Cobalt-59 Nuclear Magnetic Resonance Study of μ-Carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] Complexes

By **Wolfgang Hackbusch,* Herbert H. Rupp,** and **Karl Wieghardt,*** Anorganisch Chemisches Institut der Universität Heidelberg, 69 Heidelberg 1, West Germany

^{59}Co N.m.r. spectra of 24 μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes have been examined. Chemical-shift values are constant for all the complexes. However, the linewidths differ significantly. It is shown that the ^{59}Co relaxation is a function of the basicity of the oxygen atoms of the symmetrically bonded carboxylate bridging groups (affecting the electric-field gradient at the Co nuclei) and of the size and shape of the complexes (affecting the rotation-correlation time).

THE chemical shift in ^{59}Co n.m.r. spectra of Co^{III} complexes is known to be extremely sensitive to minor alterations of the Co^{III} co-ordination sphere. Griffith and Orgel [1] have shown that ^{59}Co chemical shifts can be interpreted according to Ramsey's expression: the diamagnetic shift, δ_d, is constant for all Co^{III} complexes with donor atoms of the second row of the Periodic Table and the observed chemical shift is due totally to the paramagnetic shift, δ_p, which is inversely proportional to the energy of the lowest optical *d–d* transition.[2]

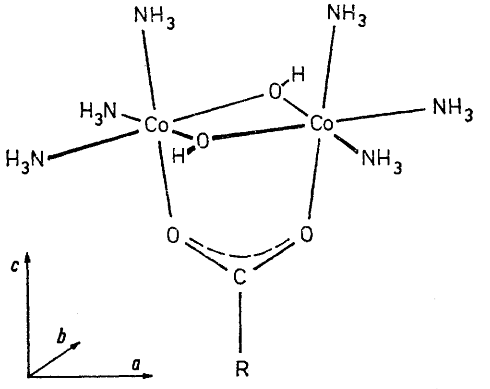

FIGURE 1 Structure of μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes including the major axes *a*, *b*, and *c*

Previous work has shown that u.v.–visible absorption spectra of μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes (Figure 1) are identical within experimental error despite very different basicities of the μ-carboxylato-bridging ligands.[3,4] [The dissociation constants, K_a, of the free organic acids vary by several orders of magnitude (Table 1).] The first absorption maximum is at 524 nm (19 100 cm^{-1}) and the molar absorption coefficient $\varepsilon = 109$ l mol^{-1} cm^{-1}.

RESULTS AND DISCUSSION

Table 1 summarises the chemical-shift and linewidth data for complexes with μ-carboxylato-bridging ligands. The chemical shifts are identical within experimental error {δ 10 525 ± 20 p.p.m. to higher frequencies relative to external $K_3[Co(CN)_6]$}. This is in excellent agreement with the theory of Griffith and Orgel [1] and demonstrates that this very sensitive method also does not detect any differences in the Co orbitals.[5] However, linewidths, $\Delta\nu_{\frac{1}{2}}$, vary from 740 to 5 000 Hz. This type of complex presents a rare opportunity to study parameters affecting the ^{59}Co relaxation by altering structural details of the complexes in a controlled and subtle fashion without changing the chemical-shift values at the same time.

^{59}Co N.m.r. linewidths are primarily controlled by quadrupolar relaxation [6,7] [equation (1)], where $V_{\alpha\alpha} = \partial^2V/\partial\alpha^2$ are the non-zero elements of the diagonalised electric-field gradient (e.f.g.) tensor with $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$, $(V_{yy} - V_{xx})/V_{zz}$ is the asymmetry parameter, and τ_r the rotation-correlation time.

$$\Delta\nu_{\frac{1}{2}} \propto \{1 + \tfrac{1}{3}[(V_{yy} - V_{xx})/V_{zz}]^2\}V_{zz}^2\,\tau_r \qquad (1)$$

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[5] W. Hackbusch, H. H. Rupp, and K. Wieghardt, *J.C.S. Dalton*, 1975, 1015.

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The Asymmetry Parameter.—The Co atoms of all investigated complexes have an identical facial A_3B_2C octahedral environment (three N atoms of the ammonia ligands, two O atoms of the μ-hydroxo-bridges, and one O atom of the μ-carboxylato-bridging group). According to point-charge calculation of the e.f.g. tensor, V_{zz} parallels the cobalt–carboxylic oxygen bond and $V_{xx} = V_{yy}$ $(= -V_{zz}/2)$.[8] Taking into account the actual charge distributions, slight deviations from octahedral symmetry may occur leading to non-vanishing asymmetry parameters. However, from the definition of the e.f.g. tensor, $1 \leqslant 1 + [(V_{yy} - V_{xx})^2/3V_{zz}^2] \leqslant 1.33$. Furthermore, from the very similar geometries of the investigated molecules, it is concluded that the asymmetry parameters do not vary considerably. Thus, any error introduced by the assumption of a constant asymmetry parameter for all complexes in solution is much smaller than the maximum 33% and can be neglected with respect to quadrupolar line broadening due to variations in τ_r and/or V_{zz}^2 (up to factors of two and five respectively).

TABLE 1

^{59}Co N.m.r. data for μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes, $[(H_3N)_3Co\mu(OH,OH,RCO_2)Co(NH_3)_3][ClO_4]_3$

				$10^{11}\tau_r$ [c]/s				
R	δ [a]/p.p.m.	$\Delta\nu_{\frac{1}{2}}$/Hz	c [b]/Å	Ellipsoid	Mutual viscosity	pK_a [d]	$\tilde{\nu}_{asym}$(CO [e]/ cm^{-1}	Ref.
H	10 525	980	3.25	0.690	2.15	3.75	1 550	4
Me	10 530	740	3.67	0.795	2.40	4.76	1 535	4
CH_2F	10 535	1 560	3.74	0.815	2.55	2.59	1 595	4
CHF_2	10 510	2 370	3.81	0.833	2.67		1 625	4
CF_3	10 510	3 960	3.88	0.845	2.76	0.23	1 655	4
CH_2Cl	10 530	1 640	3.82	0.823	2.69	2.87	1 580	4
$CHCl_2$	10 525	2 780	3 97	0.866	2.88	1.48	1 605	4
CCl_3	10 535	4 220	4.13	0.907	3.04	0.63	1 630	4
CH_2Br	10 515	1 710	3.86	0.828	2.87	2.90	1 581	[f]
$CHBr_2$	10 520	2 830	4.05	0.886	3.09		1 600	[f]
CBr_3	10 545	5 000	4.24	0.928	3.29		1 618	[f]
CH_2I	10 515	1 470	3.91	0.848	3.00	3.18	1 572	[f]
CH_2OH	10 540	1 320	3.70	0.797	2.53	3.83	1 580	[g]
Et	10 525	740	3.71	0.800	2.52	4.87	1 540	[f]
Bu^t	10 530	810	3.81	0.829	2.71	5.05	1 528	[f]
Ph	10 515	1 320	5.42	1.18	3.73	4.20	1 540	3
2-Py [h]	10 515	3 570	5.42	1.18	3.74		1 596	3
3-Py [h]	10 505	3 320	5.42	1.18	3.75		1 580	3
4-Py [h]	10 515	3 200	5.42	1.18	3.75		1 586	3
$3\text{-}O_2NC_6H_4$	10 515	2 490	5.42	1.18	4.01	3.46	1 560	[i]
$4\text{-}O_2NC_6H_4$	10 515	2 540	6.09	1.32	4.51	3.41	1 562	[i]
$3\text{-}HOC_6H_4$	10 525	1 860	5.42	1.18	3.85	4.08	1 543	[j]
$4\text{-}HOC_6H_4$	10 525	1 660	5.71	1.24	4.19	4.55	1 530	[j]
$MeCO_2C_6H_4$ [k]	10 535	2 830	6.47	1.39	4.88		1 547	[i]

[a] Relative to external $K_3[Co(CN)_6]$, estimated error ±20 p.p.m. [b] Estimated length of the *c* axis of the complex cations (Figure 1). [c] Calculated rotation-correlation times using the hydrodynamic and mutual-viscosity models. [d] Values of the dissociation constants of the free organic acids were taken from Landolt-Börnstein, 'Zahlenwerte und Funktionen,' vol. 2, ed. K.-H. Hellwege, Springer-Verlag, Berlin, 1960 and 'Stability Constants of Metal–Ion Complexes,' Special Publ. Nos. 17 and 25, ed. G. Sillén, The Chemical Society, London, 1964 and 1971. [e] I.r.-active antisymmetric (CO) stretching frequencies of symmetrically bonded carboxylate groups. [f] This work. [g] B. Kipling, K. Wieghardt, and A. G. Sykes, *J.C.S. Dalton*, submitted for publication. [h] The solvent was 1.0M-perchloric acid; under these conditions the basic pyridine nitrogen atoms are fully protonated. [i] M. Hery and K. Wieghardt, unpublished work. [j] H. Spiecker and K. Wieghardt, unpublished work. [k] The ligand is methyl terephthalate.

The Rotation-correlation time.—In order to separate the influences of e.f.g. and rotation-correlation time on linewidths we employed two independent models to calculate τ_r. The first model is a hydrodynamic one approximating the shapes of the solute molecules by ellipsoids. The molecular structure of the solvent is taken into account by introducing a microfriction factor. The appropriate rotation-correlation time for n.m.r. is given by (2) with

$$\tau_r = f_r\left(\frac{1}{\tau_a} + \frac{1}{\tau_b} + \frac{1}{\tau_c}\right)^{-1} \qquad (2)$$

τ_a, τ_b, and τ_c the dipolar correlation times for rotation of the molecules about the semi-major axes *a*, *b*, and *c* of the ellipsoid (Figure 1);[7,9,10] f_r is the rotational microfriction factor[11] [equation (3)] where a_s and $\bar{a}$ are the averaged

$$f_r = [6a_s/\bar{a} + (1 + a_s/\bar{a})^{-3}]^{-1} \qquad (3)$$

radii of the solvent and solute molecules respectively. For our calculation of τ_r: $a_s = 1.93$ Å (radius of H_2O molecules[11]); τ_a, τ_b, and τ_c were extrapolated from values listed by Budó *et al.*;[10] *a* and *b* are the half diameters of the investigated complexes in Co–Co and HO–OH directions respectively, *c* the averaged radius perpendicular to *a* and *b*, and $\bar{a} = (a + b + c)/3$. The magnitudes of *a*, *b*, and *c* were estimated using interatomic distances from refs. 12 and 13 (Figure 1).

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[8] J. R. Sams, 'Some Applications of Mössbauer Spectroscopy in Chemistry and Chemical Physics,' *MTP Internat. Rev. Sci.*, Physical Chemistry, series 1, Butterworths, 1972, vol. 4, ch. 3.

[9] F. Perrin, *J. Phys. (F)*, *Ser. VII*, 1934, **5**, 497.

[10] A. Budó, E. Fischer, and S. Miyamoto, *Z. Physik.*, 1939, **40**, 337.

[11] A. Spernol and K. Wirtz, *Z. Naturforsch.*, 1953, **A8**, 522; A. Gierer and K. Wirtz, *ibid.*, p. 532.

[12] 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' Special Publ. No. 18, The Chemical Society, supplement 1956—1959.

[13] W. H. Baur and K. Wieghardt, *J.C.S. Dalton*, 1973, 2669.

The second model used is that of mutual viscosity between solvent and solute.[14,15] According to this model the actual structure of the solute molecules and the interaction between solvent and solute molecules are taken into account. The rotation-correlation time is given by (4), where I is the average of the principal moments of inertia of the solute molecules, I_s' the moment of

$$\tau_r = \frac{II_s'(a_s + \bar{a})\eta}{(I + I_s')\mu kT} \qquad (4)$$

inertia of the solvent molecules about the centre of the solute molecules during collision, $(a_s + \bar{a})$ is taken as an average distance between solvent and solute molecules, μ the reduced mass of the solvent–solute system, and η the viscosity of the solvent. The principal axes of the moment of inertia tensor were assumed to be parallel to the major axes of the complex cations, *i.e.* parallel to the Co–Co (*a*) and HO–OH (*b*) directions, the third axis (*c*) being perpendicular to either of them (Figure 1). Free rotatory groups of the complexes (*e.g.* NH_3 groups) were treated like circular mass distributions described by Dirac δ functions.

The accuracy of the hydrodynamic and mutual-viscosity models is in general rather poor. τ_r Values calculated from formulae (2) and (4) may differ considerably from actual rotation-correlation times.[10,15,16] However, it is noted that the τ_r values calculated here by the two different models agree quite well if allowance is made for a nearly constant factor of *ca.* 3.3 (Table 1). Consequently, the two models are assumed to provide a rough estimate (except for constant factors) of the rotation-correlation times of the investigated complexes.

The Electric-field Gradient.—From the calculated rotation-correlation times, $\omega\tau_r \leqslant 7 \times 10^{-3} \ll 1$, indicating that equation (1) holds (extreme narrowing limit). Therefore, the maximum e.f.g. at the ^{59}Co nuclei may be qualitatively estimated from the measured n.m.r. line-widths, from the calculated τ_r, and the assumption of a constant asymmetry parameter. Since the immediate environment of the Co^{III} atoms is essentially identical for all the complexes, the e.f.g. can only be a function of the basicity of the O atoms of the μ-carboxylato-bridge. Figure 2 shows plots of the calculated e.f.g. values of 17 complexes against pK_a values of the corresponding free organic acids. (Values of seven complexes could not be included because the dissociation constants are lacking in the literature.) It can be seen that the pK_a and the logarithm of the e.f.g. obtained from the hydrodynamic and mutual-viscosity models are connected by a linear relation. The gradient of the lines calculated by a least-squares method gave $K_a \propto |\text{e.f.g.}|^{13.9\pm1.9}$ for the hydrodynamic model and $K_a \propto |\text{e.f.g.}|^{14.0\pm0.7}$ for that of mutual viscosity. The agreement is excellent. For the results given above the correlation coefficients[17] are quite satisfactory: $R = -0.959$ for the hydrodynamic model and -0.977 for that of mutual viscosity.

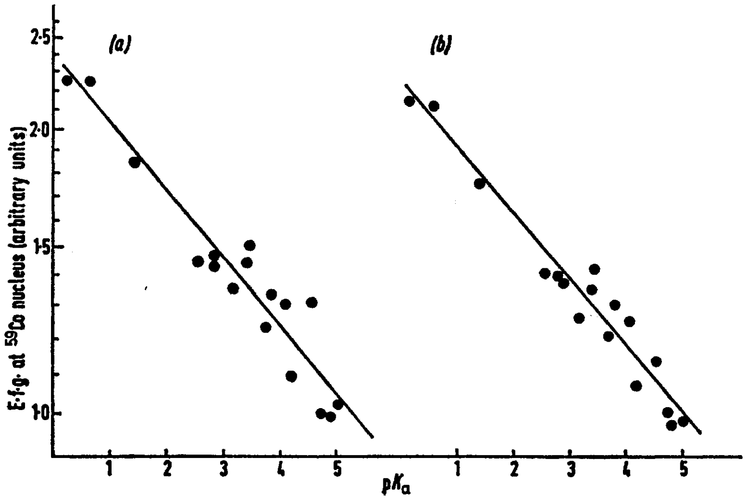

FIGURE 2 Calculated e.f.g. at ^{59}Co nuclei as a function of pK_a values of the free organic acids using (*a*) the hydrodynamic model and (*b*) the mutual-viscosity model for calculation of τ_r (the e.f.g. was arbitrarily set at unity for the μ-acetato-complex)

It has previously been shown that a linear relationship exists between the i.r.-active antisymmetric ν_{asym} (C–O) stretching frequencies of symmetrically bonded bridging carboxylate groups and the pK_a values of free organic acids.[3] Thus a relation can be obtained between e.f.g. and K_a from i.r. data. From the pK_a and ν_{asym} (C–O) values (Table 1) equation (5) can be derived. The

$$pK_a = 5.98 - 3.81 \times 10^{-2}\{[\nu_{asym}\,(\text{C–O})/\text{cm}^{-1}] - 1\,500\} \qquad (5)$$

correlation coefficient, R, is -0.970. Plots of e.f.g. against ν_{asym} (C–O) values for 24 complexes are shown in Figure 3. From (5) $K_a \propto |\text{e.f.g.}|^{13.8\pm1.5}$ for the hydro-

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[14] N. E. Hill, *Proc. Phys. Soc.*, 1954, **B67**, 149.

[15] R. W. Mitchell and M. Eisner, *J. Chem. Phys.*, 1960, **33**, 86.

[16] A. S. Agishev, *Soviet Phys. JEPT*, 1963, **16**, 815; 1964, **19**. 1.

[17] L. G. Parrat, 'Probability and Experimental Error in Science,' J. Wiley, London, 1961.

dynamic model and $K_a \propto |\text{e.f.g.}|^{13.7\pm1.3}$ for that of mutual viscosity. There is hardly any difference between these results and those above, though the correlation coefficients are less satisfactory (R 0.887 for the hydrodynamic model and 0.911 for that of mutual viscosity).

The ^{59}Co n.m.r. line width is thus a powerful and sensitive experimental method of detecting minor changes in the electron density of the carboxylic O atoms which is itself a function of the electron-withdrawing capacity of the organic substituents attached to the carboxylic group. Measurements of the actual rotation-correlation times and solid-state n.m.r. and n.q.r. investigations of these complexes are desirable for a more detailed discussion.

EXPERIMENTAL

Materials.—The binuclear complexes were prepared by procedures described in the literature.[3,4] Some of the complexes have not been characterised previously. Only the perchlorate salts were prepared and analysed (Table 2).

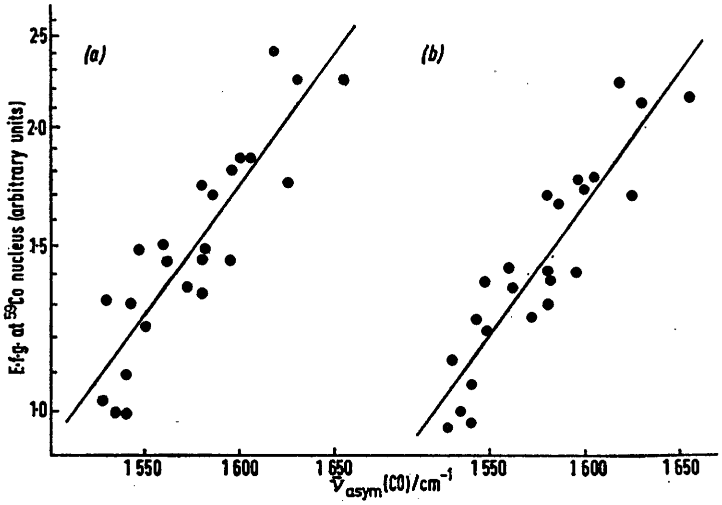

FIGURE 3 Calculated e.f.g. at ^{59}Co nuclei as a function of the (C–O) antisymmetric stretching frequencies of complexes using (*a*) the hydrodynamical model and (*b*) the mutual-viscosity model for calculation of τ_r (the e.f.g. was arbitrarily set at unity for the μ-acetato-complex)

TABLE 2

Analytical data [a] for μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] perchlorates, [b] $[(H_3N)_3Co\mu(OH,OH,RCO_2)Co(NH_3)_3][ClO_4]_3 \cdot x\,OH_2$

R	x	Analyses(%) Co	NH_3	C	H
CH_2Br	3	16.0 (15.8)	13.8 (13.7)	3.5 (3.25)	3.5 (3.80)
$CHBr_2$	0	15.5 (15.3)	13.0 (13.3)	3.3 (3.10)	3.1 (2.75)
CBr_3 [c]		9.4 (9.55)	8.0 (8.25)	2.2 (1.95)	3.1 (2.95)
CH_2I	4	14.7 (14.55)	12.6 (12.6)	3.0 (2.95)	3.3 (3.75)
Et	1	18.1 (18.3)	15.6 (15.9)	5.8 (5.60)	4.5 (4.2)

[a] Calculated values are given in parentheses. [b] Peak positions of the first absorption maximum in the u.v.–visible spectrum are identical for all complexes: $\lambda_{max.} = 524$ nm and $\varepsilon = 109 \pm 4$ l mol^{-1} cm^{-1}. [c] Extremely soluble, crystallises with $2Na[ClO_4] \cdot 8OH_2$.

Physical Measurements.—^{59}Co N.m.r. spectra were recorded on a Bruker pulse spectrometer SXP 4-100/15 at 21.6 MHz and ambient probe temperature 25 °C. Aqueous perchloric acid (1×10^{-3}M) was used as solvent. In an effort to ascertain whether ^{59}Co n.m.r. linewidths are concentration dependent, spectra of the μ-acetato- and μ-trifluoroacetato-complexes were recorded over a five-fold range of concentration. The linewidths obtained were identical within experimental error.

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