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ELECTRONIC TRANSMISSION IN SOME ORGANOMETALLIC DERIVATIVES OF COBALT(III) BAE AND SALEN COMPLEXES

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The transmission of electronic effects throughout metal complexes is often apparent in the dependence of the rates and equilibria of ligand replacement reactions on the properties of a ligand elsewhere in the complex. Kinetic and thermodynamic *trans*- and *cis*-effects have been studied most extensively in square-planar platinum and palladium complexes. However, in tetragonally-distorted octahedral cobalt(III) complexes of planar conjugated ligands the thermodynamic *trans*-effect, that is, the effect of one axial ligand on replacements involving the other, has been observed in cobalamins[1,2] and also in cobalt(III) BAE*, and SALEN*[,3] complexes. The effect of the axial ligand on the physical and chemical properties of the planar ligands, that is, the *cis*-effect, is reflected in the dependence of the chemical shift of hydrogens in the corrin ligand in cobalamins[4] and in cobalt(III) dimethylglyoxime complexes[5], on the nature of axial ligand. In this paper we describe the study by NMR of such effects in cobalt(III) SALEN and BAE derivatives.

RESULTS

Cobalt(III) BAE complexes

In chloroform the cobalt(III) BAE complexes are presumably five-coordinate[6]. The NMR spectra of the five-coordinated BAE derivatives with axial alkyl ligands are given in Table 1, and the spectrum of the methyl derivative is shown in Fig. 1a. The assignment of the spectrum is quite straightforward though we have not yet differentiated between the two different types of methyl groups in the BAE ligand. Most of the resonances are first order. However, the resonance assigned to the bridging methylene hydrogens is complex. This is probably because the hydrogens above the plane of the BAE ligand are not equivalent to those below and therefore form a A_2B_2 system [structure (A)]. The non-equivalence of the methylene hydrogens is strikingly apparent when phenyl is the axial ligand, due presumably to the marked effect of the ring current of the phenyl group on the chemical shift of the hydrogens above the plane.

When pyridine and other bases are added to the chloroform solutions of the cobalt(III) BAE complexes it is known that they form weak complexes giving six-

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* BAE = bis(acetylacetone) ethylenediimine; SALEN = bis(salicyl aldehyde) ethylenediimine.

TABLE 1

τ-VALUES FOR RCo(BAE), 0.1 *M* IN $CDCl_3$

(w) = weak, (d) = doublet, (t) = triplet, (q) = quartet.

R	*=CH−*	*$=N-CH_2-CH_2-N=$*	*$OC-CH_3$, $NC-CH_3$*	*R*
CH_3	4.88	6.50 (w), 6.59, 6.61, ~6.70 (w)	7.91, 7.97	7.75
C_2H_5	4.92	6.60, 6.63	7.93, 7.99	CH_2: 6.56; $J \simeq 7.5$ (q) CH_3: 10.29; $J \simeq 7.5$ (t)
C_2H_3[a]	4.76	~6.55 (w), 6.64, 6.66 (w), ~6.77 (w)	7.89, 7.92	CH: 3.40; $J \sim 4.5$ (d) 3.27; $J \sim 4.5$ (d) CH_2: 5.86; $J \sim 4.5$ (d) 6.01; $J \sim 4.5$ (d) 6.18; $J \sim 4.5$ (t)
C_6H_5	4.58	6.38 (w), 6.46 (d), 6.55 (t), 6.67 6.77 (d), 6.86 (t), 6.95 (w)	7.84, 7.86	*o*-H: 3.78, 3.86 *m*, *p*-H: 3.06 (w), 3.14, 3.22, 3.30 (w)

[a] The preparation of $C_2H_3Co(BAE) \cdot H_2O$ here used will be published elsewhere.

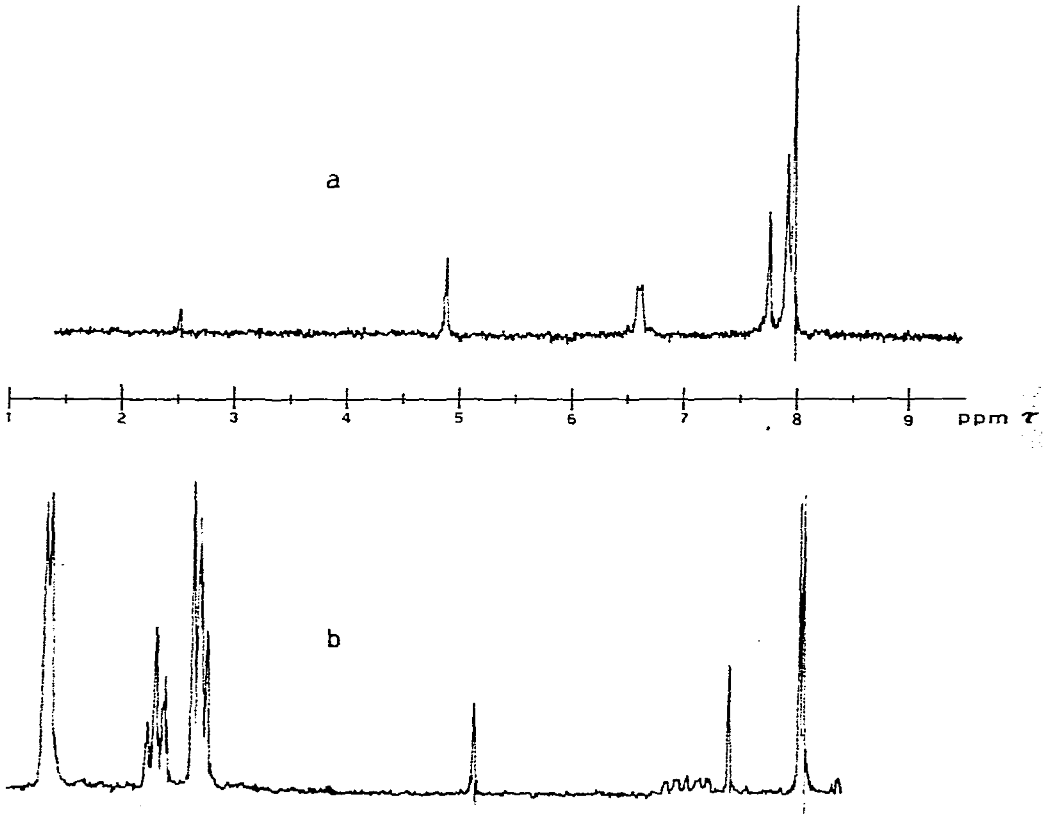


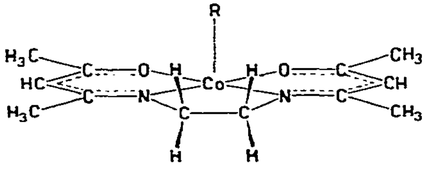
Fig. 1.

TABLE 2

τ-VALUES FOR $RCo(BAE)\cdot Py \rightleftarrows RCo(BAE) + Py$ EQUILIBRIUM IN $CDCl_3$
(w) = weak, (d) = doublet, (t) = triplet, (q) = quartet.

R	$\frac{RCo(BAE)\cdot Py}{RCo(BAE)}$	*=CH–*	$=N{-}CH_2{-}CH_2{-}N=$	$OC{-}CH_3$, $NC{-}CH_3$	*R*
CH_3	7	5.16 (5.20)	6.79 (w), 6.88 (d), 6.97 (t), 7.06, 7.16(t), 7.25 (d), 7.34 (w)	8.07, 8.10	7.43
C_2H_5	3	5.14 (5.23)	6.97, 7.01	8.07, 8.11	CH_2 (q): 6.31; $J \sim 7$ CH_3 (t): 9.63; $J \sim 7$
C_2H_3	7	5.10 (5.15)	6.75 (w), 6.83 (d), 6.93 (t), 7.03, 7.13 (t), 7.22 (d), ~7.30 (w)	8.06, 8.07	CH: 1.82, 1.88, 1.97, 2.03 $J = 6$ CH_2: [5.07d][a], 5.22 (t), 5.29
C_6H_5	4	5.11 (5.26)	6.71 (w), 6.79, 6.82, 6.91 (w)	8.06, 8.09	3.04

[a] Partially hidden by =CH– peak.



(A)

coordinate species. This is reflected in the change in absorption spectra[6] and is also apparent in the NMR spectra as shown in Table 2 and Fig. 1b. Treating the cobalt(III) BAE derivatives with pyridine causes the resonances of the BAE hydrogens and those of the axial ligand R to change.

Using an iterative method we have calculated the approximate stability constants for the equilibrium

$$RCo(BAE) + Py \overset{K}{\rightleftarrows} RCo(BAE)\cdot Py$$

using the change in the chemical shift of the methine hydrogens as an indication of the position of equilibrium. The values obtained were:

$$R \quad = C_2H_3;\; CH_3;\; C_6H_5;\; C_2H_5$$

$$K(\text{mole}\cdot l^{-1}) = 12 \;;\; 9 \;;\; 6 \;;\; 1$$

which decrease in the same order as those determined spectrophotometrically[3] in benzene. The chemical shifts calculated for the methine hydrogens in the fully-formed RCo(BAE)·Py complexes are given in parentheses in Table 2. The observation of a single resonance for both free and complexed pyridine and also single resonances for

TABLE 3

τ-VALUES FOR $CH_3Co(BAE)\cdot L$ IN $CDCl_3$
(w) = weak, (d) = doublet, (t) = triplet.

L	*=CH–*	*$=N-CH_2-CH_2-N=$*	*$OC-CH_3$, $NC-CH_3$*	*$CoCH_3$*
None	4.88	~6.50 (w), 6.59, 6.61, ~6.70 (w)	7.97, 7.91	7.75
4-Cyano-pyridine	5.12	6.73 (w), 6.83 (d), 6.92 (t), 7.01, 7.10 (t), 7.19 (d), 7.28 (w)	8.07, 8.09	7.41
Pyridine	5.16	6.79 (w), 6.88 (d), 6.97 (t), 7.06, 7.16 (t), 7.25 (d), 7.34 (w)	8.07, 8.10	7.43
4-Methyl-pyridine	5.18	6.81 (w), 6.89 (d), 6.99 (c), 7.07, 7.15 (c), 7.25 (d), 7.34 (w)	8.08, 8.11	7.46
Piperidine	5.26	6.87	8.10, 8.12	7.66
Triphenyl-phosphine[a]	4.99	6.80	7.97, 8.10	7.64

[a] Complex not fully formed.

the hydrogens of the BAE ligand shows that the rate of exchange of the pyridine ligand is fast.

We have mentioned above the effect of the axial ligand on the non-equivalence of the methylene hydrogens. This is also noted in the pyridine complexes, *e.g.* the methylcobalt(III) BAE pyridine complex (Fig. 1b). Presumably the ring current of the pyridine effects the non-equivalence (Fig. 1b).

Methylcobalt(III) BAE complexes with other bases

The NMR spectra of methylcobalt(III) BAE in the presence of excess 4-methylpyridine, 4-cyanopyridine and piperidine are given in Table 3 and it will be seen that the chemical shift depends on the base. The complexes were assumed to be fully-formed since the addition of further amounts of the bases did not alter the NMR spectra. As with pyridine, the substituted pyridines have the same effect on the equivalence of the methylene hydrogens. In contrast the methylene hydrogens give rise to a single resonance when piperidine is the ligand. Triphenylphosphine forms only a limited amount of six-coordinate complex even in the presence of 20 equivalents of the ligand. The BAE methine resonance in six-coordinate species obtained from RCo(BAE) ($R = CH_3$, C_2H_5, C_2H_3, C_6H_5) and pyridine and from CH_3Co-(BAE) and 4-methylpyridine, 4-cyanopyridine, piperidine occurs at higher field than in free BAE; *i.e.* the methine resonance is shifted in the same sense as in the BAE complexes of Ni^{II}, Pt^{II}, Pd^{II} [7].

Cobalt(III) SALEN complexes

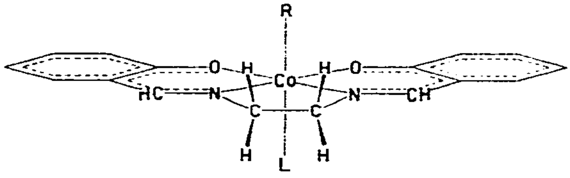
The spectra of cobalt(III) SALEN complexes measured in dimethyl sulphoxide are much more complex (see Table 4). We have not analysed the spectra of the aromatic hydrogens but the resonance of the sharp singlet due to the methine proton depends on the axial ligand R. In these complexes the equivalence of the methylene hydrogens

TABLE 4

τ-VALUES FOR RCo(SALEN)·H_2O IN $(D_3C)_2SO$

Compound	*=CH–*	*Aromatic hydrogens*	*=N–CH_2–CH_2–N=*	*R*	*H_2O*
$CH_3Co(SALEN)\cdot H_2O$	2.05	2.84, 2.91, 3.00, 3.18, 3.27, 3.56, 3.63, 3.71	6.30 (w), 6.39, 6.43, 6.60 (w)	7.88	6.66
$C_2H_5Co(SALEN)$	1.99	2.82, 2.90, 2.98, 3.14, 3.23, 3.55, 3.62, 3.69	6.12 (w), 6.22, 6.33, 6.39, 6.45, 6.54, 6.64 (w)	CH_2: 6.55, 6.62, 6.70, 6.77 CH_3: 10.06 (t); $J \simeq 7$	
$C_6H_5Co(SALEN)\cdot H_2O$	1.91	2.69, 2.77, 2.84, 2.91, 3.15, 3.23, 3.30, 3.44, 3.54, 3.61	6.28, 6.38, 6.48	[a]	6.65

[a] In same region as SALEN aromatic hydrogens.



(B)

[structure (B)] appears to have a different dependence on the axial ligand from that observed in the BAE complexes. Although the methyl and phenyl were added as aquo complexes, hydrogens of the water have the same chemical shift in both complexes and this shift is not significantly different from that of free water in di(methyl-d_3) sulphoxide. Owing to coordinating properties of $(CD_3)_2SO$ the complexes are presumably six coordinate, with di(methyl-d_3) sulphoxide as the sixth ligand.

DISCUSSION

Cis-effects

In all the complexes studied the resonances of the hydrogens of the planar ligands depend on the axial ligands coordinated to the cobalt(III). Previous NMR work on the *cis*-effect in cobalt(III) dimethylglyoxime complexes has shown that there is a good correlation between the proton resonances of the in-plane hydrogens and the Hammett σ *para*-function of the axial ligands[5]. In the five-coordinate complexes of BAE we see that the resonance of the CH hydrogen moves to higher field in the order ethyl > methyl > vinyl > phenyl. This can be interpreted simply in terms of increasing electron density on the cobalt(III) being transmitted to the methine hydrogen thereby causing a greater shielding. Though the shifts for the methyl resonances of the BAE ligand are smaller they are in the same order.

In the six-coordinate cobalt(III) BAE complexes the resonance of all the hydrogens in the BAE ligand depend on the coordinated base. That due to the methine hydrogen is the most sensitive, the chemical shift moving to higher field in the order piperidine > 4-methylpyridine > pyridine > 4-cyanopyridine. This is the order of decreasing basicity. The simplest explanation of this effect is that as in the five-coordinate species, the increasing electron density on the cobalt(III) is reflected in an increased electron density on methine hydrogen with a concomitant increase in the shielding. Much smaller shifts, but again in the same order, are noticed for the methyl hydrogens. The dependence of the chemical shift of the methine hydrogen on the nature of the coordinated carbon ligand is different from that observed in the five-coordinate complexes. The resonance shifts to higher field in the order phenyl > ethyl > methyl > vinyl. We have not, as yet, an explanation for this order.

Trans-effect

Using NMR we can obtain an indication of the groundstate *trans*-effect, as shown in the dependence of the chemical shift of the cobalt(III) axial methyl hydrogens in $CH_3Co(BAE) \cdot L$ on the other axial ligand, L. It moves to higher field in the order piperidine > 4-methylpyridine > pyridine > 4-cyanopyridine. This is the same order as that observed for the *cis*-effect and presumably may again be correlated with an increased shielding of the cobalt(III) methyl hydrogens.

An interesting factor is that if the chemical shift reflects changes in the electron density, then the methine hydrogens show a lower electron density in the five-coordinate complexes than in the six-coordinate complexes, whereas the cobalt methyl shows a higher electron density in the five-coordinate complexes than in the six-coordinate complexes. This is rather strange, but the simple explanation of chemical shifts in terms of electron density neglects possible changes in the bond lengths, second-order Zeeman effects and direct shielding by non-bonding electrons of the cobalt(III). However, when the ligand atoms are constant, that is the sixth ligand is a nitrogenous base, then the other factors remain constant and an explanation in terms of electron densities is sufficient.

EXPERIMENTAL

All the PMR spectra were measured on a JEOL–JNM 100 spectrometer. The shifts were measured in cycles per second from TMS as an internal standard using a built-in frequency counter. The quoted shifts are accurate to 0.01.

All the complexes were prepared by previously reported methods[6,8]. The solvents used, deuterated chloroform and dimethyl sulphoxide were CIBA materials. The solutions were prepared in the absence of direct light and precautions were taken to exclude air.

SUMMARY

The proton magnetic resonance spectra of some organometallic derivatives of cobalt(III) BAE and SALEN complexes have been measured. The chemical shift of the methine hydrogens in the planar BAE ligand in the five-coordinate complexes, $RCo^{III}(BAE)$, depends on the axial ligand, the shift to high field being in the order; R = ethyl > methyl > vinyl > phenyl. The chemical shift of the methine hydrogens in the complexes, $RCo^{III}(BAE) \cdot L$, where L is a nitrogenous base, depends on the basicity of L. The shift to high field is in the order; piperidine > 4-methylpyridine > pyridine >

4-cyanopyridine. These *cis*-effects are discussed in terms of changes of electron density in the complexes. Approximate stability constants have been calculated for the equilibria; $RCo^{III}(BAE) + Py \rightleftharpoons RCo^{III}(BAE) \cdot Py$ and they show a marked dependence on R. Another example of the *trans*-effect studied was the dependence of the chemical shift of the cobalt methyl hydrogens in $CH_3Co^{III}(BAE) \cdot L$ on the basicity of L.

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