Equilibria in *N*-Heterocyclic Complexes.
Part 45.* Ligand Electron Densities in Coordinated Pyridine

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(Received March 23, 1987)

Abstract

Results of INDO calculations on the species pyridine (py), $(pyH)^+$, $[py\text{-}CH_3]^+$, $[Fe(NH_3)_x(py)_{6-x}]^{2+}$, $[Fe(NH_3)_5(py)]^{3+}$, $[Fe(CN)_5(py)]^{3-}$, and $[Co(CN)_5(py)]^{2-}$ are presented and discussed, comparing quaternization and coordination.

Recently, two articles have discussed (using qualitative arguments) whether a heterocycle might be expected to show enhanced activation towards nucleophilic attack when coordinated to a metal ion [2, 3]. One view [2] argued that π back donation of electrons from the metal would counterbalance any inductive loss of electron density from the rings via σ donation to the metal. On this basis, the effect produced by quaternization would differ from that caused by coordination to a metal. The other discussion [3] likened the π orbitals of a metal–pyridine moiety to those of the benzyl anion and suggested that positions C2 and C4 of the ring would be deactivated by π-back donation, while on the other hand implying also that these same two positions on the ring would interact most strongly with orbitals of an approaching nucleophile if orbital overlap criteria were important.

Qualitative arguments of this kind are unlikely to be useful when discussing reactivity at various sites of coordinated heterocycles and may result in confusion.

Our INDO calculations [4] yield values for electron densities in both σ and π orbitals of the heterocyclic ring. Results are given in Table I for pyridine when quaternized and for a number of model cationic pyridine complexes of Fe(II) and Fe(III), together with those for the free molecule for comparison. These show that for free pyridine, positions C2 and C4 are deficient in π-electrons, in keeping with its resonance structures. Moreover, these atoms are also deficient in σ electrons (position C2 more so than C4) which leads to an overall positive charge on them.

Interestingly, on coordination to a metal ion, there is a net flow of electrons from the ring to the metal–ligand fragment as shown by the total charges. Thus, the heterocyclic ring becomes more positive on coordination and might therefore be expected to be more reactive towards nucleophiles. Most of the electron loss from the ring occurs through the σ

TABLE I. π Electron, σ Electron Densities, and Total Resultant Charges at Pyridine Ring Positions

		Uncoord. py	$(py\text{-}Me)^+$	$[Fe(NH_3)_5py]^{2+}$	$[Fe(NH_3)_4py_2]^{2+}$	$[Fe(NH_3)_3py_3]^{2+}$	$[Fepy(NH_3)_5]^{3+}$
π Density	N	1.075	1.303	1.176	1.169	1.162	1.264
	C2	0.956	0.936	0.978	0.978	0.967	0.974
	C3	1.030	0.985	0.983	0.987	0.991	0.965
	C4	0.951	0.851	0.887	0.892	0.896	0.839
σ Density	N	4.115	3.580	3.840	3.839	3.846	3.782
	C2	2.889	2.911	2.869	2.870	2.885	2.856
	C3	2.999	3.003	3.013	3.011	3.011	3.015
	C4	2.980	3.023	3.007	3.005	3.004	3.025
Total charge	N	−0.190	+0.117	−0.016	−0.008	−0.009	−0.046
	C2	+0.155	+0.153	+0.153	+0.152	+0.148	+0.170
	C3	−0.029	+0.012	+0.004	+0.002	−0.002	+0.020
	C4	+0.069	+0.126	+0.106	+0.103	+0.100	+0.136

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*For Part 44, see ref. 1.

0020-1693/88/$3.50

framework, with very little change overall for the total π electrons of the ring.

The charge distribution should be contrasted with that implied [3] in the analogy with the benzyl anion where C2 and C4 are shown as carrying a negative charge. The π electron distribution within the pyridine ring is of course modified upon both coordination and quaternization as a result of changing electronic repulsion between σ and π electrons as σ electrons are pulled out of the ring. However, there appears to be no increase in π electron density for the ring as a whole. Such an increase, of course, is frequently assumed using a qualitative model. Our finding arises because the metal d_π orbitals lie approximately midway in energy between the ring π levels, both occupied and empty (*i.e.* HOMO and LUMO), with which they interact, and consequently are essentially non-bonding.

Moreover, contrary to an earlier suggestion [2], the heterocyclic ring is very similar electronically in both its σ and π electron distributions when quaternized and when it is coordinated to a metal ion, the nitrogen atom as expected showing the greatest differences.

The calculations also yield a more quantitative picture of the lowest unoccupied orbitals of the complexes, important if orbital interactions with an approaching nucleophile are to be considered. It is invariably true for transition metal complexes containing extended ligands (e.g. CN^-, CO, py, bz, cp, etc.) that the LUMO (d_σ apart) resembles a ligand antibonding level, and our calculations show that this situation also occurs for those model pyridine complexes examined herein. This orbital (LUMO) is represented in Fig. 1, alongside that of ψ_4 for the benzyl anion [3]. Although our LUMO does have significant location at C_2 and C_4, there is also a non-trivial contribution from C_3 and a very substantial involvement of the nitrogen $2p_\pi$ orbital. This orbital is very similar in composition to the lowest vacant orbital of pyridine itself as expected. Thus the comparison of the LUMO of a pyridine metal complex with that of the benzyl system is a naive oversimplification. In fact, if ψ_4 of benzyl anion were to represent the LUMO of a metal complex ion in the absence of back bonding [3], then ψ_4 would be largely metal d_π in character and would therefore have little contribution from C2 and C4 of the ring.

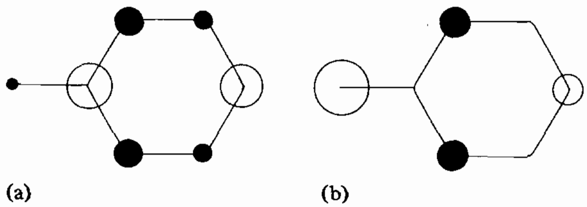

Fig. 1. (a) LUMO of $Fepy(NH_3)_5^{2+}$, (b) ψ_4 (LUMO) of benzyl.

In summary, the results of the present calculations on cationic systems do not support earlier conclusions drawn either from qualitative considerations of metal–ligand back bonding effects [2] or by modelling a metal–pyridine moiety on the benzyl group [3].

Is the situation different for anionic complexes? We have previously reported calculations [4] for anionic complexes of type $[Fe^{II}(N–N\ heterocycle)(CN)_4]^{2-}$ using the π bonding ligand CN^- as an alternate for further heterocyclic groups for computational expediency. However, much of the experimental work [5, 6] has been carried out on cationic complexes of type $[M(N–N\ heterocycle)_3]^{n+}$ and the charges on their ring heterocycle atoms will probably be better reflected by the cationic model $[M(N–N\ heterocycle)(NH_3)_4]^{n+}$. On the other hand, ^{13}C NMR spectra have been reported [7] for a number of heterocycles including pyridine, and the shifts for the ring carbons of the heterocycle when protonated, quaternized (methyl) and coordinated to both $[Fe^{II}(CN)_5]^{3-}$ and $[Co^{III}(CN)_5]^{2-}$ compared with the values for the free ligand. Changes in the C(4) shifts were interpreted in terms of π back bonding for $[Fe^{II}(CN)_5py]^{3-}$, but with little such bonding for $[Co^{III}(CN)_5py]^{2-}$. Although the shifts for carbon centres remote from the site of quaternization or coordination did correlate with changing electron densities at these atoms, with several factors contributing to the α carbon shifts it was not possible to compare directly with electron densities at this position.

The cyanide group, CN^-, as a π bonding ligand is likely to affect the π electron densities of the coordinated heterocycle to a much greater extent than the essentially σ bonding NH_3 group, and therefore full results for the complexes $[Fe(CN)_5py]^{3-}$ and $[Co(CN)_5py]^{2-}$ are given in Table II. These show that the total π electron density within the pyridine ring is (significantly) greatest when it is coordinated to $[Fe^{II}(CN)_5]^{3-}$ (6.154 electrons), and the total π electron density in the ring varies little between uncoordinated pyridine, methyl quaternized pyridine, $[Fe^{II}(py)_2(NH_3)_4]^{2+}$ or even $[Co^{III}(CN)_5(py)]^{2-}$ (from 5.991–6.027 electrons). For $[Fe^{II}(CN)_5(py)]^{3-}$ about half of the small total additional π electron charge, compared with free pyridine, is accumulated at position C4.

The calculations also show that generally as π electron density at a particular ring position is changed as a result of coordination to a metal–ligand moiety, or by quaternization, then the σ electron density is also modified but in a smaller and opposite sense to that of the π electrons. This effect (which clearly results from the one-centre electronic repulsion between σ and π electrons) has also been observed

TABLE II. Electron Densities (σ and π) and Total Resultant Charges at Pyridine Ring Positions in Anionic Complexes

		Uncoord. py	$[Fe^{II}(CN)_5py]^{3-}$	$[Co^{III}(CN)_5py]^{2-}$	$(py\text{-}H)^+$	$(py\text{-}Me)^+$
π Density	N1	1.075	1.107	1.083	1.358	1.303
	C2	0.956	0.976	0.948	0.913	0.936
	C3	1.030	1.038	1.037	0.992	0.985
	C4	0.951	1.019	0.974	0.832	0.851
σ Density	N1	4.115	3.803	3.799	3.568	3.580
	C2	2.889	2.915	2.923	2.913	2.911
	C3	2.999	2.994	2.999	2.998	3.003
	C4	2.980	2.959	2.977	3.029	3.023
Total charge	N1	–0.190	+0.090	+0.118	+0.074	+0.117
	C2	+0.155	+0.109	+0.129	+0.175	+0.153
	C3	–0.029	–0.032	–0.036	+0.010	+0.012
	C4	+0.069	+0.022	+0.049	+0.139	+0.126

[8, 9] for the *para* position in substituted benzene derivatives. Moreover, the observed relationship between the changes in σ and π electron densities at the 4-position ($\Delta\sigma \approx -0.41\ \Delta\pi$) in these coordinated pyridines is very similar to that derived previously [8] for substituted benzenes. $[Co^{III}(CN)_5(py)]^{2-}$ is an exception: there, the calculated changes are very small for both σ and π densities. Consequently, the calculated total charges parallel the π electron charges but are somewhat smaller. The calculated charges, particularly at the 4-position, are in agreement with the ^{13}C NMR results, where, compared with free pyridine, resonance occurs upfield for $[Fe^{II}(CN)_5(py)]^{3-}$ but downfield for $[Hpy]^+$ and $[Mepy]^+$. The conclusion drawn [7] from the ^{13}C-shifts that little π back bonding to the pyridine ring occurs for the $[Co^{III}(CN)_5(py)]^{2-}$ complex is supported by the present calculations.

Finally, it is evident from the calculations that the variation in charge distribution around the pyridine ring which occurs on coordination is dependent both on the metal and on any other coordinated ligands. Thus carbon atoms C2 and C4 both accumulate negative charge compared with uncomplexed pyridine in the complex $[Fe^{II}(CN)_5py]^{3-}$, while in the cationic complexes $[Fe^{II}(NH_3)_n(py)_{6-n}]^{2+}$ there appears to be little change in overall charge at position C2; however atom C4 becomes substantially more positive. Thus simple models for a metal–pyridine system are unlikely to be generally applicable.

Our calculations, of course, refer to isolated ('vapour-phase') species and the nucleophilic substitutions whose pre-equilibria and rates are of interest [5] are done in solutions. Solvation (particularly localized effects) of factors and intermediates render tentative any conclusions based on such calculated electron populations. Nevertheless rates of nucleophilic reactions in isomeric tris-complexes of bidiazines (bipyridazines, bipyrimidine, and bipyrazine) do correlate [4b] with INDO calculated positive changes on particular carbon atoms.

A comparison of the total charges calculated for analogous compounds differing only in the oxidation state of the metal ion (and naturally overall ionic charge) indicates that, as originally predicted, [5b], the higher charged metal ions polarize the ligands more. For $[M(CN)_5(py)]^{n-}$ (Table II): $M = Fe^{II}$, $n = 3$, $C(2) = +0.109$; $M = Co^{III}$, $n = 2$, $C(2) = +0.129$. For $[M(NH_3)_5py)]^{x+}$ (Table I): $M = Fe^{II}$, $x = 2$, $C(2) = +0.152$; $M = Fe^{III}$, $x = 3$, $C(2) = +0.170$.

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