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Ligand Reactivity in Coordinated Heterocycles; a Comment

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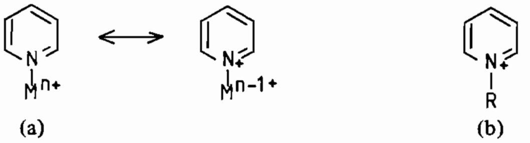
In the past decade, there has been considerable interest in the chemistry of coordinated ligands. In particular, there has been some controversy over the activation of coordinated π-deficient heterocycles [1]. Gillard and his school have presented evidence purporting to show a close analogy between a pyridine or 2,2′-bipyridine coordinated to a metal ion (Fig. 1a) and a quaternary pyridinium salt (Fig. 1b). It was claimed that coordinated heterocycles were activated towards attack by nucleophiles such as hydroxide ion, and the anomalous kinetic and chemical properties frequently encountered in complexes of this type were ascribed to these reactions. These results have been questioned by a number of workers, and it is now apparent that the observations reported by the Cardiff school are open to alternative explanations. Whilst this is not the forum to resurrect this particular issue, it is necessary to correct some misconceptions which appear to have arisen from the matter.



(a) (b)

Fig. 1. (a) Pyridine coordinated to metal ion, (b) pyridinium salt.

Although the question of nucleophilic attack upon coordinated pyridines must at present be regarded as *sub judice,* the somewhat heated discussions have led to a widespread view that there is no activation of the ligand. This particular argument has been clearly presented by Lay, and it is the purpose of this note to question this view [2].

Lay maintains that the analogy drawn between a coordinated heterocycle and a quaternary salt is over-naive. If one only considers an inductive effect transmitted through the σ-bonding framework of the heterocycle, positive charge should be built up on the ring, decreasing with the distance from the metal ion; *i.e.* N(1) > C(2) > C(3) > C(4). However, synergic back-bonding is expected to counter this, and result in the build-up of electron density on the heterocycle. The crux of Lay's argument is that these two effects are expected to be of similar, but opposite, magnitude, as predicted by the Pauling neutrality principle, and that the overall electron density on the heterocycle is unlikely to be greatly altered. He, very correctly, points out that the modification of ligand properties is expected to be greatest for complexes with highly charged ions (+3 or greater), but that no major effects are to be expected with lower charged ions. This is particularly germane to the results obtained by the Cardiff school, since the majority relate to complexes of ruthenium(II) and iron(II).

Whilst there is no doubt that the arguments presented by Lay are substantially correct, it is not a necessary consequence of the back-bonding that the ligand properties are unaltered. Low-level calculations (INDO) by the Cardiff group have indicated that in the model complex $[Fe(py)_2(CN)_4]^{2-}$, positive net electron density (σ and π components summed) is associated with N(1), C(2) and C(4) (Fig. 2) [3]. However, even if the overall electron density at each site on the pyridine ring is not altered from that in the free ligand, there will be significant differences in the σ and π components at each site. The inductive effect is likely to result in a diminution of σ electron density, whereas back-bonding will result in an increase of π electron density (assuming the pyridine to act as a nett π-acceptor). Specifically, back-donation will result in occupancy of levels which may be equated with the ligand antibonding levels, and thus reduce the π-bonding order of the ligand. It is the combination of these two effects which will be important in the observed reactivity (in which both kinetic and thermodynamic terms will be expressed).

Fig. 2. Calculated charges (×1 000) at ring atoms in pyridine and iron(II) complexes, INDO method [3].

The inductive effect of the positively charged metal ion is predominantly electrostatic in origin, and is transmitted through the bonding framework. As such, it decreases with increasing distance from the cationic centre. This increases the electrostatic attraction experienced by the incoming nucleophile. In contrast, the back-donation of electron density from the metal to the antibonding levels of the ligand will tend to repel the incoming nucleophile. To a first approximation, the electron densities may be modelled by the benzyl anion (Fig. 3) [4]. Whilst the model is crude, and the electron densities will

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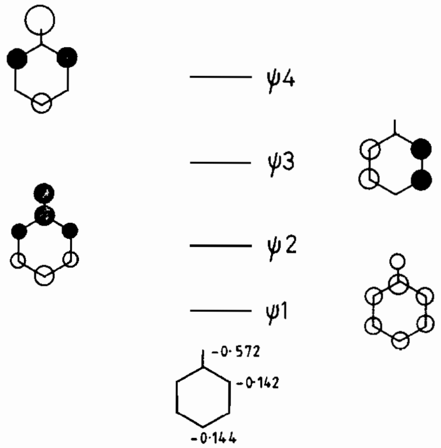

Fig. 3. Occupied π-orbitals of the benzyl anion and calculated excess charge density associated with the π-electron population [4].

not be accurate, it qualitatively confirms our predictions that charge density will be built up at C(2) and C(4).

However, a more subtle effect is also operative. The approach of a nucleophile to the coordinated heterocycle will involve orbital overlap between the HOMO of the nucleophile and the LUMO of the ligand. Whereas the inductive effect is dominated by the distance from the centre of the charge, the π interaction is dominated by the symmetry properties of the orbitals. Significantly, ψ_4 which represents the LUMO (in the absence of significant back-donation) has electron density at C(2) and C(4), and nodes at C(3) and C(N)(1). Thus, symmetry considerations indicate that the incoming nucleophile will interact with the 2– and the 4– positions.

The important factors from the above discussion are that significant alterations in the σ and π components of the ligand will and must occur upon coordination to a metal ion. The nett balance of effects may result in little overall change in the electron densities in any position, but reactions which are dominated by interaction with orbitals of π symmetry will be susceptible to change.

Whether such modification of ligand reactivity is observable in any particular case is entirely another matter.

There are, however, a number of observations which indicate that π-deficient heterocycles do undergo a genuine modification of reactivity upon coordination to a transition metal ion. The displacement of chloride ion from $[RuL_3]^{2+}$ (L = 5-chloro-1,10-phenanthroline or 4,4′-dichloro-2,2′-bipyridine) is more rapid than that in the free ligand [5, 6]. It is also significant that the coordinated heterocycles are also activated with respect to attack by electrophiles, usually at the same positions. Thus $[M(phen)_3]^{n+}$ (M = Ru, n = 2; M = Co, n = 3) readily nitrates at the 5-positions under remarkably mild conditions [1].

References

1 R. D. Gillard, *Coord. Chem. Rev., 16,* 67 (1975); N. Serpone, G. Ponterini, M. A. Jamieson, F. Bolletta and M. Maestri, *Coord. Chem. Rev., 50,* 209 (1983); E. C. Constable, *Polyhedron 2,* 551 (1983); R. D. Gillard, *Coord. Chem. Rev., 50,* 209 (1983).
2 P. A. Lay, *Inorg. Chem., 23,* 4775 (1984).
3 D. W. Clack, L. A. P. Kane-Maguire, D. W. Knight and P. A. Williams, *Transition Met. Chem., 5,* 376 (1980).
4 I. Fleming, 'Frontiers Orbitals and Organic Chemical Reactions', Wiley, New York, 1976.
5 E. C. Constable, *Inorg. Chim. Acta, 82,* 53 (1984).
6 K. Jackson, J. H. Rid and M. L. Tobe, *J. Chem. Soc., Perkin Trans., 2,* 607, 611 (1979).