Cobalt-59 Nuclear Magnetic Resonance Study of some Polynuclear Cobalt(III) Complexes

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The ^{59}Co n.m.r. spectra of 12 polynuclear cobalt(III) complexes are reported. Chemical shifts and linewidths are discussed in relation to the spectra of mononuclear species. Complexes containing chemically non-equivalent cobalt(III) atoms exhibit discernible resonances with differing chemical shifts. ^{59}Co N.m.r. spectroscopy is shown to be a useful tool in elucidating the structures of polynuclear cobalt(III) complexes.

In recent years ^{59}Co n.m.r. spectra of diamagnetic cobalt complexes have been studied intensively. It is now well established that relatively small alterations in the co-ordination sphere surrounding the cobalt nucleus will give rise to marked differences in chemical shift.[1,2] A classical example is the asymmetric position of ^{13}C satellites relative to the central line in the ^{59}Co n.m.r. spectrum of $K_3[Co(CN)_6]$.[3] It has also been shown that the chemical shift is due to a large extent to paramagnetic contributions, δ_p: the shift to higher resonance frequencies is inversely proportional to the energy of the lowest optical *d–d* transition.[4,5] Linewidths of ^{59}Co resonances ($I = \frac{7}{2}$) are almost exclusively determined by quadrupolar relaxation.[1,6] Therefore, the linewidth provides useful additional information in elucidating structures of diamagnetic Co complexes.[7]

Cobalt-59 n.m.r. studies of Co^{III} have been reported for mononuclear complexes only. Because of the sensitivity of position and linewidth of ^{59}Co resonances to minor changes in the co-ordination sphere, ^{59}Co n.m.r. spectroscopy should be a very useful method of determining structures of polynuclear Co^{III} complexes. In the present paper we report the ^{59}Co n.m.r. spectra of 12 polynuclear complexes in aqueous solution.

RESULTS AND DISCUSSION

Formulae of the complexes investigated are shown below. Polynuclear Co^{III} complexes containing chemically non-equivalent Co atoms should exhibit lines in the ^{59}Co n.m.r. spectrum with discernible chemical shifts. The spectrum of complex (I) provides an excellent example. Two distinct resonances with different linewidths were observed (Table). The chemical shifts differed by 4 790 p.p.m. and the ratio of intensities (3 : 1) allows an unambiguous assignment. Spectra for the binuclear complex (III), which contains two equivalent Co atoms, and for the related mononuclear complex, *cis*-$[(H_3N)_4Co(OH_2)_2]Cl_3$,[8] support the above assignment of the lowest-frequency resonance. Mononuclear Co^{III} complexes with an octahedral environment of six

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[1] Y. Koike, F. Yajima, A. Yamasaki, and S. Fujiwara, *Chem. Letters*, 1974, 177; *Bull. Chem. Soc. Japan*, 1974, **47**, 1442.

[2] A. Johnson and G. W. Everett, *Inorg. Chem.*, 1973, **12**, 2801.

[3] P. C. Lauterbur, *J. Chem. Phys.*, 1965, **42**, 799.

[4] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 1957, **53**, 601.

[5] G. P. Betteridge and R. M. Golding, *J. Chem. Phys.*, 1969, **51**, 2497.

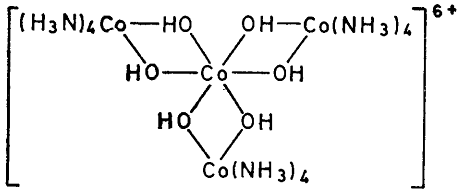
[6] A. Abragam, 'The Principles of Nuclear Magnetism,' Oxford University Press, 1961, ch. 8.

[7] R. A. LaRossa and T. L. Brown, *J. Amer. Chem. Soc.*, 1974, **96**, 2072.

[8] A. Yamasaki, F. Yajima, and S. Fujiwara, *Inorg. Chim. Acta*, 1968, **2**, 39.

oxygen atoms give rise to large chemical shifts (Figure). The central Co atom of (I) exhibits the largest chemical shift to higher frequencies so far observed, resulting from a weak ligand field of six hydroxo-bridges (δ = 14 850 p.p.m.).

The electric-field gradient for octahedral symmetry is relatively small and sharp n.m.r. signals are to be expected. However, the experimental linewidth of the second resonance of (I) was quite broad ($\Delta\nu_{\frac{1}{2}}$ 1 710 Hz) compared with correspondingly co-ordinated mononuclear species {*e.g.* for $K_3[Co(C_2O_4)_3]$ $\Delta\nu_{\frac{1}{2}}$ 250 Hz [8]}. This cannot be explained by a larger rotation-correlation time, τ_c, alone. The *X*-ray structure of the ethylenediamine derivative of (I) clearly shows that the octahedral symmetry of the central Co atom is distorted (D_3).[9] This distortion of symmetry accounts for the observed line broadening.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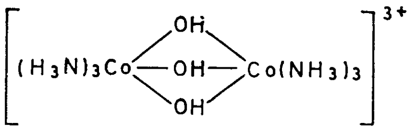
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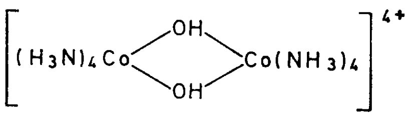
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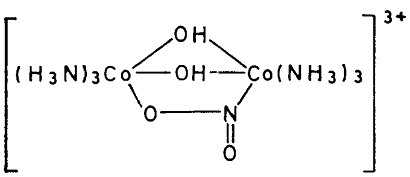
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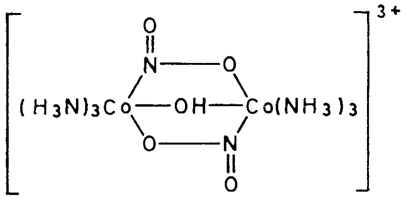
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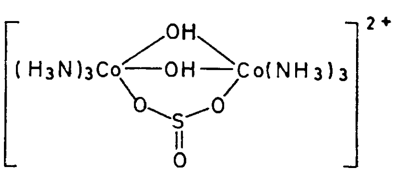
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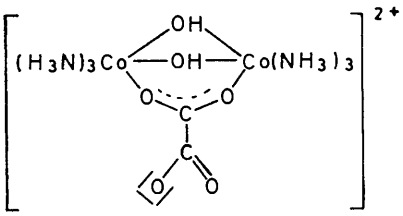
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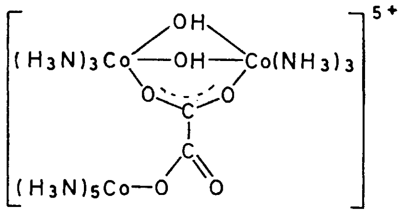
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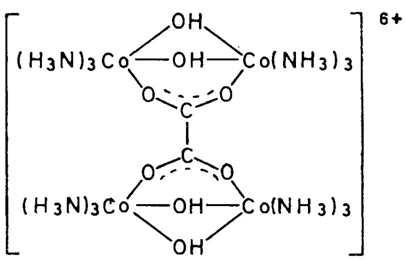
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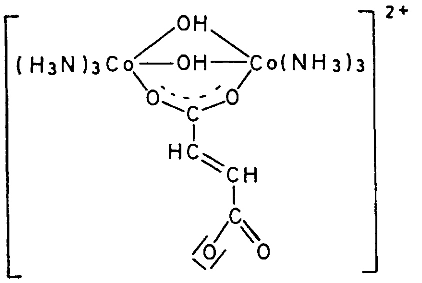
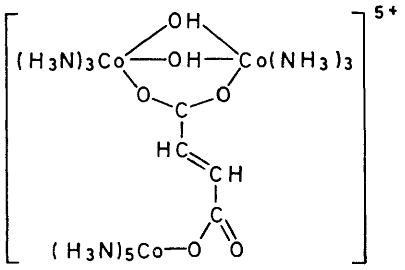

(X)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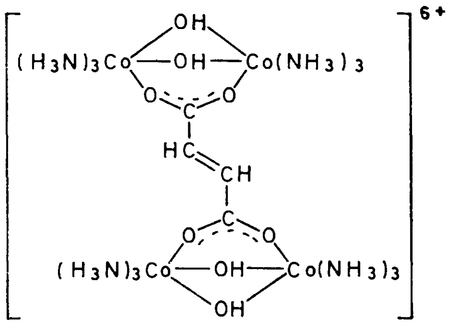
(XII)

The sensitivity of chemical shift to minor structural changes in the Co^{III} co-ordination sphere is demonstrated by the spectra obtained for binuclear complexes with NO_2-bridging ligands. The ^{59}Co n.m.r. spectrum of (IV) showed two resonances of equal intensity indicating two chemically non-equivalent Co^{III} atoms. The difference in chemical shift was quite pronounced ($\Delta\delta$ 1 280 p.p.m.). It has previously been shown by *X*-ray[10] and i.r.[11] measurements that N_3CoO_3 and N_4CoO_2 co-ordination for the two Co atoms of complex (IV) originates from unsymmetrical bonding of one bridging NO_2 group. In the ^{59}Co n.m.r. spectrum of (V), a binuclear complex with two NO_2 bridges, only *one*

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[9] U. Thewalt, *Chem. Ber.*, 1971, **104**, 2657.

[10] U. Thewalt, *Acta Cryst.*, 1970, **B26**, 81.

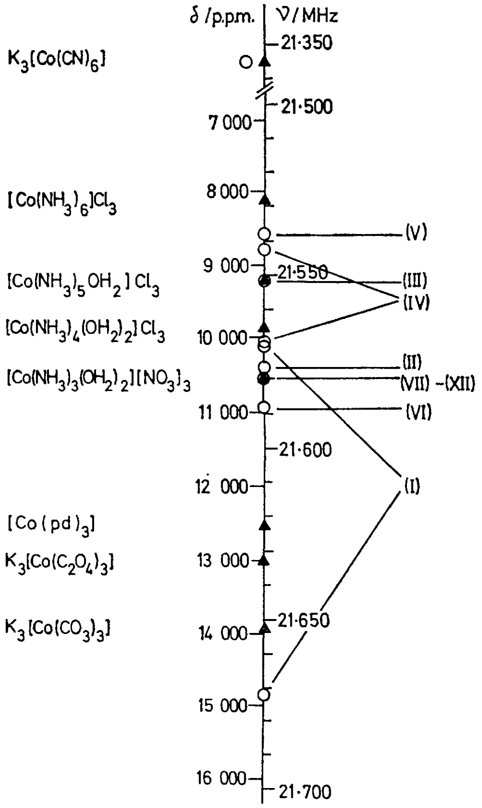
[11] K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.

resonance in the proximity of the lower signal of (IV) could be detected. Again this is in excellent agreement with an X-ray determination of the structure of complex (V)[10] which indicates that both Co atoms are equivalent (N_4CoO_2 co-ordination) due to '*anti*' orientation of two unsymmetrically bonded NO_2 bridges. By comparison of the observed resonances for (IV) and (V) the above assignment of the two resonances in (IV) is unambiguous.

^{59}Co N.m.r. data for polynuclear cobalt(III) complexes

Complex	Assignment	Chemical shift, δ [a]	Linewidth, $\nu_{\frac12}$/Hz	Refs. [b]
(I)	N_4CoO_2	10 060	6 230	9
	CoO_6	14 850	1 710	
(II)	N_3CoO_3	10 410	770	14
(III)	N_4CoO_2	9 180	170	*c*
(IV)	N_4CoO_2	8 760	540	11
	N_3CoO_3	10 040	2 510	
(V)	N_4CoO_2	8 520	4 150	10
(VI)	N_3CoO_3	10 910	440	12
(VII)	N_3CoO_3	10 520	2 490	*d*
(VIII)	N_3CoO_3	10 520	3 600	*d*
	N_5CoO	9 100 (?)	Very broad	
(IX)	N_3CoO_3	10 480	5 860	*e*
(X)	N_3CoO_3	10 500	2 300	*f*
(XI)	N_3CoO_3	10 500	2 320	*f*
	N_5CoO	Not detected		
(XII)	N_3CoO_3	10 520	3 170	*f*

[a] In p.p.m. relative to external $K_3[Co(CN)_6]$; data were obtained in 10^{-3}M-$HClO_4$ solutions at the ambient temperature of 25 °C. [b] These refer to X-ray structure determinations or, if the latter were not carried out, to preparations. [c] C. K. Prout, *J. Chem. Soc.*, 1962, 4429. [d] K. Wieghardt, *Z. anorg. Chem.*, 1972, **391**, 142. [e] H. Siebert and G. Tremmel, *Z. anorg. Chem.*, 1972, **390**, 292. [f] K. Wieghardt, *J.C.S. Dalton*, 1973, 2548.



Comparison of chemical-shift values of mono- (▲) and polynuclear (○) Co^{III} complexes; pd = pentane-2,4-dionate

The detection of only one resonance in the ^{59}Co n.m.r. spectrum of (VI) strongly supports the proposed structure[12] with two equivalent Co atoms. The SO_3-bridging group is bonded symmetrically *via* two oxygen atoms to the Co atoms. On the other hand, it is noted that a N_3CoO_2S co-ordination (unsymmetrically bonded SO_3 bridge) would give an extremely broad signal due to a very large electric-field gradient and the resonance might not have been detected.

Since the nuclear relaxation of ^{59}Co is predominantly determined by quadrupolar interactions, the linewidth is therefore very sensitive to minor alterations in the co-ordination sphere of the cobalt atom. An expression for the linewidth is given by (1),[6] where η is the asymmetry parameter, $(\partial^2V/\partial z'^2)_0$ the electric-field gradient,

$$\Delta\nu_{\frac12} \propto \left(1+\frac{\eta^2}{3}\right)\left(\frac{\partial^2 V}{\partial z'^2}\right)_0 \tau_c \qquad (1)$$

and τ_c the rotation-correlation time. Complexes (VII)—(IX) and (X)—(XII) are ideally suited to test the applicability of the correlation because chemical-shift values of ^{59}Co resonances of complexes (VII)—(XII) with N_3CoO_3 co-ordination are identical within experimental error (Table) but linewidths vary significantly. This behaviour is in agreement with the simple Griffith and Orgel theory.[4] Peak positions of the lowest optical *d-d* transition of complexes (VII) and (IX) and (X) and (XII) are also identical (19 100 ± 100 cm^{-1}). The linewidth broadens within the series of μ-oxalato- and μ-fumarato-complexes as the number of bonded Co atoms increases. This effect appears to be much more marked for the μ-oxalato-series.

Assuming identical values of η for complexes (VII)—(XII), there are two main factors which could cause the smaller increase in $\Delta\nu_{\frac12}$ observed for the μ-fumarato-series. First, the two molecular parts of the tri- and tetra-nuclear complexes (XI) and (XII), which are linked by a fumarato-bridge, are more flexible compared with their relatively rigid μ-oxalato-analogues. Therefore, the increase in the rotation-correlation time is more pronounced for the μ-oxalato-complexes. Secondly, the electric-field gradient, and therefore the linewidth, is a function of the basicity of the oxygen atoms in the μ-carboxylato-bridges.[13] The basicity is strongly increased by the number of cobalt atoms attached to the carboxylate groups. It seems reasonable that the inductive effect caused by bonding additive Co atoms to one carboxylate group may have a greater effect on the basicity in the case of the μ-oxalato-complexes than when fumarate is the bridge.

Conclusion.—Cobalt-59 n.m.r. spectra of polynuclear Co^{III} complexes containing mixed *O*- and *N*-donor ligands have been measured in order to test the usefulness of this method for structure determinations. From this study it can be concluded that the ^{59}Co n.m.r.

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[12] H. Siebert and G. Wittke, *Z. anorg. Chem.*, 1974, **406**, 282.

[13] W. Hackbusch, H. H. Rupp, and K. Wieghardt, unpublished work.

spectra of polynuclear $\mathrm{Co^{III}}$ complexes are closely related to those of mononuclear species if the individual Co atoms are in an environment of similar ligands (Figure). In other words, ^{59}Co n.m.r. spectroscopy clearly shows that there are no Co–Co interactions in polynuclear $\mathrm{Co^{III}}$ complexes. This has previously been considered a possibility on the grounds of a relatively short Co–Co intramolecular distance in complex (II)[14] and the extremely large circular dichroism exhibited by (I).[15,16] Mixed-donor complexes of $\mathrm{Co^{III}}$ have large quadrupole coupling constants leading to large linewidths. Because of this one cannot be absolutely sure that all possible ^{59}Co resonances of a given complex have been observed. This limits the applicability of ^{59}Co n.m.r. spectroscopy for structure determinations.

EXPERIMENTAL

The polynuclear complexes were prepared by procedures described in the literature (see refs. in the Table). ^{59}Co N.m.r. spectra were recorded on a Bruker pulse spectrometer SXP 4-100/15″ at ambient probe temperature (25 °C). In an effort to ascertain whether ^{59}Co n.m.r linewidths are concentration dependent spectra of complex (V) were recorded over a five-fold range of concentration. The linewidths observed were identical within experimental error.

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[14] P. Andersen, *Acta Chem. Scand.*, 1967, **21**, 243.

[15] S. F. Mason and J. W. Wood, *Chem. Comm.*, 1967, **209**.

[16] R. D. Kern and R. A. D. Wentworth, *Inorg. Chem.*, 1967, **6**, 1018.