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Structural, NMR and Theoretical Study of Delocalization in Cobaloximes

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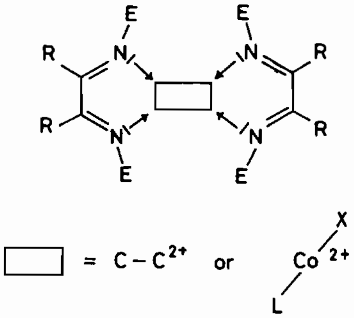
Despite the wealth of structural and NMR spectral information available for cobaloximes, a great deal of interest is now being devoted to the study of correlations between the NMR spectral data and the molecular structure of such compounds [1–8]. In this paper we present preliminary experimental and theoretical results suggesting that the ring-current model might be useful for the interpretation of the NMR spectra of cobaloximes with nitrogen donors occupying an axial coordination position. The existence of an induced π-electron ring-current is a well established criterion for determining the aromatic nature of a cyclic organic system [9], but in the field of metallacycles it has been studied only for porphyrins and phthalocyanines [10].

Neutral cobaloximes of the type $[CoX(DH)_2L]$ have been obtained through ligand substitution reactions on $[CoCl(DH)_2(H_2O)]$ or $[CoBr(DH)_2PPh_3]$, where $X = Cl^-$, B^-; DH = dimethylglyoximato (dmgH) or diphenylglyoximato (dpgH); L = pyrazine (pz), 2,6-dimethylpyrazine (Me_2pz), 2,6-dichloropyrazine (Cl_2pz), 4-cyanopyridine (CNpy), 3,5-dimethylpyrazol (DMP), or pyridazine (pdz). Substitution of the chloro ligand in these compounds produces the corresponding neutral or cationic derivatives $[CoX(DH)_2L]$, $X = CN^-$, H_2O, PPh_3.

The new compounds have been characterized by their combustion analysis, and their IR, UV, ^1H and ^{13}C NMR spectra (except for those cases in which the solubility in the usual NMR solvents was too low). The crystal structures have been determined for $X = Cl^-$, $L = Me_2pz$, Cl_2pz, CNpy, DMP; $X = Br^-$, $L = Me_2pz$ [11].

Cobaloxime is a bicyclic system with 12 π electrons, eight from the C=N bonds and four from the metal d_{xz} and d_{yz} orbitals. MO calculations of the EH type [12] show that these electrons occupy six π-type orbitals delocalized throughout the planar cobaloxime moiety, with topologies analogous to those reported previously for $L_2MC_4H_4$ metallacycles [13].

It will be useful for the subsequent discussion to establish a comparison of the delocalization in the coordination compounds under study and in a related aromatic system. Although there is no organic system in which only one atom is shared by two aromatic rings, it has been previously found useful to formally replace the d orbitals of a metal atom by combinations of the s and p orbitals of a C_2 fragment [14]. Such a replacement would take us from cobaloximes to biimidazole or the biimidazolato dianon, as schematically shown in Scheme 1, where the E groups represent either lone pairs (in the biimidazolato dianion) or the electron pair involved in the N–O bond (in cobaloximes).



Scheme 1.

MO calculations on both systems at the Extended Hückel level show the same pattern for the π^* orbitals of both systems, the main difference being that the interaction between the orbitals of the central fragment (the box in Scheme 1) and those of the organic part is poorer in the case of the transition metal; hence the delocalization is much smaller than for the organic analogue as reflected in a longer C–C distance in the ring (1.45 *vs.* 1.37 Å).

Several effects are acting simultaneously upon a particular atom to determine the shift of its NMR signal from the free to the coordinated ligand. The three main effects to consider here are: (a) the inductive effect, generally assumed to act in a deshielding way on all the ligand's atoms through the σ backbone and to decrease with the distance to the metal atom; (b) long-range effects of magnetic anisotropy, such as ring-currents arising from either the metallacycles, the axial ligand, L, or the phenyl group of the oxime (for DH = dpgH), and (c) metal-to-ligand back-bonding which can in turn alter the intensity of the ring-currents in (b).

A ring-current resulting from the delocalized electron system of the cobaloxime would affect the nuclei in different ways, depending on their relative position to the metallacycles: shielding those on top and deshielding those at the sides of the ring. This

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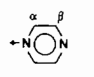
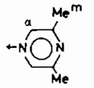
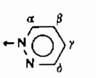
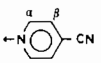
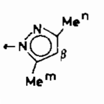
TABLE I. ^{1}H NMR Chemical Shifts (in $CDCl_3$ Relative to TMS; Varian XL-200 Spectrometer, 200 MHz) and Charge Transfer Bands (in CH_2Cl_2) for the Compounds [CoCl(dmgH)$_2$L]

	Proton[a]	Free ligand	Complex	Co → DH charge transfer band (nm)
	α		8.32	
	β	8.58	8.52	
	x		2.42	261
	α	8.28	7.94	
	m	2.54	2.48	
	x		2.42	274
	α δ	9.23	9.04	
	β γ	7.57	7.53	
	x		2.40	266
	α	7.60	7.48	
	β	8.80	8.54	
	x		2.41	271
	β	5.55	5.59	
	m	2.20	2.10	
	n		2.21	
	x		2.48	259

[a]The x protons are those corresponding to the methyl groups of the dimethylglyoximato ligands.

effect is well known for organic aromatic rings [15]. For the dimethylglyoxime methylic protons, the inductive and ring-current effects work in the same direction; consequently, those protons appear downfield (Table I) from the neutral free ligand or its dianionic form (2.0 ppm) [16]. The magnitude of this shift (*ca.* 0.4 ppm), though, is significantly smaller than in organic aromatic rings (*ca.* 1.5 ppm) because of the smaller delocalization previously noted.

The α protons of the axial ligands, on the other hand, are shifted upfield, in agreement with previous observations on other cobaloximes [7]. The same trend appears for the α methyl in the DPM complexes. Furthermore, no correlation is found between the shifts for the α protons and the pK_a of the ligands. All this indicates that the ring-current shielding predominates over the inductive deshielding on those protons.

Although the downfield shifts of protons on equatorial or axial positions in transition metal complexes can be rationalized in terms of the magnetic influence of the d electrons only [17], the simultaneous observation of a downfield shift for the methylic protons of the oxime and an upfield shift for the protons of the axial ligands can be taken as a proof of the existence of an aromatic-like ring-current in the cobaloxime. That both shifts have the same origin can be seen in the nice correlation shown in Fig. 1 for the new series of compounds; the same trend is seen for the α protons of the pyridine [7] and tert-butylpyridine [8] cobaloximes previously reported. The shift of the methyl signal of dimethylpyrazine from the free ligand is also correlated to δ_{CH_3} (dmgH) but with a much smaller slope, as those methyl groups are farther apart from the metallacycles and are consequently less affected by the ring current.

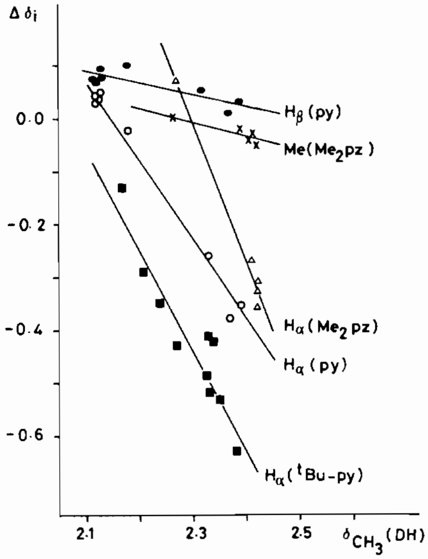


Fig. 1. Correlation between the ^{1}H chemical shift of the equatorial ligands methyl groups (δ_{CH_3}) and the displacement of the signals of the axial ligand L ($\Delta\delta_i = \delta_i$ (complexed ligand) $- \delta_i$ (free ligand)) in three series of compounds [CoX(dmgH)$_2$L]. Linear regression lines are shown; experimental values for L = py and ^{t}Bu-py are from refs. 7 and 8, respectively.

If the upfield shifts, relative to the free ligand, of the signals corresponding to the H_α or the C_α atoms of the axial ligand L are used as a measure of the cobaloxime ring-current intensity, the following series can be established:

$$Cl^- \simeq H_2O \geqslant Br^- > PPh_3 \gg CN^- \qquad (1)$$

$$Me_2pz > CNpy > pdz > pz > DMP \qquad (2)$$

Notice that the ligand ordering in eqn. (2) is the same as that of their charge transfer wavelengths (Table I). This is also true for eqn. (1): for L = Me_2pz the observed wavelengths are 275 (X = Cl^-), 270 (X = Br^-) and 245 nm (X = CN^-).

For the new series of cobaloximes, the shifts of the axial ligand protons can be correlated with their position relative to the rings (defined through their cylindrical coordinates ρ and z, taking the metal atom as the origin of coordinates) as should be expected for a ring-current effect, but also with the wavelength of the Co → DH charge transfer band, according to eqn. (3) (multilinear regression coefficient for eight experimental points: 0.99; standard error of estimate: 0.03 ppm).

$$\Delta\delta_{L}(^{1}H) = 2.211 + 0.118\rho + 0.078z - 0.011\lambda \qquad (3)$$

If one pays attention to the cobalt d_{xz} and d_{yz} orbitals, the dependence on λ can be easily understood, because these orbitals are involved simultaneously in the Co → axial ligand back-bonding and in the π system of the cobaloxime moiety. In other words, an increase in Co → L back-bonding would produce a depopulation of these orbitals and consequently the energy of the charge transfer band, as well as the intensity of the ring-current in the cobaloxime, would decrease. Therefore, the orderings of eqns. (1) and (2) can be regarded as the order of increasing π-acceptor ability of the axial ligands.

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