequent ligand atoms. However, each oxidation state must be regarded as a different acceptor.

2.1 Classification of Acceptors : Hard and Soft Acids

Most of the metals in their common oxidation state belong to class (a). It also includes hydrogen. The affinity of the ligands for class (a) acceptors tends to run roughly parallel to the basicity

except when steric and other factors intervene. The acceptors of class (b) which are less numerous, occupy a more or less triangular area in the periodic table¹. Obviously, there is a border region. Thus Cu(I) is definitely a class (b) acceptor, while Cu(II) is in the border between two classes.

According to Pearson², the features which bring out class (a) behaviour are small size and high oxidation state. Class(b) behaviour is associated with a low or zero oxidation state and/or with a large size. Since the features which promote class(a) behaviour are those which lead to low polarisability, and those which create type(b) behaviour lead to high polarisability, the class(a) and class(b) acceptors have conveniently been classified as 'hard' and 'soft' acids respectively. Then, we have the useful generalisation that 'hard acids' prefer to associate with 'hard bases' and the opposite.

2.2. The Relative Coordinating Affinities of Ligand Atoms

In case of the ligand atoms of the group Vb a more or less uniform behaviour is observed. Thus, with the class (a) acceptors the coordinating abilities diminish as $N \gg P > As > Sb > Bi$ and with class (b) as $N \ll P > As > Sb > Bi$. The relative affinity sequence of ligand atoms of group VIIb is similar to that observed in group Vb for class (a) acceptors, e.g., $F \gg Cl > Br > I$, but in case of class (b), is $F \ll Cl < Br < I$. In the border region of (a) and (b) identical stabilities and mixed sequences may occur. With the metal atoms of strong class (a) character, ligand atoms of group VIb exhibit the sequence $O \gg S > Se > Te$, but with the

acceptors of class(b) any sequence of S, Se and Te may occur.

2.3. Ligand Atoms in Organic Reagents and Classification of Acceptors

The general approach presented above is too broad. But if we confine our attention to the ligand atoms N, O and S, one or more of which is present in almost all the important organic reagents, a more useful classification of the common metal atoms and ions is obtained. Thus, for analytical purposes the metals (or ions) have been divided into three groups³.

(a) Ions in which the electronic distributions approximate to those of the inert gases (e.g., Be, Al etc.). Oxygen containing ligands, e.g., carboxylate ions, 1,3-diketones etc. preferentially react with the acceptors of this group. Thus, quinalizarine is used as a colorimetric reagent for Be, Mg, B and Al.

(b) Ions in which the d- or f- orbitals are only partially filled, i.e., the transition metal ions (e.g., Ti, V, Fe, U etc.). They form stable complexes with ligands containing polarisable portions, e.g., amino groups and heterocyclic nitrogen atoms. However, there may be some overlapping in the border region. Thus, Zn, Cd and Hg, with complete d-orbitals react strongly with ethylene-diamine.

(c) Ions with filled d-orbitals (e.g., Hg, Pb, Bi etc.). They also prefer highly polarisable ligands, especially those having suitable vacant d-orbitals into which some d-electrons

can be back bonded. The conditions favour sulphur-containing ligands. Thus, thionilide form insoluble complexes with Hg(II), Tl, Bi etc. Here again some overlapping with some higher transition metals is evident.

2.4. Analytical properties of Some Metal Ions

When a particular organic reagent is given, with the help of the above classification, it is possible to predict to which class of metal ions the reagent will find suitable applications. On the otherhand, when a new organic reagent is prepared it is worth trying to apply it to different members of each class. Later, in the experimental part, the use of some new β -ketoanilides as reagents have been described. These reagents have been used in the analysis of one typical member of each of the above three groups, viz., beryllium, uranium(VI) and mercury(II). Some of the important properties of these three ions related to their analytical determinations are given below.

2.4.1. Beryllium (Giving ions with electron distribution similar to inert gas, He)

Due to its small size, Be^{2+} (electronic configuration, $[\text{He}]$) has a higher tendency to form at least partially covalent bonds than any other group IIA metal ions. The ion is highly aquated in solution and strong ion-dipole reactions lead to the formation of 'oxo' (Be-O-Be) and 'hydroxo' (Be-OH-Be) ions. The hydroxide, $\text{Be}(\text{OH})_2$ may be precipitated by ammonia, but at a high pH, there is a tendency

to form the beryllate anion. As oxygen is a strong donor for Be^{2+} , most of its reagents bond through oxygen rather than nitrogen. Thus, morin^{4,5} and aluminon^{6,7} in colorimetry and fluorimetry, acetylaceton⁸ in extraction and cupferron⁹, N-benzoyl-N-phenyl-hydroxylamine¹⁰ etc. in gravimetry are familiar reagents for Be^{2+} . The complex forming tendency with nitrogen is so weak, that the universal complexing agent, ethylenediamine tetraacetate (EDTA) has been freely used for masking other elements in their separation from Be^{2+} .

2.4.2 Uranium (Giving ions with partially filled d- or f-orbitals)

The electronic configuration is $[\text{Rn}]5f^3 6d^1 7s^2$. In aqueous solution uranium(VI) is the most important form, though U(III) and U(IV) are possible, and the tendency towards hydrolysis decreases in the order $\text{U}^{4+} > \text{UO}_2^{2+} > \text{U}^{3+}$. Uranium(VI), usually present as UO_2^{2+} form strong complexes with oxygen containing ligands, e.g. carboxylic acids, acetylaceton and other β -diketones, than with nitrogen containing ligands. The energy needed to promote electrons from 5f or 6d in uranium is within the range of chemical bonding energies, so that 5f electrons can be used in U for complex formation. In solvated UO_2^{2+} ion, the 'O-U-O' arrangement is linear, while upto six ligands may be disposed around U in a plane perpendicular to it. Uranium(VI) gives coloured complexes with many organic reagents, but the reactions, in general, lack specificity. Here also, the ligands are mostly oxygen containing, though

some less selective reagents like 8-hydroxyquinoline have been used.

2.4.3. Mercury [Giving ions with filled d-orbitals]

In mercury (II), the electronic configuration, $[\text{Xe}]4f^{14}5d^{10}$ affords a much increased cation deformability and a much greater tendency towards covalent bond formation. Mercury(II) will form stable complexes only with highly polarisable ligands which will provide opportunities for back-bonding. Consequently, dithizone^{11,12} type reagents have been extensively used in the determination of Hg^{2+} . Among the oxygenated reagents, N-benzoylphenylhydroxylamine¹³, phenoxyacetic acid¹⁴ etc., may be mentioned. However, the number of organic reagents for either Hg^{2+} or Hg_2^{2+} is limited when compared to other metal ions.

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