

Cobalt-59 Nuclear Magnetic Resonance Spectra of
Unsymmetrical Cobalt(III) Complexes*

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The Cobalt-59 nuclear magnetic resonance (NMR) spectra of aqueous solutions of the ions, $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$ ($\text{X} = \text{OH}_2, \text{OH}^-, \text{NO}_2^-, \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{and } \text{I}^-$) and $\text{Co}^{\text{III}}(\text{CN})_5\text{X}$ ($\text{X} = \text{OH}_2, \text{OH}^-, \text{Br}^-, \text{and } \text{I}^-$), have been obtained at 14.45 MHz and 32°C. The ^{59}Co nucleus in the complexes having $\text{X} = \text{Cl}, \text{Br}, \text{and } \text{I}$, are more shielded than predicted by the linear correlation that has been established for complexes of Co^{III} with oxygen, carbon, and nitrogen donors: ^{59}Co chemical shift vs. the reciprocal of the energy of the first « d-d » electronic transition. The deviation of the ^{59}Co shifts from the linear correlation is consistent with a reduction of the second order paramagnetism of Co^{III} resulting from the delocalization of the cobalt 3d electrons to the ligands, $\text{Cl}^-, \text{Br}^-, \text{and } \text{I}^-$. The line widths of the NMR signals are discussed briefly in terms of the electric field gradient at the Co^{III} nucleus in the unsymmetrical complexes.

Introduction

Diamagnetic cobalt(III) complexes exhibit extremely large chemical shifts of the ^{59}Co nuclear resonance.^{1,4} For complexes in which Co^{III} is bonded to C, N, or O donors, the ^{59}Co chemical shift is a linear function of the wavelength of the first « d-d » electronic transition ($^1\text{A}_1 \rightarrow ^1\text{T}_1$) and the shifts have been interpreted in terms of the magnetic field induced mixing of the $^1\text{T}_1$ electronic states localized on Co^{III} .^{1,2}

Recently it has been shown that the ^{59}Co shifts of complexes in which Co^{III} is bonded to $\text{S}^{5,6}$ and As^7 donors exhibit large deviations from such a linear correlation. It appears that the deviations can be attributed to the delocalization^{5,8} of the 3d electrons of Co^{III} to the ligands. We report here the ^{59}Co chemical shifts of compounds of the type $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}]$ and $[\text{Co}^{\text{III}}(\text{CN})_5\text{X}]$ ($\text{X} = \text{OH}_2, \text{OH}^-, \text{NO}_2^-, \text{F}^-, \text{Br}^-, \text{and } \text{I}^-$). The chemical shifts of these complexes also

deviate from the linear correlation in a manner that is qualitatively consistent with a delocalization effect. Also included in this report are the line widths of the ^{59}Co resonances which show that the electric field gradient at the Co nucleus in these unsymmetrical complexes is less than that which has been suggested on the basis of a simple point charge model.⁸

Experimental Section

Materials. The following salts of the substituted Co^{III} amines used in this study were prepared using the methods of Haim and Taube:⁹ $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{ClO}_4)_3$ and $[\text{Co}(\text{NH}_3)_5\text{X}](\text{ClO}_4)_2$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$, and NO_2^-). The salt $[\text{Co}(\text{NH}_3)_5\text{F}](\text{NO}_3)_2$ was prepared using the method of Basolo and Murmann.¹⁰ The potassium salts of the ions, $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ and $[\text{Co}(\text{CN})_5\text{X}]^{3-}$ ($\text{X} = \text{OH}^-, \text{Br}^-, \text{and } \text{I}^-$), were prepared following the procedures of Haim and Wilmarth¹¹ and Adamson, *et al.*¹² The purity of the complexes was checked spectrophotometrically.^{12,13,14}

Measurements. ^{59}Co NMR spectra were recorded as the derivative of the absorption signal obtained at 14.45 MHz with a Varian DP-60 spectrometer operated in the broadline mode. Samples were contained in 12 mm (i.d.) tubes and chemical shifts were measured with respect to the external standard, saturated aqueous $[\text{Co}(\text{en})_3]\text{Cl}_3$ (en = ethylenediamine). Bulk magnetic susceptibility corrections are negligible. Saturated aqueous solutions (~0.1 M) of the substituted Co^{III} amines and 0.4 M solutions of $\text{K}_2[\text{Co}(\text{CN})_5\text{OH}_2]$ and $\text{K}_3[\text{Co}(\text{CN})_5\text{X}]$ were used in recording the spectra. The solutions of the $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{and } \text{I}^-$) and $[\text{Co}(\text{NH}_3)_5\text{OH}_2]^{3+}$ ions also contained 1 M HClO_4 .

Results and Discussion

Chemical Shifts. The ^{59}Co chemical shifts obtained in this study are summarized in Table I. A plot of

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Table I. ^{59}Co NMR Data for Aqueous Solutions of Cobalt(III) Complexes at 14.45 MHz and 32°C

Entry	Complex	Chemical shift ^a (ppm)	Line width ^b	Modulation Amplitude ^c
1	$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	-2400.	1.0	1.1
2	$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	-1730.	1.0	0.41
3	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	-1700.	1.0	0.25
4	$\text{Co}(\text{NH}_3)_5\text{I}^{2+}$	-1640.	1.2	0.41
5	$\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$	-1940.	1.7	0.41
6	$\text{Co}(\text{NH}_3)_5\text{OH}^{2+}$	-1997.	1.1	1.1
7	$\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$	-510.	0.1	0.042
8	$\text{Co}(\text{CN})_5\text{OH}_2^{2-}$	+5298.	3.5	2.06; 1.68
9	$\text{Co}(\text{CN})_5\text{OH}^{3-}$	+5280.	3.0	1.68
10	$\text{Co}(\text{CN})_5\text{Br}^{3-}$	+5900.	6.5	2.06
11	$\text{Co}(\text{CN})_5\text{I}^{3-}$	+6340.	5.7	1.68
12	$\text{Co}(\text{CN})_6^{3-}$	+7120.	0.1	0.042

^a Shifts, ± 5 ppm for entries 1-6 and ± 60 ppm for entries 7-11, are with respect to the external standard aqueous Coen_3Cl_3 ; the negative sign denotes a downfield shift. ^b Width peak to peak, in gauss ($\pm 3\%$), of the derivative of the absorption line. ^c Modulation amplitude in gauss at a modulation frequency of 20 Hz.

the chemical shifts vs. the wavelength of the first «d-d» electronic transition of the complex is provided in Figure 1. The line drawn in that figure is the correlation line established by Freeman, Murray, and Richards² for «symmetrical» Co^{III} complexes with C, N, and O donors [e.g. $\text{Co}(\text{CN})_6^{3-}$, Coen_3^{3+} , and $\text{Co}(\text{CO}_3)^{3-}$]. The ^{59}Co nucleus in the $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Co}(\text{CN})_5\text{X}^{3-}$ ions ($\text{X} = \text{Cl}^-$, Br^- , or I^-) is substantially more shielded than predicted by the correlation line in Figure 1. It is not possible to account for these shielding effects within the framework of the theory developed by Griffith and Orgel¹ and Freeman, *et al.*² who treated the ^{59}Co shifts in terms of magnetically induced mixing of d electronic states localized on Co^{III} . Betteridge and Golding⁸ have shown that in the crystal field approximation, the most likely causes of deviations from the linear correlation (e.g. low symmetry crystal fields, spin orbit and configurational interaction effects) should lead to additional deshielding effects at Co^{III} . However, Betteridge and Golding have also shown that if some

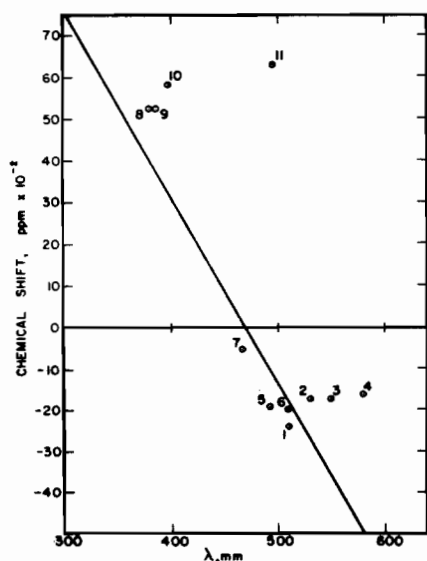


Figure 1. Plot of ^{59}Co chemical vs. wavelength of the lowest energy «d-d» electronic transition for the complexes listed in Table I. The line drawn is the correlation line established for Co^{III} complexes with C, N, and O donors.²

delocalization of the Co^{III} 3d electrons to the ligands occurs, then the paramagnetic terms which lead to the deshielding of Co^{III} will be reduced. The deviation of the shifts from the linear correlation in the order, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} < \text{Co}(\text{NH}_3)_5\text{Br}^{2+} < \text{Co}(\text{NH}_3)_5\text{I}^{2+}$, and $\text{Co}(\text{CN})_5\text{OH}^{3-} < \text{Co}(\text{CN})\text{Br}^{3-} < \text{Co}(\text{CN})_5\text{I}^{3-}$, is qualitatively consistent with the trend in electron delocalization expected from the nephelauxetic series¹⁵ of ligands, $\text{OH}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$.

The ^{59}Co resonance of Co^{III} complexes with sulfur donors (e.g. diethyldithiophosphate and diethyldithiocarbonate) also occur at much higher fields than predicted by the correlation line in Figure 1.^{5,6} Khanekar, *et al.*⁵ have suggested that the relative shielding of the Co nucleus is associated with an expansion of the radius of the 3d electrons in the sulfur complexes compared with those containing C, N, and O donors. Betteridge and Golding,⁸ however, have interpreted this shielding effect in terms of the loss of electron orbital angular momentum which is due to the delocalization of 3d electrons from Co^{III} to the ligands and which is reflected in a reduced value of the Stevens orbital angular momentum factor, k .¹⁶

In a qualitative sense, both the orbital expansion and the orbital angular momentum reduction factors should be directly related to the nephelauxetic effect. However, as recently discussed, a quantitative analysis of the relationships among these parameters and their implications regarding metal ion ligand covalent bonding will prove to be difficult.^{17,18} For example, it has been shown that the Stevens orbital reduction factor is not simply related to a loss of electron orbital angular momentum,^{17,18} and that it may be necessary to define different nephelauxetic ratios for different electronic states.^{18,19}

Line Widths. The line widths of these unsymmetrical Co^{III} complexes (Table I) should be determined by quadrupole relaxation via the modulation of the electric field gradient at the nucleus.²⁰ It has been

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suggested⁶ that a point charge (or point dipole) model for the electric field gradient at Co^{III} accounts qualitatively for the trends in the line widths of unsymmetrical Co^{III} complexes in solution. It is evident that such a model cannot account for the line widths we have observed. We note especially that, in contrast to the predictions of the point charge model, the line widths decrease in the order [after correction for modulation broadening effects^{21,22} of the ^{59}Co resonance of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$], $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+} > \text{Co}(\text{NH}_3)_5\text{X}^{2+}$ ($\text{X} = \text{OH}^-$, Cl^- , Br^- , or I^-) $\gg \text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and $\text{Co}(\text{CN})_5\text{OH}_2^{2-} > \text{Co}(\text{CN})_5\text{OH}^{3-}$.²³ A quantitative analysis of the field gradients in these complexes must

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(23) We have observed that the line widths of the ammine complexes depend upon the solution concentration and the nature of the counter ion. These medium effects are probably due to changes in the size of the complex ion via ion-pairing, and changes in the rotational correlation time via viscosity effects. These medium effects are currently under study.

await the results of pure quadrupole resonance and single crystal nmr studies from which the quadrupole coupling constants can be obtained directly. Of interest in this regard is the fact that a molecular orbital model, which treats the asymmetry in the population of the Co^{III} 3d and 4p orbitals, has been applied with some success to the calculation of the quadrupole coupling constant and the electric field gradient at the Co^{III} nucleus in single crystals of *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.²⁴

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