Contribution from Gilman Hall,
Iowa State University, Ames, Iowa 50011

Cobalt-59 Nuclear Magnetic Resonance Studies on Hexakis(phosphite)-Cobalt(III) Complexes

R. Weiss and J. G. Verkade*

Received August 18, 1978

The linear correlation of rising energy of the longest wavelength d–d transition with increasing applied field for $\delta(^{59}Co)$ in six-coordinate cobalt(III) complexes of oxygen- and nitrogen-containing ligands and cyanide ion (Figure 1) has long been known.[1,2] Before the present work was undertaken, the only reported ^{59}Co shifts for complexes containing second row ligating atoms was restricted to the sulfur-containing ligands $R_2NCS_2^-$, $ROCS_2^-$, $RSCS_2^-$, RCS_2^-, and $ROPS_2^-$.[3–6] Very recently the spectrum of the hexakis(trimethyl phosphite) complex was reported.[7]

The dashed line in Figure 1, drawn through the previously reported sulfur ligand points and the phosphite ligand points taken from the data given in Table I, unambiguously confirms the existence of a second linear correlation for second-row elements, which contrary to earlier conjectures[5,8] does not have an intercept common with the line for first-row element ligands. The trend among the phosphorus ligands to exhibit stronger ligand fields and higher ^{59}Co chemical shifts in the order **1** < **2b** < **2a** < **3** < **4** parallels their decreasing σ-basicity order **1** > **2a** > **2b** > **3** > **4**,[9] except for the reversal of **2a** and **2b**. While the reason for the reversal in the isomeric **2** species is presently obscure, the rise in ligand field with generally decreasing basicity may be rationalized by postulating a dominance of phosphorus π acidity in these ligands or a decrease in ligand–ligand repulsion upon increased ligand constraint. Evidence for the former postulate was recently published from our laboratories in the form of a monotonic rise in energy of the lowest d–d transition with decreasing charge in two series of phosphite complexes NiL_5^{2+}, CoL_5^+, and FeL_5.[10]

The paramagnetic contribution to the shielding tensor which dominates the ^{59}Co chemical shifts is given by (1).[11,12] The

$$\sigma_p = (-32\beta^2/\Delta E)\langle r_d^{-3}\rangle \qquad (1)$$

high-field ^{59}Co shifts of the sulfur ligand complexes have been ascribed to an increase in the metal–ligand distance,[3,4] corresponding to a decrease in $\langle r_d^{-3}\rangle$ wherein r_d is the cobalt d-orbital radius. These shifts have also been associated[5,6,8] with an increase in covalency which can be expressed by introducing a $(\kappa')^2$ term into eq 1, where κ' (the orbital reduction factor[12]) is the coefficient of the d_{z^2} and $d_{x^2-y^2}$ AO's on cobalt in the ligand field treatment. Inclusion of the diamagnetic contribution of the cobalt ion[12] into eq 1 gives (2), where i denotes

$$\delta(^{59}Co) \propto \sigma_d + \sigma_p = (e^2/3mc^2)\sum_i\langle r_i^{-1}\rangle + 32\beta^2(\kappa')^2\langle r_d^{-3}\rangle\Delta E^{-1} \qquad (2)$$

all doubly occupied orbitals. The slope of the lines in Figure 1 is therefore given by $32\beta^2(\kappa')^2\langle r_d^{-3}\rangle$ and the intercept by σ_d. The ratio of the intercepts of the first- and second-row elements given by $\sum_i\langle r_i^{-1}\rangle_1/\sum_i\langle r_i^{-1}\rangle_2 = 1.60$ strongly suggests that cobalt radius changes are important in comparing correlations involving ligands from different periods. Moreover, the lower field intercept of the second row element line accords with the expectation of a larger cobalt radius for such complexes. The present data do not allow assessment of the relative importance of the κ' and $\langle r_d^{-3}\rangle$ terms in determining the slopes.

Experimental Section

Materials. $Co(BF_4)_2\cdot 6H_2O$ was obtained from Alfa Products (Ventron) and used as received. The ligands $(CH_3O)_{ax}POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O$,[13] $(CH_3O)_{eq}POCH(CH_3)_{eq}CH_2CH(CH_3)_{eq}O$,[13] $CH_3OPOCH_2CH_2O$,[14] and $P(OCH_2)_3CCH_3$[15] were prepared by literature methods. Trimethyl phosphite and 2,2-dimethoxypropane were obtained from Eastman Kodak Co. and used as received. The preparation followed for the tervalent complexes was essentially that reported earlier.[16] In a typical preparation, 1.33 g (3.9 mmol) of $Co(BF_4)_2\cdot 6H_2O$ was dissolved in 10 mL of dry acetone and 20 mL of 2,2-dimethoxypropane, and the solution was allowed to stir for 30 min under a N_2 atmosphere. The ligand $CH_3OPOCH_2CH_2O$ (4.02 g, 33.0 mmol) was then added to the stirred Co(II) solution and the reaction mixture was stirred for 1 h. The white $Co(CH_3OPOCH_2CH_2O)_6(BF_4)_3$ was then filtered off under a N_2 atmosphere, washed with ether, and recrystallized from acetonitrile–ether solution.

Spectra. UV–visible electronic spectra were recorded in acetonitrile solution using a Cary Model 14 spectrometer. Cobalt-59 NMR spectra were recorded in acetonitrile-d_3 solution on a Bruker HX-90 spectrometer operating at 21.35 MHz in the Fourier mode. Chemical

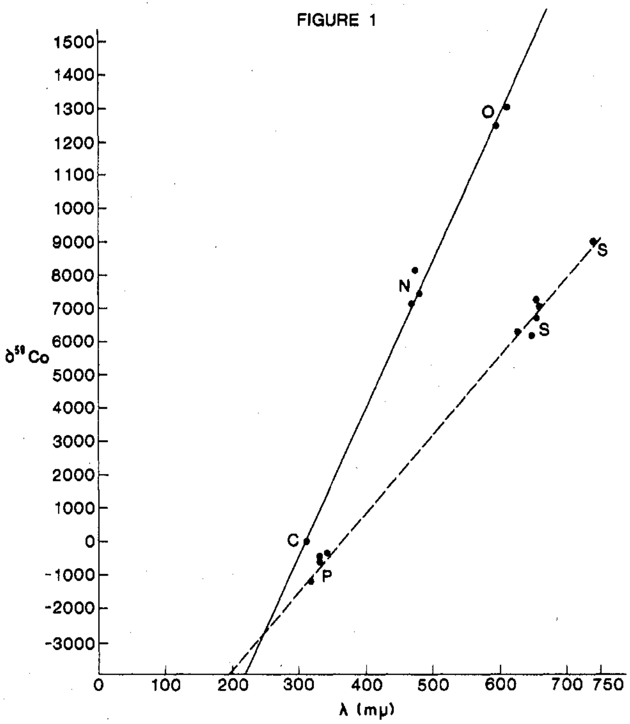
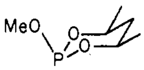
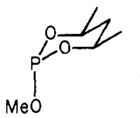
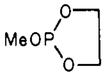
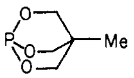


Figure 1.

Table I. Spectroscopic Data for $[CoL_6](BF_4)_3$ Complexes

	L	δ^a	λ, nm	$^1J(^{59}Co-^{31}P)$, Hz	$\Delta\nu_{1/2}$, Hz
1	$P(OMe)_3$	−305	340	443^b	150
2b		−307	341	*c*	ca. 3000
2a		−356	339	*c*	ca. 3000
3		−1185	317	*c*	ca. 2500
4		−1243	ca. 300^d	412	75

[a] $K_3Co(CN)_6 = 0$; negative sign indicates upfield shift. [b] Taken from the spacing in the septet ^{59}Co resonance. [c] Unobservable due to rapid Co relaxation. [d] Partially obscured by charge-transfer band.

0020-1669/79/1318-0529$01.00/0

shifts are reported relative to external (aqueous, saturated) $K_3Co(CN)_6$, contained in a capillary which was held coaxially in the sample tube by a Teflon vortex plug.

Acknowledgment. J.G.V. thanks the National Science Foundation for support of this research in the form of a grant and also for funds which permitted the purchase of the ^{59}Co probe for the Bruker HX-90 NMR spectrometer.

Registry No. **1**, 66083-03-2; **2**, 68258-11-7; **2b**, 68330-53-0; **3**, 68258-13-9; **4**, 68258-14-0.

References and Notes

(1) R. Freeman, G. R. Murry, and R. E. Richards, *Proc. R. Soc. London, Ser. A*, a**242**, 455 (1957).
(2) S. S. Dharmatti and C. R. Kanekar, *J. Chem. Phys.*, **31**, 1436 (1960).
(3) C. R. Kanekar, M. M. Dhingra, V. R. Marathe, and R. Nagarajan, *J. Chem. Phys.*, **46**, 2009 (1967).
(4) A. Yamasaki, F. Yajima, and S. Fujiwara, *Inorg. Chim. Acta*, **2**, 39 (1968).
(5) R. L. Martin and A. H. White, *Nature (London)*, **223**, 394 (1969).
(6) S. Fujiwara, F. Yajima, and A. Yamasaki, *J. Magn. Reson.*, **1**, 203 (1969).
(7) F. A. Yamasaki, T. Aoyama, S. Fujiwara, and K. Nakamura, *Bull. Chem. Soc. Jpn.*, **51**, 643 (1978).
(8) G. P. Betteridge and R. M. Golding, *J. Chem. Phys.*, **51**, 2497 (1969).
(9) See, for example: J. G. Verkade, *Phosphorus Sulfur*, **2**, 251 (1976).
(10) C. A. Tolman, L. W. Yarbrough, II, and J. G. Verkade, *Inorg. Chem.*, **16**, 479 (1977).
(11) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).
(12) J. S. Griffith, "The Theory of the Transition Metal Ion", Cambridge University Press, London, 1961.
(13) J. A. Mosbo and J. G. Verkade, *J. Am. Chem. Soc.*, **95**, 4659 (1973).
(14) R. D. Kroshefsky, R. Weiss, and J. G. Verkade, *Inorg. Chem.*, in press.
(15) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).
(16) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1 (1972).