Electronic Transmission in Schiff-base Complexes of Cobalt(III)

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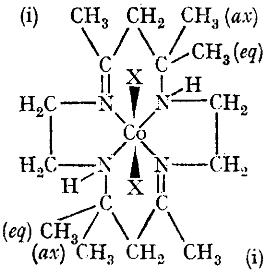
HILL, MORALEE, and COLLIS[1] have recently reported the ^{1}H n.m.r. spectra of cobalt(III) dimethylglyoximates of the form "$XCo(DH)_2PPh_3$" where the axial ligand X was varied [DH represents the dimethylglyoximate anion]. The chemical shifts of the methyl hydrogens ($\tau_{\rm Me}$) of the dimethylglyoxime ligands were found to be dependent upon the axial ligand X, and the shifts were correlated with the Hammett σ values for X. We have been investigating some very closely related Co^{III} complexes[2,3] (I) and have observed that the chemical shifts of the imine methyl groups (i) in these complexes also exhibit considerable sensitivity to the ligands X. However, X groups which cause upfield shifts in the dimethylglyoximates appear to cause downfield shifts ($\tau_{\rm i}$) in the Schiff-base complexes.



Co(A)X$_2$ (I)

Complexes of the Curtis macrocycle (I) contain equatorial alkyl methyl groups (*eq*) which have about the same geometrical relationship to magnetically polarizable groups in the $CoAX_2^{n+}$ complex and to the solvent as do the imine methyl groups. The resonance due to these equatorial alkyl methyl groups occurs upfield, ($\tau_{eq} \simeq 9$ p.p.m.) and the difference ($\tau_{eq} - \tau_{\rm i} = \Delta_{\rm i}$) between the chemical shifts of the two kinds of equatorial methyl groups is very sensitive to X (Table). These differences indicate very strongly that electronic effects are transmitted from the axial ligand X to the imine methyl group, as suggested by Hill *et al.*[1]

On the other hand the difference ($\tau_{eq} - \tau_{ax} = \Delta_{\rm a}$) in chemical shifts of the equatorial and axial geminal dimethyl groups is also a sensitive function of X, and illustrates the magnitudes of variation in chemical shift to be expected from the proximity of magnetically polarizable groups (in this case the nonbonding electron density of the Co^{III}). The imine methyl groups in both the $XCo(DH)_2PPh_3$ and $CoAX_2^{n+}$ complexes are similarly disposed relative to the central metal ion. Much of the difference in the observed chemical shifts for these two series of complexes may arise from the very large magnetic polarizability of the phenyl groups of the PPh_3 ligand. It is well known that alkyl groups above the plane of a phenyl ring are shifted upfield.[5]

Insofar as the chemical shifts represent changes in electron density at the imine methyl carbon, the downfield shifts (or large $\Delta_{\rm i}$) might be expected to reflect a decrease in acidity of the methyl protons. We have investigated the imine-methyl H/D(D_2O)

TABLE

Chemical shift data for methyl protons of $XCo(DH)_2PPh_3$[c] *and* $CoAX_2^{n+}$ [a]

X	$\tau_{\rm Me}$[b,c]	$\tau_{\rm Me(i)}$	$\tau_{\rm Me(\it eq)}$	$\tau_{\rm Me(\it ax)}$	$\Delta_{\rm i}$(p.p.m.)	$\Delta_{\rm a}$(p.p.m.)	$\sigma_{\rm para}$[e]
NO_2^-	7·71	7·66	9·15	8·47	1·49	0·68	0·78
CN^-	7·79	7·60[d]	8·73[d]	8·54[d]	1·13	0·19	0·66
Cl^-	7·99	7·54	8·86[f]	8·56	1·32	0·30	0·23
Br^-	8·00	7·37	8·98	8·41	1·61	0·57	0·23
OH^-		7·48[d]	8·84[d]	8·47[d]	1·36	0·37	−0·37
SCN^-		7·50	8·94	8·45	1·44	0·49	
H_2O		7·50[d]	8·85[d]	8·42[d]	1·35	0·43	

[a] Measured in $(CD_3)_2SO$.

[b] Ref. 1.

[c] Measured in CH_2Cl_2.

[d] Measured in D_2O.

[e] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p. 173.

[f] The $Co(Ab)Cl_2^+$ and $Co(Aa)Cl_2^+$ isomers[3] differ in n.m.r. spectra only in τ-Me$_{(eq)}$. The value for $Co(Aa)Cl_2^+$ is 8·90.

exchange rates[2] and find the rates decrease for $X = OH^- > CN^-$. This is consistent with the trend in Δ_1 but contrary to Hammett σ values.

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[1] H. A. O. Hill, K. G. Moralee, and R. E. Collis, *Chem. Comm.*, 1967, 888.

[2] R. E. Ball, J. C. Charkoudian, and J. F. Endicott, Abstracts, 154th National Meeting, American Chemical Society, Chicago, Illinois, September, 1967, No. 0–034.

[3] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 1967, **6**, 770.

[4] M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, 1966, 908.

[5] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon, Oxford, 1965, Ch. 4.