

⁵⁹Co Nuclear Magnetic Resonance Spectra of Some Alkyl Cobalt(III) Derivatives and Related Complexes

By BERNHARD E. REICHERT and BRUCE O. WEST*

(Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, Australia 3168)

Summary The considerable variation in the ⁵⁹Co resonance positions of some six-co-ordinate alkyl Co^{III} and related complexes is interpreted in terms of the relative field strength of the equatorial ligands, *viz.* (dmgH)₂ > salen > acacen.

dimethylglyoxime and its δ value lies close to its (dmgH) analogue. Thus one can qualitatively observe a marked effect on ⁵⁹Co resonances due to the nature of the equatorial ligand and a much smaller influence due to varying axial ligands when the equatorial group remains the same.

ORGANOMETALLIC compounds of Co^{III} have been prepared¹ containing a wide variety of ligands, particularly those such as dimethylglyoxime or tetradentate Schiff bases which can occupy four equatorial positions around the metal ion. The influence of axial groups on the properties of such six-co-ordinate cobalt complexes having the same equatorial ligands has been studied for such compounds² as well as vitamin B₁₂ derivatives³ but there has been little comparison of compounds having different equatorial ligands other than the electrochemical studies of Costa *et al.*⁴

We have accordingly examined the ⁵⁹Co n.m.r. spectra of a number of Co^{III} complexes having (dmgH)₂, salen, or acacen as the equatorial ligands and alkyl groups and/or monodentate Lewis bases in the axial positions. The chemical shifts were measured relative to an aqueous solution of K₃Co(CN)₆ and defined by the expression $\delta = (B_r - B_i)/B_1$ ($B =$ magnetic induction) at constant frequency under which condition the measurements were made ($\nu = 7.6596$ MHz). Subscripts r and i refer to the reference and the compound under study, respectively. Results are presented in the Table. It is apparent that the δ values of the (dmgH)₂ complexes are distinctly lower than those of the corresponding compounds containing the Schiff-base ligands salen or acacen. The single complex examined which is derived from 1,3-bis(biacetylmono-oximeimino)propane (bmip) is closely similar in structure to the derivatives of

TABLE

Complex ^a	δ (%) ^b	Solvent
[Co(dmgh) ₂ (NH ₃) ₂]Cl	0.512	H ₂ O
MeCo(dmgh) ₂ H ₂ O	0.402	MeOH
MeCo(dmgh) ₂ (py)	0.337	CHCl ₃
MeCo(dmgh) ₂ (ba)	0.332	CHCl ₃
BuCo(dmgh) ₂ (py)	0.342	CHCl ₃
Ph ₃ SnCo(dmgh) ₂ (py)	0.309	CHCl ₃
Ph ₃ SnCo(dmgh) ₂ (ba)	0.315	CHCl ₃
[Co(bmip)(NH ₃) ₂]Cl ₂	0.551	H ₂ O
[Co(salen)(NH ₃) ₂]Cl	0.806	H ₂ O
MeCo(salen)H ₂ O	0.682	MeOH
MeCo(salen)(ba)	0.680	CHCl ₃
[Co(acacen)(NH ₃) ₂]Cl	0.830	H ₂ O
MeCo(acacen)H ₂ O	0.715	MeOH
MeCo(acacen)(py)	0.696	CHCl ₃
MeCo(acacen)(ba)	0.69	CHCl ₃

^a dmgh⁻ = Dimethylglyoximato anion, salen²⁻ = NN'-ethylenebis(enebis(salicylaliminato) anion, acacen²⁻ = NN'-ethylenebis(acetylacetonato) anion, ba = benzylamine. ^b Measured at 7.6596 MHz at 295 K. δ Values are accurate to ± 0.005%, except for MeCo(acacen)(py) where excessive line width reduced accuracy to *ca.* ± 0.02%.

The chemical shifts are linearly related to the nuclear shielding constants σ by expression (1) and hence related

$$\sigma_1 = \sigma_r - (2\pi\nu/\gamma B_r)\delta_1 \quad (1)$$

to the ability of the co-ordinating groups in complexes to split the electronic energy levels.⁵ Dharmatti and Kanekar⁶

have used such a relationship to place a series of ligands in order of increasing field strength, their results indicating that ligands in complexes showing the smallest chemical shifts produced the largest ligand field splitting. More recently it has been shown⁷ that the linear relationship breaks down when covalent contributions to bonding become more important and this factor would apparently also account for the lower δ values of the alkyl derivatives in this work as compared with the diammine complexes.

The complexes under examination can be classified into series in which the axial ligands remain constant and the equatorial ligands vary. In each case the order of chemical shifts is $(\text{dmgH})_2 < \text{salen} < \text{acacen}$ and it may be concluded that this represents the order of *decreasing* ability to split the energy levels of Co^{III} .

The $\text{Co}^{\text{III}}\text{-C}$ bonds in complexes involving $(\text{dmgH})_2$ ligands appear stronger or at least more stable to dissociation than those in complexes involving Schiff-base ligands. The

present indication that two linked dmgH ligands have a greater ability to split Co^{III} energy levels than the tetradentate Schiff-base ligands may thus explain the greater stabilisation of Co-C bonds in these complexes by increasing the separation between the lowest (empty) antibonding level associated with the molecular orbitals defining the Co-C bond and the highest filled level in the general sense first suggested by Chatt and Shaw⁸ but without any specific need to postulate a π -bonding interaction.

As a further extension of these results it may be significant that stable Co-M bonds have been formed when cobalt is co-ordinated by $(\text{dmgH})_2$ and M is a metal such as Sn ,⁹ in complexes such as $\text{Ph}_3\text{SnCo}(\text{dmgH})_2(\text{py})$, whereas preliminary experiments have shown that such bonds are much less stable and difficult to form when salen is the ligand concerned.¹⁰

(Received, 9th October 1973; Com. 1396.)

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