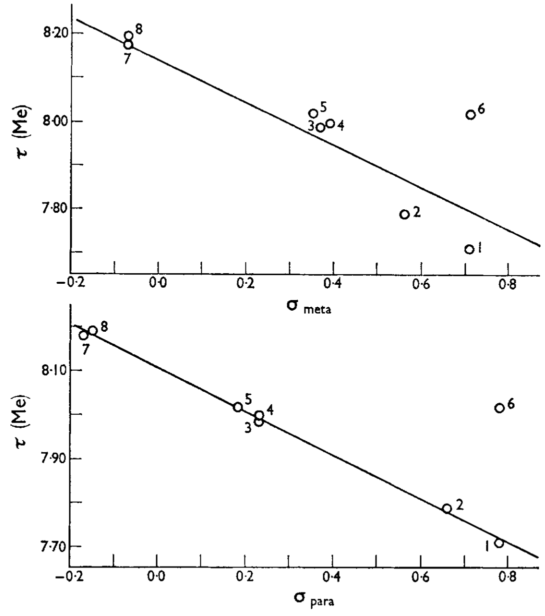
# Study of Electronic Transmission in Cobalt(III) Dimethylglyoxime Complexes by Nuclear Magnetic Resonance

By H. A. O. HILL* and K. G. MORALLEE,
(*Inorganic Chemistry Laboratory, Oxford University*)
and R. E. COLLIS
(*Chemistry Department, Southampton University*)

IT is well-known that one ligand in a metal complex influences the kinetics and thermodynamics of the replacement reactions involving other ligands in the same complex. Such effects have been observed in cobalt(III) dimethylglyoximates,[1] cobalamins (derivatives of vitamin $B_{12}$)[2] and cobalt(III) complexes of Schiff bases.[3] An understanding of these effects would be aided if the ligand dependence of the electron-density in the ground-state was known. We have measured the $^1H$ n.m.r. spectra of some cobalt(III) dimethylglyoximates of the form, $RCo(DH)_2L$, where L is $PPh_3$ in deuterochloroform and dichloromethane, and we have found that the chemical shifts of the methyl hydrogens in the dimethylglyoximate planar ligand depend on the axial ligand (Table). The resonance assigned to the dimethylglyoximate methyl protons is always a doublet $J \sim 2$–3 c./sec., due to long-range coupling with the $PPh_3$ phosphorus.[4] The chemical shift and the line width of the resonance assigned to the hydrogen-bonded hydrogens is also dependent on the axial ligand. We must assume that the relaxation time of the hydrogen-bonded hydrogens is axial-ligand dependent and that in some complexes they are broadened so as to be unobservable. They are, however, observable in other solvents, *e.g.*, Gillard and Wilkinson assigned[5] a resonance at $\tau$ $-8{\cdot}28$ to them in $Co[DH]_2pyCl$ measured in dimethyl sulphoxide. Schrauzer has reported[6] that they have chemical shifts of $\sim 0\,\tau$.



FIGURE

*Plot of* $\tau$(Me) versus *Hammett* $\sigma$*-functions of* R *for* $RCo(DH)_2PPh_3$ *complexes in* $CH_2Cl_2$.

TABLE

$\tau$ *Values of dimethylglyoximate protons in* $RCo(DH)_2PPh_3$ *complexes and the Hammett* $\sigma$ *functions of* R.

| Figure Number (*cf.* Table) | R | $\tau_{(Me)}$ | | $\tau_{O\ H\cdot O}$ | | $\sigma_{para}$[e] | $\sigma_{meta}$[e] |
|---|---|---|---|---|---|---|---|
| (1) | $NO_2$[A] | 7·71[a] | | C | | 0·78 ± 0·02[d] | 0·71 ± 0·02[d] |
| (2) | CN | 7·79[a] | | C[a] | | 0·66 ± 0·02 | 0·56 ± 0·05 |
| (3) | Cl | 7·99[a] | | C[a] | | 0·23 ± 0·02 | 0·37 ± 0·02 |
| (4) | Br | 8·00[a] | 7·98[b] | C[a, b] | | 0·23 ± 0·02 | 0·39 ± 0·02 |
| (5) | (I) | 8·02[a] | 8·01[b] | C[a, b] | | 0·18 ± 0·1 | 0·35 ± 0·02 |
| (6) | $NO_2$[B] | 8·02[a] | | C[a, b] | | 0·78 ± 0·02[d] | 0·71 ± 0·02[d] |
| — | $CH_2{\cdot}CF_3$ | — | 8·16[b] | — | 8·16[b] | — | — |
| (7) | $CH_3$ | 8·18[a] | 8·18[b] | −8·22[a] | −8·10[b] | −0·17 ± 0·02 | −0·07 ± 0·02 |
| (8) | $CH_2{\cdot}CH_3$ | 8·19[a] | 8·19[b] | −8·15[a] | −8·02[b] | −0·15 ± 0·02 | −0·07 ± 0·1 |
| — | $CH_2{\cdot}CH_2{\cdot}CH_3$ | — | 8·19[b] | — | −8·02[b] | — | — |

[a] = measured in $CH_2Cl_2$; [b] = measured in $CDCl_3$; [c] = not observed; [d] = values for ← $NO_2$.

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

We have found that a good correlation of the $\tau$ (Me) values, measured in dichloromethane, with the Hammett $\sigma_{\text{para}}$ function of R as shown in the Figure. The attempted correlation with the $\sigma_{\text{meta}}$ function shows much more scatter. We conclude, from the correlation observed here, that changes in the electron density in the $\sigma$-orbitals are mainly responsible for the change in chemical shift with each ligand having some additional influence on the $\pi$-electron density of the dimethylglyoximate ligand.

The two values for $NO_2$ as the axial ligand are due to the two complexes isolated which both analyse for $Co(DH)_2NO_2(PPh_3)$. We assume they are the nitro- and nitrito-complexes and this may be reflected in their different i.r. spectra; the following bands did not appear in the i.r. spectra of other $RCo(DH)_2PPh_3$ complexes:

A 1408 s 1310 vs 817 w 810 vw cm.$^{-1}$

B 1410 s 1313 vs 806 s cm.$^{-1}$

The chemical shift of the dimethylglyoximate methyl hydrogens of isomer A corresponds, if our correlation between Hammett $\sigma_{\text{para}}$ function and chemical shift is meaningful, to a Hammett $\sigma_{\text{para}}$ function of 0·78 which is that for the nitro-group. We therefore assume that iosmer A is the nitro-complex and isomer B the nitrito-complex. Indeed the chemical shift of the isomer B corresponds to a Hammett $\sigma_{\text{para}}$ function of approximately 0·15 which is in the correct region for some oxygen-containing substituents.

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