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Neo-classical Coordination Chemistry: Principles of Ligand Reactivity in Coordination Compounds

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Abstract

The coordination of an organic ligand to a metal ion has a profound effect upon both the ligand and the metal. The ways in which the properties and reactivity of a ligand may be perturbed are discussed.

Introduction

The chemistry of coordination compounds has commonly emphasised the reactivity and properties of the metal ions involved. Ligand Field Theory in one of its manifestations has provided an excellent basis for the empirical and semi-quantitative interpretation of metal ion properties in coordination compounds. The fundamental tenet of such theories is that the metal-centred energy levels are perturbed by the number, type and geometrical arrangement of the ligands bonded to the metal. In the same way, the molecular orbitals of the ligands are perturbed by the proximity of the metal ion. Our interests are in the chemical consequences of this aspect of the metal–ligand interaction, and in this paper we discuss the ways in which coordination to a metal ion may affect an organic molecule.

Although the reactivity of carbon-bonded organic fragments is the rationâle for much organometallic chemistry, reactions of coordinated ligands are less familiar to the 'normal oxidation state' coordination chemist. In particular, reactivity at carbon atoms is commonly only discussed in terms of organometallic systems; such reactions in systems bonded to the metal atom through other donor atoms offer an interesting addition to the existing organometallic methodology.

This aspect of the metal–ligand interaction has received little recent attention, although a number of schemes have been proposed for the rationalisation of ligand reactivity [1]. Whilst all of these schemes have their merits, they are generally based upon empirical observations. We wish to discuss the reactivity of coordinated ligands in terms of the origins of the interaction, and present in this paper a simple scheme to rationalise the effects of coordination upon a ligand.

We consider there to be three ways in which the metal–ligand interaction may be manifested in the properties of the coordinated ligand:

(1) Conformational
(2) Inductive (or σ-type)
(3) Mesomeric (or π-type)

We shall consider each of these effects in turn, and demonstrate how the properties of ligands may be modified.

Conformational Effects

These effects become apparent when the conformation or geometry of the ligand in the complex differs from that of the equilibrium conformation or geometry in the free ligand. The geometry of any molecule is a subtle balance of steric and electronic effects. In principle, any ligand should, upon coordination to a metal ion, undergo changes associated with the conversion of a lone pair of electrons to a bonding pair. In practice, such changes are relatively minor, if detectable at all, with much more marked changes occurring in the acceptor rather than the donor molecule. This is in accord with experience from main group chemistry; the formation of $R_3N\cdot BF_3$ from R_3N and BF_3 results in a change from trigonal planar to near-tetrahedral at boron, whilst the nitrogen atom remains in a pyramidal environment.

Rather more marked changes occur when polydentate ligands interact with metal ions. In these cases, it is frequently found that the conformation adopted by the ligand in the complex differs from that observed in the free ligand. Classical examples are seen in complexes of 1,2-diaminoethane (ethylenediamine) or 2,2′-bipyridine (bipy), where the chelated bonding mode requires a *cis* arrangement of the donor atoms. In both cases, the equilibrium conformation of the free ligand exhibits a *trans* arrangement of the donor atoms, with free rotation about C–C bonds (Fig. 1). The chemical consequences of these geometrical changes are well-documented. The formation of the five-membered non-planar chelate ring in 1,2-diaminoethane complexes results in the introduction of a new element of chirality in the

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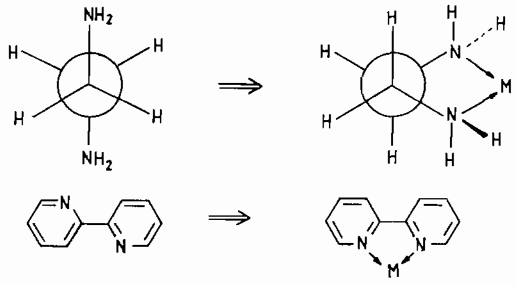

Fig. 1. Conformational changes in 1,2-diaminoethane and 2,2′-bipyridine upon formation of chelate complexes.

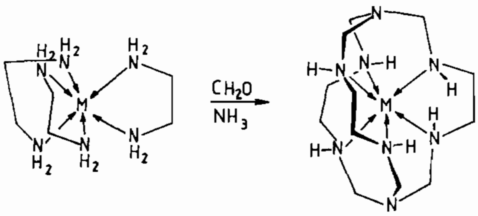

Fig. 2. Conformational control in the synthesis of an encapsulating ligand.

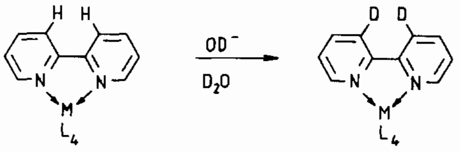

Fig. 3. Specific deuterium exchange at the 3,3′-positions in $[Ru(bipy)_3]^{2+}$.

molecule [2]. This chirality is carried through in one of the most remarkable examples of ligand reactivity yet reported; the formation of encapsulating ligands from the reaction of $[M(en)_3]^{n+}$ with ammonia and formaldehyde (Fig. 2) [3]. This reaction also utilises the *cis* conformation of the 1,2-diaminoethane ligand in the complex! In the case of 2,2′-bipyridine complexes, the adoption of the *cis* configuration results in a steric interaction between the 3- and 3′-protons [4]. This results in unusual spectroscopic properties, and an enhanced acidity at these positions (Fig. 3) [5].

Inductive (σ-type) Effects

These have a more obvious origin in the polarisation resultant from interaction with a charged metal ion. Bonding of a donor atom to a positively charged metal ion is expected to result in the build-up of positive charge upon the donor atom in particular, and the ligand in general. The transmission of charge through the molecule is expected to decrease with distance from the site of positive charge, although symmetry considerations associated with the ligand bonding may modify this. Even if the ligand is bonded to a neutral metal fragment, there is still expected to be some polarisation of the ligand, since most metals are more electropositive than ligand donor atoms [6]. The polarisation in the metal–ligand bond will be in accord with the electronegativities of the donor and acceptor atoms, and the Pauling electroneutrality principle [6].

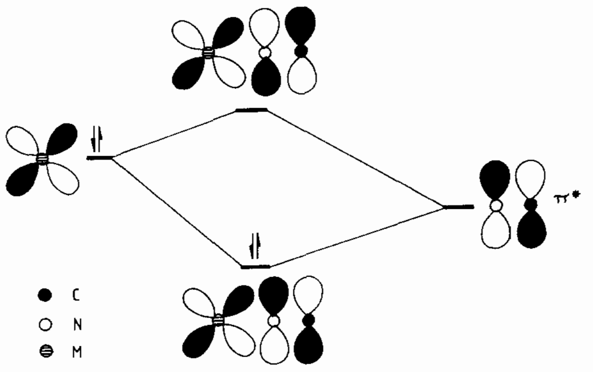

Fig. 4. Overlap of filled d orbitals with a ligand π^* orbital.

This polarisation of the ligand may be expressed in a number of ways, the simplest of which are the enhancement of attack at the ligand by nucleophiles, or the facile loss of positively-charged fragments from the ligand. The attack of nucleophiles upon carbonyl groups is enhanced in the presence of metal ions, and rate enhancements of amide or amino acid ester hydrolysis of the order of 10^8 have been described in the presence of copper(II) (Fig. 4) [7].

$$RCONH_2 \xrightarrow{H_2O,\ Cu^{2+}} RCO_2H + NH_3$$

Similarly, PF_3 only reacts with water or alcohols relatively slowly, but upon coordination to a transition metal the rate of attack is considerably enhanced [8].

The most commonly encountered examples of metal ion modification of ligand properties are undoubtedly observed in the aqua ions. It has been known since the pioneering researches of Werner that metal aqua complexes show a tendency to form hydroxy and oxo species by the loss of protons. This represents the effect of the positively charged metal ions on the pK_a of the coordinated water ligand.

$$M(H_2O)^{n+} \rightleftharpoons M(OH)^{(n-1)+} + H^+ \rightleftharpoons M{=}O^{(n-2)+} + 2H^+$$

The increase in acidity of the coordinated water may be dramatic, from 15.6 for the free ligand to 1.4 in $[Pd(H_2O)_4]^{2+}$ and 2.0 in $[Fe(H_2O)_6]^{3+}$ [9].

Mesomeric (π-type) Effects

This is a somewhat disparate term which is meant to include any of the plethora of interactions between orbitals on the metal and the ligand which possess π symmetry. In general, interactions of this type are limited to transition metals, in which the d orbitals are of the correct symmetry for π overlap with the ligand (Fig. 4).

The inductive effect of a charged metal ion upon a coordinated ligand results in a polarity in the metal—ligand bond. In accord with the Pauling electroneutrality principle, the system will attempt to minimise this charge separation. One of the ways in which this can be achieved is by the donation of electron density to or from the metal by interaction of a p, π or π^* orbital on the ligand with a d orbital on the metal. This will result in a nett redistribution of charge within the metal—ligand bonding system, although the individual σ and π contributions may differ radically.

Examples of this type of interaction are well-known in organometallic chemistry, and provide the basis of the stabilisation of low-oxidation states by π-acceptor ligands. Similarly, in high-oxidation state chemistry the rôle of π-donor ligands is explained. A typical chemical application is seen in the stabilisation of imines towards hydrolysis by coordination to a transition metal ion. Hydrolysis of an imine involves attack by water upon the vacant π^* orbital of the ligand; occupancy of this level results in a reduced water—ligand interaction, and hence stabilisation.

Clearly, the balance of these effects will determine the overall pattern of reactivity in the coordination compound, and, in particular, the σ and π effects may oppose each other in their action. This is demonstrated in the case of a coordinated imine discussed above; in some cases the imine is stabilised by coordination to a metal, but in others the build up of positive charge on the ligand is the dominant factor, and hydrolysis is accelerated. A clear understanding of the magnitude and the operation of the various factors in the metal—ligand interaction is necessary before making any predictions regarding ligand reactivity. In particular, a distinction between thermodynamic and kinetic control of reactivity is necessary; the symmetry of frontier orbitals may control interactions with incoming reactants. These are precisely the orbitals which will be most affected by any π interactions [10].

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