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Effect of Ionizing Radiation on the Hexanitrocobaltate(III) Ion: E.s.r. Spectra of the Hexa- and Pentanitrocobaltate(II) Ions

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Exposure of the alkali metal hexanitrocobaltate (III) salts to ^{60}Co γ-rays gave nitrogen dioxide as the major electron loss center together with two centers both considered to be formed by electron capture. One, identified as $Co(NO_2)_5^{3-}$, showed strong hyperfine coupling to one ^{14}N nucleus and normal e.s.r. parameters for ^{59}Co with an unpaired electron in the $3d_{z^2}$ orbital. At 77K the other center had an e.s.r. spectrum comprised of a set of nearly isotropic features centered at g = 2.090 and separated by 11G; these are thought to arise from hyperfine coupling to six equivalent ^{14}N nuclei. On cooling to 4.2K a broad, unresolved asymmetric band was recorded with $g_\perp$ = 2.133 and $g_\parallel$ = 2.000. We conclude that this center is $Co(NO)_6^{4-}$ undergoing a dynamic Jahn–Teller distortion at 77K which is largely quenched at 4.2K. This requires the coincidence that $A_{av}(^{59}Co) \approx 0$. The latter center was also formed by partial reduction of $Na_3[Co(NO_2)_6]$ with sodium borohydride.

Introduction

Continuing our studies of the effect of ionizing radiation on diamagnetic transition metal complexes [1, 2] we have turned our attention to the hexanitrocobaltate(III) ion. This ion was expected to give electron gain and loss centers displaying hyperfine coupling to ^{14}N as well as ^{59}Co in their e.s.r. spectra. Elliott *et al.* [3] studied the X-ray powder patterns and electronic and infrared spectra of a range of hexanitro complexes and concluded that the cobalt (II) and copper(II) salts had tetragonal environments. However, their e.s.r. spectra for the undiluted powders consisted of single isotropic features and hence they postulated a rapid dynamic Jahn–Teller distortion. One interesting feature of their results was that on cooling to 77K, the $K_2Pb[Cu(NO_2)_6]$ salt gave an e.s.r. spectrum typical of copper(II) ion with an unpaired $3d_{x^2-y^2}$ electron, while the $K_2Ba[Cu(NO_2)_6]$ complex gave a spectrum typical of a copper(II) ion with an unpaired $3d_{z^2}$ electron. Although this indicated a "freezing out" of the Jahn–Teller distortion for the copper complex, no such change was observed for the cobalt complexes.

Experimental

Commercial sodium hexanitrocobaltate(III) was used to prepare the hexanitrocobaltate(III) salts of potassium, rubidium, cesium, lead(II) and silver by precipitation from warmed aqueous solution. The solids were washed thoroughly with water, methanol, and diethyl ether and dried in a vacuum desiccator over calcium sulfate. Chemical reduction was accomplished by adding a small amount of solid sodium borohydride to a concentrated solution of hexanitrocobaltate(III) and immediately freezing to a glass at 77K. The hexanitrocobaltate(III) salts were irradiated at 77K as fine powders in a ^{60}Co Vickrad source at a dose rate of 1.7 M.Ci.h^{-1} for up to 2h. E.s.r. spectra were measured at 77K on a Varian E3 X-band Spectrometer. Samples were annealed above 77K in the empty insert Dewar, and recooled to this temperature whenever significant changes were detected in the continuously monitored e.s.r. spectra.

Results and Discussion

Sodium Borohydride Reduction

Partial reduction of sodium hexanitrocobaltate (III) with sodium borohydride gave a species (A) with an e.s.r. spectrum at 77K having a similar isotropic g-value to that detected by Elliott *et al.* [3] except that well-defined hyperfine splitting was observed

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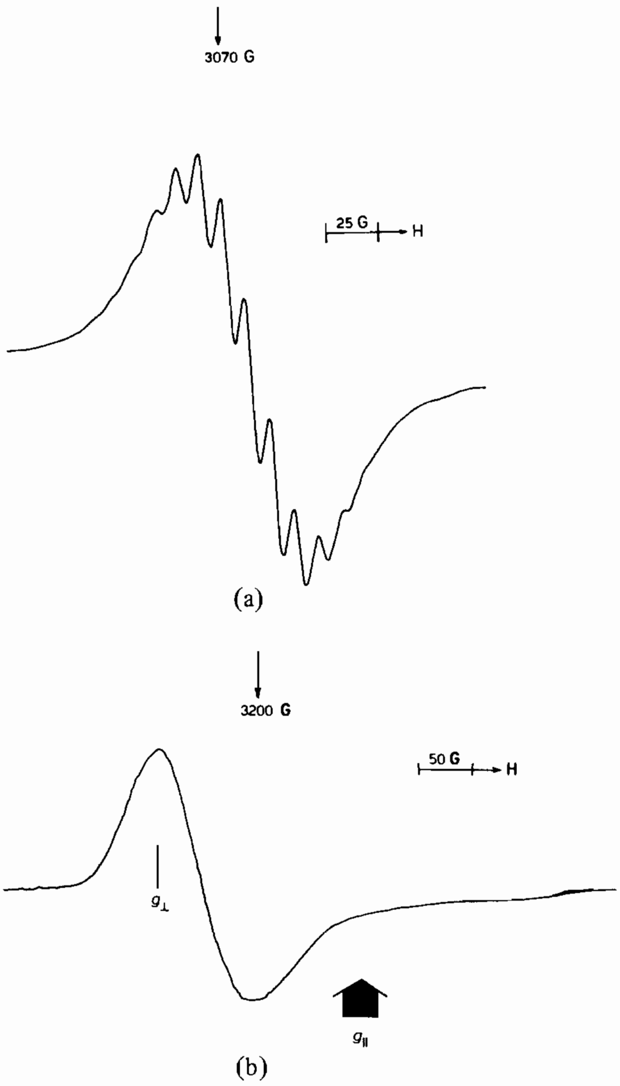

Figure 1. First derivative X-band e.s.r. spectra for species A $[Co(NO_2)_6^{4-}]$ formed by sodium borohydride reduction, (a) at 77K and (b) at 4.2K.

(Fig. 1a). Also, their line width, estimated from their diagram, is apparently much greater. There are clearly an odd number of lines in our spectrum which become severely, but almost symmetrically broadened in the wings. There are certainly eleven and probably thirteen components. One possible analysis gives an isotropic octet from ^{59}Co with $A \approx 11G$ split further by one coupled ^{14}N nucleus with half this coupling. However, reconstructions on this basis gave very poor agreement with experiment. A more reasonable postulate is that six equivalent ^{14}N nuclei give rise to 13 features, with the coupling to ^{59}Co too small to be resolved. On this basis the spectrum is well produced.

At a temperature just above 4.2K this multiplet gave way to an asymmetric feature as shown in Figure 1b. From this spectrum we have obtained very approximate values for $g_\parallel$ and $g_\perp$ (Table).

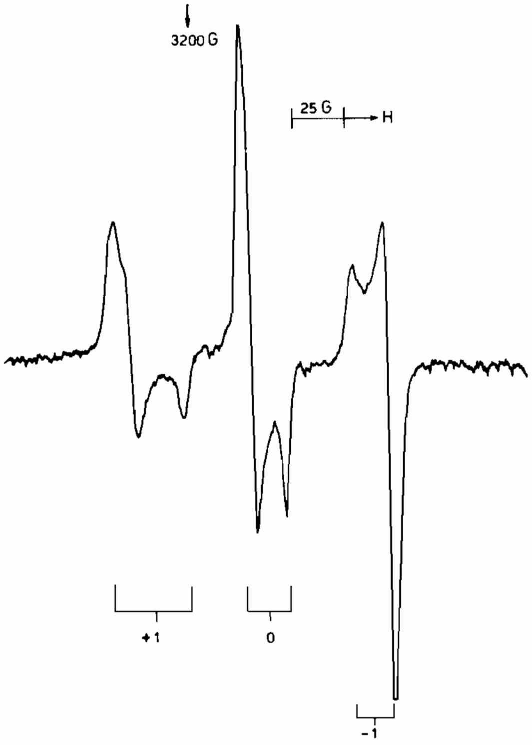

Figure 2. First derivative, X-band e.s.r. spectrum for γ-irradiated $Na_3Co(NO_2)_6$, assigned to the NO_2 radical.

TABLE. E.s.r. Data for Paramagnetic Cobalt Centers Derived from $Na_3Co(NO_2)_6$.

Center	^{59}Co Hyperfine Coupling (G)[a]			^{14}N Hyperfine Coupling (G)			g-Values	
	∥	⊥	*av.*	∥	⊥	iso	∥	⊥
A. $[Co(NO_2)_6^{4-}]$	–	–	*ca.* 0	–	–	11	2.004 *av.* 2.09	2.133[b]
B. $[Co(NO_2)_5^{3-}]$	⩽(+)35	(–)70	–35	–	16	–	2.00[c]	–

[a] $G = 10^{-4}T$. [b] At 4.2K. [c] Assumed.

γ-Radiolysis

By far the most intense feature in the e.s.r. spectrum of the irradiated salts at 77K is a triplet which we assign to NO_2 radicals [4] (Fig. 2). The derived ^{14}N hyperfine data for NO_2 displayed a wide range of values for the different salts, as has been previously observed for this radical. Sharp and Symons showed that most available data could be rationalized by considering restrictions on the rotation and vibration of NO_2 caused by the environment [5]. Converting the calculated A_{iso} and 2B values to apparent 2*s* and 2*p* populations on nitrogen and plotting the 2*p*/2*s* ratio against the total population, 2*p* + 2*s*, they obtained the linear correlation that is reproduced in Figure 3. Data obtained in the present experiments give results which fit well on this line and hence we conclude that the variations in our data result entirely from restricted motions, which are absent only for the sodium salt.

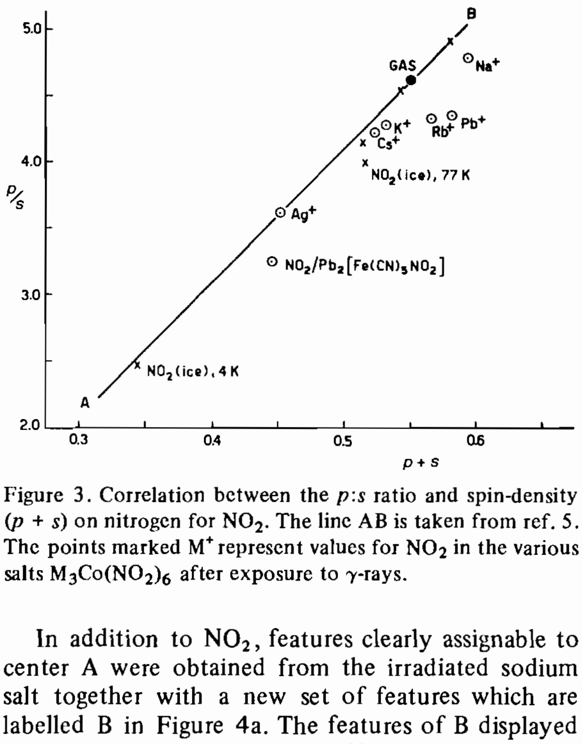

Figure 3. Correlation between the *p*:*s* ratio and spin-density (*p* + *s*) on nitrogen for NO_2. The line AB is taken from ref. 5. The points marked M^+ represent values for NO_2 in the various salts $M_3Co(NO_2)_6$ after exposure to γ-rays.

In addition to NO_2, features clearly assignable to center A were obtained from the irradiated sodium salt together with a new set of features which are labelled B in Figure 4a. The features of B displayed a curious variety of slightly different forms for the different salts, one particular variation is shown in Figure 4b. However, the paramagnetic centers are all basically identical. We think that the complicating feature is a non-axial effect which is least marked for the sodium salt. We have utilized only data derived from this salt (Table).

Center A

This center is clearly the $Co(NO_2)_6^{4-}$ ion studied by Elliott *et al.* [3]. A dynamic Jahn–Teller distortion should result in a spectrum displaying the average g and A (^{59}Co) values, probably together with the isotropic ^{14}N coupling in the powder spectrum, although the anisotropic ^{14}N coupling is not averaged by the migration effect of the ligands. It thus seems that, coincidentally, A_{av} (^{59}Co) is close to zero. The only reasonable way to explain the small magnitude of the ^{59}Co isotropic coupling is to invoke a relatively large positive contribution from the 4 *s* cobalt orbital to balance the normal negative contribution (*ca.* – 100G) from inner shell polarization effects. This, in turn, is only possible for a symmetrical complex if the major population is $3d_{z^2}$. This also fits the form of the g-tensor, the $3d_{z^2}$ configuration requiring $g_{\parallel} \approx 2.00$ and $g_{\perp} > 2.00$, as observed. Thus, the distortion that is rapidly migrating from *x* to *y* to *z* at 77K must be a slight outward movement of two *trans* nitro-groups.

The large isotropic coupling of 11G to six equivalent ^{14}N nuclei represents a total 2*s* population of *ca.* 0.12 [6]. If we make the reasonable assumption of *ca.* sp^2 hybridization at the nitrogen atoms, this gives a total spin-density of *ca.* 0.36 on the ligands. If this spin-density were confined to the two *z*-axis ligands in the distorted complex, it would be unusually high, as would the A_{iso} (^{14}N) values of 33G. However, there is probably a minor contribution from the four equatorial ligands that would reduce these values. Thus, for example, if $A_{iso} \cong 5G$ for the equatorial ligands, then the axial ligands must contribute 23G, which is closer to expectation.

Center B

Since this center was formed in every salt together with NO_2, sometimes in the absence of center A, we consider that this is also an electron excess species, formed by dissociative electron capture:

$$Co(NO_2)_6^{3-} + e^- \longrightarrow Co(NO_2)_5^{3-} + NO_2^- \qquad (1)$$

The main factor that establishes the $Co(NO_2)_5^{3-}$ structure is the large hyperfine coupling to one ^{14}N nucleus. Assuming a $3d_{z^2}$ configuration for Co, the value of $A_{\perp}$ (^{14}N) = 16G is in good accord with expectation. Unfortunately we were never able to study the e.s.r. spectrum of this species in the absence of the dominating features for NO_2, so only a rough estimate can be made for $A_{\parallel}$. If we assume that $g_{\parallel} \approx 2.00$, then absence of any parallel hyperfine features on the high-field side of the NO_2 spectra sets an upper limit for $A_{\parallel}$ (^{59}Co) of *ca.* 35G. Neglecting any orbital magnetic corrections these values give A_{iso} = (–) 35G and 2B = (+) 70G (this is based on $A_{\perp}$ = –70G and $A_{\parallel}$ = +35G: other sign combinations give unacceptable values. Corrections for orbital magnetism would be small and, in view of the large uncertainty in $A_{\parallel}$, have been omitted). These results are quite normal for Co(II) complexes and we feel that this strongly supports our identification. Again, if we assume an sp^2 contribution from ^{14}N, the value of $A_{\perp}$ = 16G can be used to obtain 2*s* and 2*p* popula-

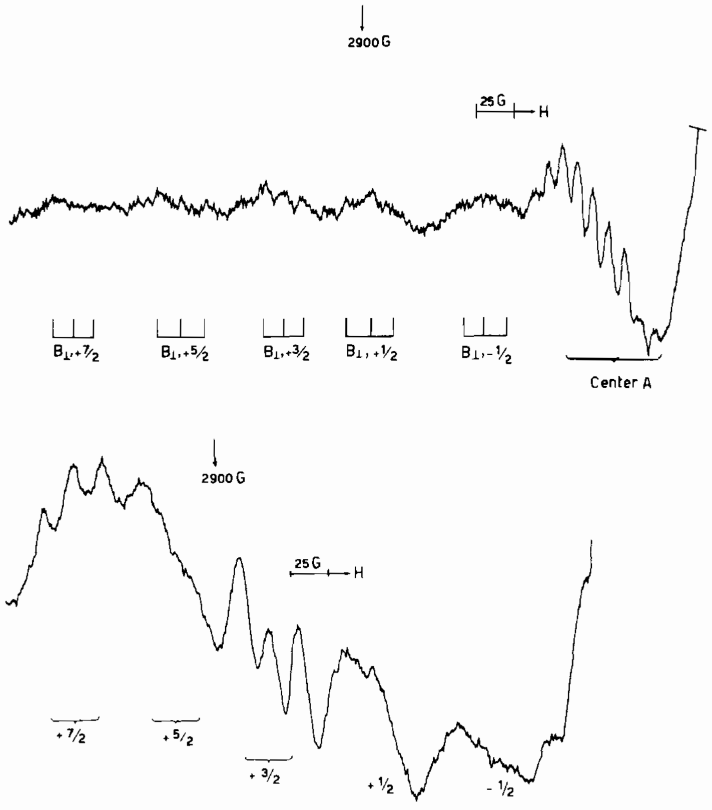

Figure 4. First derivative X-band e.s.r. spectra at 77K for center B in γ-irradiated complexes, (a) $Na_3Co(NO_2)_6$ and (b) $K_3Co(NO_2)_6$.

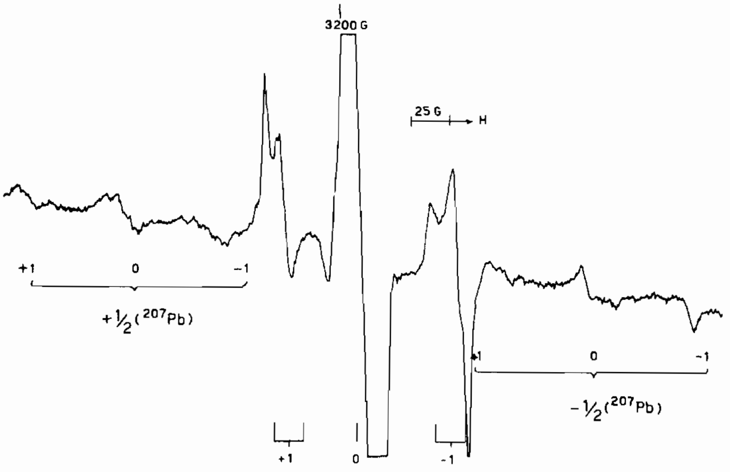

Figure 5. First derivative X-band e.s.r. spectrum at 77K for NO_2 in irradiated $Pb_2[Co(NO_2)_6]_3$ showing the high-field components for the $NO_2\cdots{}^{207}Pb^{2+}$ complex.

tions of *ca.* 0.03 and 0.06 again in good agreement with expectation.

Thus the formulations $Co(NO_2)_6^{4-}$ and $Co(NO_2)_5^{3-}$ would appear to be reasonable for centers A and B. However, we are puzzled by the low value of A_{av} (^{59}Co) for the former complex. We have previously suggested [2] that for complexes having a $3d_{z^2}$ configuration, admixture of the 4s orbital increases on going from complexes having two axial ligands to those having none. The reverse trend is exhibited in the present case. Thus we have some reservations regarding the present analysis, but can suggest no reasonable alternatives.

Aspects of Mechanism

The overall radiolysis can be summarized as

$$[Co(NO_2)_6]^{3-} + \gamma \longrightarrow [Co(NO_2)_6]^{2-} + e^- \quad (2)$$

$$[Co(NO_2)_6]^{2-} \longrightarrow [Co(NO_2)_5]^{2-} + NO_2 \quad (3)$$

$$[Co(NO_2)_6]^{3-} + e^- \begin{array}{l} \xrightarrow{a} [Co(NO_2)_6]^{4-} \\ \xrightarrow{b} [Co(NO_2)_5]^{3-} + NO_2^- \end{array} \quad (4)$$

We have previously shown that reactions such as (4a) may proceed in two stages, with initial capture into the π-framework of one of the ligands [7]. Unfortunately, no such intermediate was detected in the present studies. Reaction (4b) probably proceeds in parallel with (4a) since species A did not convert into B on annealing, nor did A, formed chemically, react to give B on heating. Situations in which different modes of electron addition are selected at the onset of reaction have been noted previously [8].

We have not detected features assignable to the electron-loss center, $Co(NO_2)_6^{2-}$. Thus, electron-loss is probably also initially from one ligand, and dissociation may be more efficient than relaxation to give the $3d^5$ complex.

Finally, we should mention that in the particular case of the lead(II) salt, the NO_2 center displayed a hyperfine interaction with one ^{207}Pb nucleus of the type recently discovered for NO_2 in irradiated lead (II) nitrate [9] (Fig. 5). The ^{207}Pb isotropic coupling of 149G is essentially isotropic, and hence arises primarily from slight electron transfer from Pb^{2+} That is to say that the excited charge-transfer state, $Pb^{3+}\cdots\cdots NO_2^-$ makes a small contribution to the ground-state.

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