

Contribution from the Department of Chemistry,  
University of Minnesota, Minneapolis, Minnesota 55455**Cobalt-59 and Nitrogen-14 Nuclear Magnetic Resonance Relaxation in Hexanitrocobaltate(III) Ion**KENNETH D. ROSE and R. G. BRYANT\*<sup>1</sup>

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The <sup>59</sup>Co and <sup>14</sup>N NMR spectra for hexanitrocobaltate(III) ion are investigated in aqueous solutions. Scalar relaxation of the second kind is shown to make a substantial contribution to the <sup>59</sup>Co relaxation accounting in part for the large cobalt line width in this symmetrical complex. The <sup>14</sup>N spectrum makes it clear that a time-dependent decomposition of the hexanitrocobaltate ion leads to the formation of nitrate ion and a cobalt(II) complex that accounts for an earlier misassignment of the <sup>14</sup>N spectrum.  $J_{\text{CoN}}$  is estimated to be  $46 \pm 4$  Hz.

**Introduction**

<sup>59</sup>Co NMR is potentially very useful for the study of structural and dynamic interactions in metal complexes because the nucleus is very easily observed. The major difficulty encountered is that interaction of the very large <sup>59</sup>Co nuclear electric quadrupole moment with field gradients at the cobalt nucleus may make the <sup>59</sup>Co NMR lines too broad for practical observation in spite of an intrinsically high sensitivity and very large chemical shift range. This difficulty is circumvented in some cases by examination of symmetrical cobalt complexes that provide narrow lines because the nuclear quadrupole coupling constant vanishes to first order as cubic symmetry is approached.<sup>2a</sup> However, in several nitrogen-liganded cobalt complexes where octahedral symmetry is approximated well, the <sup>59</sup>Co NMR line width is significantly broader than in non-nitrogen-bonded compounds. Recently we have pointed out that when the cobalt is bonded to a nitrogen, a scalar interaction of the second kind is responsible for a significant broadening of the cobalt resonance in spite of the high symmetry.<sup>2b</sup>

The present study was undertaken to investigate the generality of scalar interactions in cobalt(III) complexes and to determine whether there were important or large effects associated with changes in the nature of the ligand, the charge on the complex, or the hybridization of the nitrogen coordinated to the cobalt atom. In the present case we confirm that scalar relaxation is important and estimate the Co-N coupling constant on the basis of the relaxation data. In addition, there appears to be a significant misassignment of the spectrum for coordinated nitrite made in the earlier literature, which we correct.

**Materials and Methods**

Nuclear magnetic resonance measurements were made at 1.4 T by using an NMR spectrometer assembled in this laboratory and described previously.<sup>3</sup> <sup>14</sup>N measurements were recorded by use of Fourier transform methods at 4.3 MHz. <sup>59</sup>Co spectra were obtained by using Fourier transform methods at 14.3 MHz. Longitudinal relaxation-time measurements were made by using a two-pulse inversion recovery method. Relaxation rates in Table I are the averages of at least three trials. Error in these measurements is estimated at 5% for <sup>59</sup>Co data and 10% for <sup>14</sup>N. Sodium hexanitrocobaltate was prepared and recrystallized from water according to the method described by Brauer.<sup>4</sup> Samples were stored in the solid state until use because of the decomposition reactions.

**Results and Discussion**

The <sup>59</sup>Co NMR spectrum of  $\text{Co}(\text{NO}_2)_6^{3-}$  ion is a single line 60 Hz wide shifted +7540 ppm to higher frequency from hexacyanocobaltate ion. There is a noticeable decrease in the cobalt signal intensity as a function of time. Comparison of this cobalt line width with the cyano complex is striking since the <sup>59</sup>Co NMR line width of the cyano complex is limited by the magnet homogeneity.<sup>5</sup> Both complexes are classically

**Table I.** <sup>59</sup>Co and <sup>14</sup>N NMR Relaxation Rates (s<sup>-1</sup>) in 1.0 M Na<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub> Solutions at 30 °C

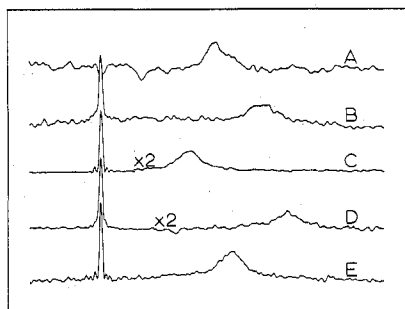
solvent	<sup>59</sup> Co		<sup>14</sup> N
	1/T <sub>2</sub>	1/T <sub>1</sub>	1/T <sub>2</sub>
H <sub>2</sub> O	188	24	996
D <sub>2</sub> O	174	28	1134

octahedral so that the nuclear-electronic quadrupole interaction should be a relatively unimportant source of relaxation because of the high symmetry.<sup>6</sup> In other nitrogen-bonded cobalt complexes we have shown that there is a contribution to the cobalt relaxation from what Abragam calls scalar relaxation of the second kind.<sup>7</sup> The coupling in this case is between the cobalt nucleus and the directly bonded nitrogen which relaxes efficiently by a nuclear-electronic quadrupole mechanism. The cobalt relaxation rate from such an interaction is given by

$$(1/T_2)_{\text{Co}} = \frac{2}{3}(2\pi J)^2 \tau_N$$

where  $J$  is the cobalt-nitrogen coupling constant in hertz and  $\tau_N$  the correlation time for the reorientation of the nitrogen spin, i.e., the nitrogen longitudinal relaxation time in the case where it relaxes rapidly compared with any chemical-exchange event. It is clear that knowledge of the nitrogen relaxation rate will provide an estimate for the coupling constant.

The <sup>14</sup>N NMR spectra for the hexanitro complex are shown in Figure 1. The top spectrum was taken from a freshly prepared solution of the sodium hexanitrocobaltate complex. The position and width of the line are not consistent with an earlier report.<sup>8</sup> The second spectrum was taken approximately 2 h later; there are clearly a shift of the coordinated nitrite signal and the appearance of a narrow component that has the same width and chemical shift that were originally reported as being due to the coordinated nitrite. This narrow line is due to the appearance of nitrate ion in the solution as the shift and width are consistent with the nitrate resonance as shown by spectrum C of Figure 1. The earlier investigators were apparently misled by a time-dependent decomposition of the complex leading to a large shift of the coordinated nitrite spectrum and the appearance of a significant amount of nitrate ion that is much easier to observe because of its smaller relaxation rate. The decomposition product appears to be a cobalt(II) species.<sup>9</sup> Several features of the data support this conclusion: (1) nitrite is oxidized to nitrate; (2) the <sup>59</sup>Co(III) NMR signal intensity decreases with time; (3) spectra in D and E of Figure 1 show that the addition of cobalt(II) to an aged sample of cobalt(III) complex shifts the coordinated nitrite spectrum to higher frequencies while the addition of excess nitrite shifts the spectrum back to lower frequencies toward the free nitrite line. These data are consistent with the reduced product of the decomposition being a cobalt(II)



**Figure 1.**  ${}^{14}\text{N}$  NMR spectra at 4.3 MHz obtained by Fourier transform. Full-scale sweep width on all spectra is 4108 Hz with frequency increasing to the right. The low-frequency nitrate signals in spectra B–E are incompletely apodized. The sample temperature was  $30 \pm 1^\circ\text{C}$ : A, spectrum of 1.25 M hexanitrocobaltate(III) ion freshly dissolved (20 000 transients); B, spectrum of solution A after standing for 2 h (10 000 transients); C, spectrum of 1 M  $\text{NaNO}_3$  and 5 M  $\text{NaNO}_2$  (5000 transients); D, spectrum of 1.25 M hexanitrocobaltate(III) ion which is 5.4 mM in  $\text{Co}^{2+}$  by addition of aqueous cobalt chloride (20 000 transients); E, spectrum of 1.25 M hexanitrocobaltate(III) ion which is 1.9 M in sodium nitrite (20 000 transients).

complex which is labile and catalyzes exchange of the free ligand with the cobalt(III) complex and also causes a large paramagnetic shift.

It is important to note that addition of the same amount of cobalt(II) ion that was used in obtaining the spectrum of Figure 1D to a solution of nitrate and nitrite ions does not cause an observable shift in the  ${}^{14}\text{N}$  spectrum of either anion. Since the  ${}^{14}\text{N}$  spectra of Figure 1B,D,E show an exchange-averaged nitrite ion line, the cobalt(II) ion apparently catalyzes rapid exchange of ligand with the cobalt(III) complex. It is likely that the catalysis involves an electron transfer.

These chemical complications make estimation of the cobalt–nitrogen coupling constant more uncertain because even extrapolation to zero time does not guarantee that the  ${}^{14}\text{N}$  line

width in the hexanitrocobaltate ion will accurately reflect  $T_1$  because of the possible exchange contributions. With this caution, the necessary relaxation data are summarized in Table I for solutions of the complex in water and deuterium oxide. The changes in the cobalt  $T_1$  and the nitrogen line width reflect the differences in the viscosity of the two solvents in the usual way. It is clear, however, that the cobalt line width has the inverted dependence on solution viscosity expected for a dominant contribution from scalar relaxation of the second kind. Coupling constants from both sets of data were used independently to calculate  $J_{\text{Co-N}}$ . Both calculations give the value of  $46 \pm 4$  Hz. This result is 20% smaller than that obtained in the same way for hexaamminecobalt(III) ion.<sup>3</sup>

In view of these results, it appears that the conclusions drawn about the nitrogen spectra in the nitro complexes of platinum and palladium<sup>8</sup> need to be reexamined and it appears that scalar relaxation mechanisms need to be considered very carefully when the metal resonances are investigated in nitrogen coordinated systems.

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**Registry No.**  $\text{Co}(\text{NO}_2)_6^{3-}$ , 15079-20-6.

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## Spectroscopic and Theoretical Analysis of the Intense ${}^1T_{1u} \leftarrow {}^1A_{1g}$ Transitions in $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$

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Optical spectra of  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}, \text{W}$ ) complexes have been measured in argon matrices at 10 K, focusing on the intense  ${}^1T_{1u} \leftarrow {}^1A_{1g}$  transitions at 286 and 230 nm. Vibrational structure is observed on the 286-nm band. A detailed band shape analysis is performed on both absorption bands, and accurate excited-state electronic parameters are obtained. The distortion of the CO moiety is found to be small for both transitions, particularly for the 286-nm one. Transition-state  $X\alpha$  calculations have been performed for the low-lying allowed metal to ligand and ligand to metal charge-transfer transitions as well as for the metal-localized  $d(t_{2g}) \rightarrow p(t_{1u})$  excitation. The results confirm assignment of the electronic absorption bands to  $d(t_{2g}) \rightarrow \text{CO}(\pi^*)(t_{1u} \text{ and } t_{2u})$ ; however, the  $\pi^*$  levels of CO in the metal hexacarbonyls prove to differ considerably from the  $\pi^*$  level in free CO. Relative amounts of charge reorganization calculated for the excited states provide a rationale of the spectroscopically derived parameters.

Both extended Hückel<sup>2</sup> and more elaborate calculations<sup>3</sup> provide a basis for understanding many aspects of the electronic structure of metal hexacarbonyl complexes. At this point satisfactory agreement between photoelectron spectra and calculated ionization potentials has been realized for  $\text{Cr}(\text{CO})_6$ .<sup>2,3</sup> Additionally, reasonable assignments of the low-resolution electronic absorption spectra of  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) have been proposed on the basis of molecular orbital calculations combined with the spectroscopic effects

of chemical variation.<sup>2</sup> These studies assign the low-energy tail in the electronic absorption spectra of the metal hexacarbonyls as ligand field transitions. In addition, two intense spectral features (found at ca. 286 and 230 nm) are assigned as allowed  ${}^1T_{1u} \leftarrow {}^1A_{1g}$  transitions arising from one-electron excitation processes which originate in the metal  $t_{2g}$  (d) orbitals and terminate in the  $t_{1u}$  and  $t_{2u}$  ligand  $\pi^*$  orbitals (i.e.,  $\text{M } d(t_{2g}) \rightarrow \text{CO}(\pi^*)$ ).<sup>2-4</sup> A detailed assignment of the electronic absorption spectra and a determination of the nature of the