whereas the aged chelate had a positive charge. If the oxidation state of the chromium in the chelated intermediate was +4 as was suggested by Beck and Bardi,[5] then the immediately formed chelate would have a zero charge on it and would not exchange with either exchange column. That there was 80% exchange of the aged chelate instead of 100% might be in part due to dimerization, which, if it did occur, would yield a neutral species. This has not yet been investigated. The unchelated, colorless intermediate, that is, the species following the loss of blue perchromic acid without DPA added, was passed through both columns and was found to exchange with the cation- and not the anion-exchange column. This was shown by adding DPA to the solution immediately after passing through the columns. The characteristic color of the chelated intermediate was obtained only from the solution which passed through the anion-exchange column.

Kinetics of the Loss of the Reactive Intermediate.— The loss of the reactive intermediate was followed by removing aliquot portions of the original reaction mixture (no DPA present) at specified time intervals and adding it to solutions containing a tenfold excess of DPA to ensure rapid and complete conversion of the reactive intermediate to the chelated form. The absorbance of these solutions was then immediately measured to prevent the slow chelation of $Cr(H_2O)_6{}^{3+}$ from interfering. The concentrations of the reactive intermediate and the hexaaquochromium(III) ion were determined from the equations

$$C^* = \frac{A_T - \epsilon Q l}{(\epsilon^* - \epsilon)l} \qquad C = Q - C^*$$

where C and C^* are the concentrations of hexaaquochromium(III) ion and reactive intermediate, respectively (which is equal to the concentration of chelated intermediate); ϵ and ϵ^* are the molar absorptivities of the hexaaquochromium(III) ion and of the chelated reactive intermediate, respectively; Q is the total chromium concentration; l is the cell length; A is the absorbance at a wavelength of 540 mμ. The values of ϵ and ϵ^* were determined to be 27.0 and 270, respectively, at 540 mμ.

The reaction, run in excess hydrogen ion and hydrogen peroxide, was found to be second order with respect to reactive intermediate (Figure 2). The pH did not change appreciably during reaction, the initial value being 0.98 and the final value 1.07. Duplicate runs were made at each of three temperatures, and an activation energy of 15.0 kcal/mole was found. The rate constants (M^{-1} sec^{-1}) are as follows: at 28.5° (1) 5.66, (2) 5.58; at 18.7° (3) 2.43, (4) 2.43; at 8.8° (5) 1.01 (6) 0.97.

The following stoichiometric equation for the loss of reactive intermediate is proposed

$$2Cr(O_2)(H_2O)_5{}^+ + 4H^+ \longrightarrow 2Cr(H_2O)_6{}^{3+} + O_2$$
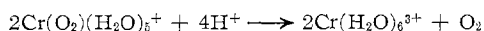
Whether this is a simple disproportionation of the peroxide groups or is a complex reaction involving a

(5) M. T. Beck and I. Bardi, *Acta Chim. Acad. Sci. Hung.*, **29**, 283 (1961).
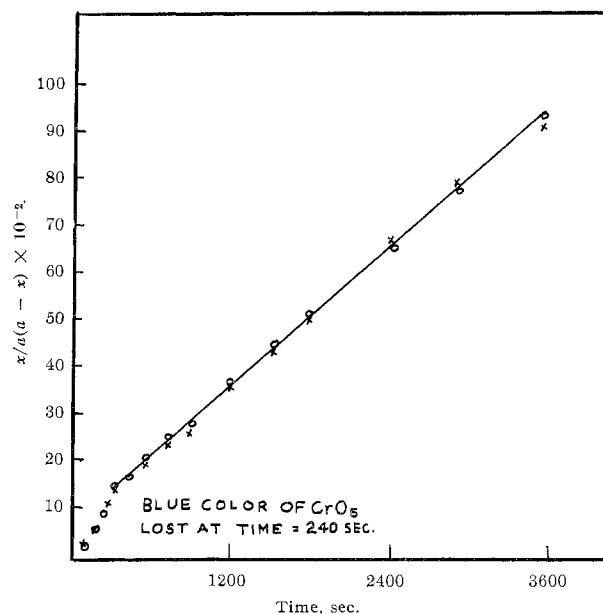

Figure 2.—Second-order plot for intermediate disappearance at 18.7°. Replicate runs are represented by $\times$ and $\bigcirc$ points. The initial pH is 0.98. The initial concentration of peroxochromic acid is a, and the concentration at any time is $a - x$.

nucleophilic displacement as the rate-determining step has not yet been determined.

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Vibrational and Electronic Spectra of Hexanitrocobalt(III) Salts

By Ronald A. Krause, Adrienne E. Wickenden,
and Carl R. Ruggles

Salts of the hexanitrocobalt(III) anion have been known for many years. Recently Schutte[1] has investigated the infrared spectra of several such salts; however, Schutte's work covered only the rock salt region. The spectrum in the cesium bromide region, where many metal–ligand vibrations absorb, was not reported. Nakamoto and co-workers,[2] examining nitro and nitrito complexes, assign the Co–N stretching frequency in K_3-$[Co(NO_2)_6]$. We have observed the infrared spectrum of $Na_3[Co(NO_2)_6]$ to be different from that reported by Nakamoto, *et al.*, for the analogous potassium salt. This has led us to examine the spectra of a number of

(1) C. J. H. Schutte, *Z. Anorg. Allgem. Chem.*, **334**, 304 (1965).
(2) K. Nakamoto, J. Fujita, and H. Murata, *J. Am. Chem. Soc.*, **80**, 4817 (1958).

TABLE I

SPECTRA OF $[Co(NO_2)_6]^{3-}$ SALTS IN THE CsBr REGION[a]

Compd				Co-N stretch			
$K_3[Co(NO_2)_6]$	630 m, sp		418 sh	414 s			291 s
$Rb_3[Co(NO_2)_6]$	627 m, sp			412 s	398 sh		<290
$Cs_3[Co(NO_2)_6]$	623 m			412 s	398 sh		<290
$Na_3[Co(NO_2)_6]$	614 m	447 m			378 sh	369 s	<290
$Ba_3[Co(NO_2)_6]_2$	623 w		425 sh	408 s			294
$[Co(en)_3][Co(NO_2)_6]$[b]	615 w		415 sh	408 s	395 sh		<290

[a] s, strong; m, medium; w, weak; sp, sharp; sh, shoulder. [b] Corrected for the $Co(en)_3{}^{3+}$ ion.

hexanitrocobalt(III) salts in the cesium bromide region and in the electronic spectral region. These results are reported and correlated below.

Experimental Section

Fisher CP grade $Na_3[Co(NO_2)_6]$ was used as received. The Cs^+, Ba^{2+}, and $Co(en)_3{}^{3+}$ salts were prepared by dissolving Na_3-$[Co(NO_2)_6]$ in a small quantity of water, cooling in ice, and adding the stoichiometric amount of cooled aqueous solution of the appropriate chloride. Precipitation occurred immediately with the Cs^+ salt and within 5 min after mixing for the Ba^{2+} and Co-$(en)_3{}^{3+}$ salts. The precipitates were allowed to stand in ice for 1 hr and were then filtered and washed with ice water. After preliminary drying, they were dried *in vacuo* over P_2O_5 at 100°. Drying was continued until no water was observed by infrared analysis, indicated by the absence of O–H absorption at 3500 cm^{-1}. The Rb^+ salt was made by the same method from Rb-ClO_4, which was dissolved in water at 80°. To prepare the K^+ salt, a solution of 4.05 g of $Na_3[Co(NO_2)_6]$ in 100 ml of cold water was added to a concentrated solution (40.0 g in 200 ml of water) of KCl. The resulting precipitate was then treated as above.

All compounds reported gave satisfactory analyses for Co and N (nitrogen by G. I. Robertson, Florham Park, N. J.).

Infrared spectra were run from 2 to 16 μ on a Perkin-Elmer Infracord as Nujol mulls between NaCl plates. A Beckman IR-5A fitted with CsBr optics was used to obtain spectra from 16 to 35 μ. Samples for the far-infrared region were mulled with Nujol in a Wig-L-Bug and spread on CsBr plates. Electronic spectra were run from 1300 to 250 mμ on a Beckman DU equipped with the standard reflectance attachment. Powdered Mallinckrodt reagent grade $MgCO_3$ was used in the reference compartment. Electronic spectra were also obtained on a Cary 14, using mineral oil mulls of samples sandwiched between quartz plates. Perforated metal filters were placed in the reference beam.

Results and Discussion

Infrared spectra of the hexanitrocobalt(III) salts under consideration are listed in Table I; electronic spectra of the cesium, sodium, and barium salts are tabulated in Table II. The most interesting aspect of the infrared spectra is the band in the 400-cm^{-1} region, which is illustrated in Figure 1. This band is assigned by Nakamoto, *et al.*,[2] as a cobalt–nitrogen stretching mode. This assignment appears to be valid, particularly since simple nitrite salts are transparent in this region. We find that the extent of splitting of this band is greatly dependent on the cation present in the crystal lattice. In the potassium, rubidium, and cesium salts splitting is almost undetectable; in the barium and tris(ethylenediamine)cobalt(III) salts two peaks may readily be discerned, one as a shoulder on the other. The extreme situation is observed in the sodium salt, where the band is split into two distinct peaks separated by 78 cm^{-1}.

Accepting the assignment of this band as a cobalt–nitrogen stretching mode we propose that the extent of

TABLE II

ELECTRONIC SPECTRA OF $[Co(NO_2)_6]^{3-}$ SALTS[a]

	Cation		Assignment
Cs^+	Na^+	Ba^{2+}	
(15,200)	12,900 w	12,700 w	$^1A_{1g} \rightarrow {}^3T_{1g}$
(15,700)	...	(13,400)	$\rightarrow {}^3T_{2g}$
(16,300)	...	...	?
...	19,200	21,300	$\rightarrow {}^1E_g$[a]
...	26,000	(23,100)	$\rightarrow {}^1A_{2g}$
(24,300)	...	...	$\rightarrow {}^1T_{1g}$
25,200	...	...	$\rightarrow {}^1T_{2g}$

[a] All values in cm^{-1}. Parentheses indicate shoulders. Very weak bands indicated by w.
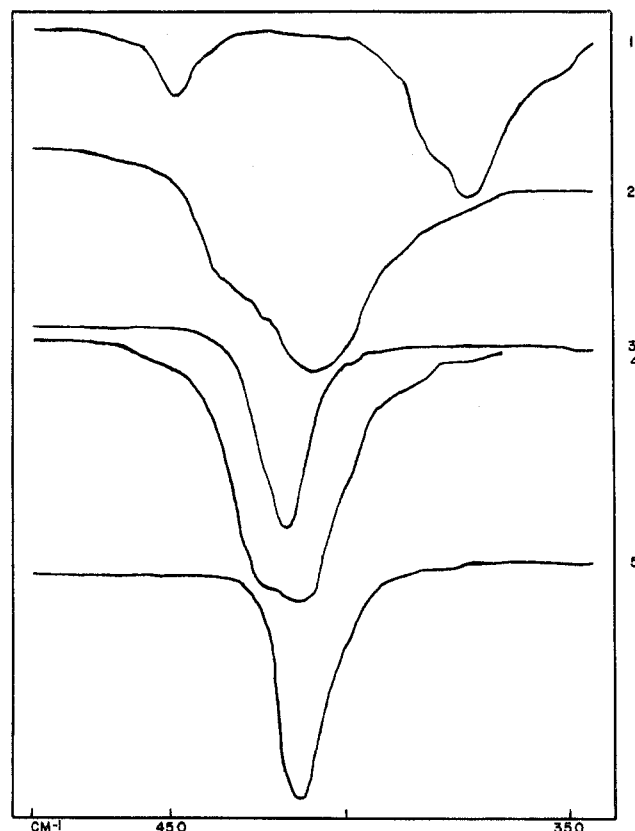
Figure 1.—The far-infrared spectra from 500 to 350 cm^{-1} of (1) $Na_3[Co(NO_2)_6]$, (2) $Ba_3[Co(NO_2)_6]_2$, (3) $K_3[Co(NO_2)_6]$, (4) $K_3[Co(NO_2)_6]$, thicker mull than 3, and (5) $Cs_3[Co(NO_2)_6]$.

splitting depends on the amount of distortion from O_h symmetry that the $[Co(NO_2)_6]^{3-}$ ion has undergone. Indeed, Schutte[1] has concluded that the sodium salt is deformed by a noncubic crystal lattice. The vibrational spectra indicate then that the potassium, rubidium, and cesium salts are essentially undistorted, and the anions may be assumed to have O_h symmetry, while the sodium, barium, and tris(ethylenediamine)cobalt-

(III) salts are distorted, presumably along one axis giving rise to D_{4h} symmetry. We feel the extent of distortion parallels the extent of splitting of the Co–N stretching mode. This indicates that the sodium salt is most distorted, followed by the barium salt, and then the $[Co(en)_3]^{3+}$ salt.

The electronic spectra of the cesium, sodium, and barium salts justify the conclusion that compounds exhibiting a split Co–N stretching mode are distorted. Wentworth and Piper[3] have developed a three-parameter crystal-field model for cobalt(III) (and chromium-(III)) complexes. Table II contains the observed electronic spectral data for hexanitrocobalt(III) salts and our assignments. The assignments for the cesium salt are self-consistent; using our assignments for the energies of the $^3T_{1g}$, $^3T_{2g}$, and $^1T_{1g}$ energy levels we calculate the energy of the $^1T_{2g}$ level. A calculated value of 25,300 cm^{-1} agrees very well with that observed (25,200). No other choice of assignments is so self-consistent, and we feel these to be correct.

Using Wentworth and Piper's model, we assume that the cesium salt possesses undistorted octahedral cobalt-(III) on the basis of the cesium bromide region spectrum and calculate the Racah parameters B and C; values of 56.2 cm^{-1} for B and 4550 cm^{-1} for C are obtained. This value of B is considerably below those observed for a number of other compounds. Wentworth and Piper[3] calculate values of 528, 502, and 418 cm^{-1} for the hexaammine-, tris(ethylenediamine)-, and hexacyanocobalt(III) complexes. However, low values of B in cobalt(III) complexes are not unknown. From data given by Jørgensen[4] we calculate a B value of 22 cm^{-1} for the diethyldithiophosphate complex of cobalt-(III). Using our value of B for $Cs_3[Co(NO_2)_6]$, we calculate the nephelauxetic parameter $1 - \beta$ and obtain a value of 0.95. From this we conclude that the hexanitrocobalt(III) complex exhibits a very high degree of covalency.

For the cesium salt we calculate a Dq of 2880 cm^{-1}. Considering that the nitrite ion lies between ethylenediamine and cyanide ion in the spectrochemical series, this appears to be a logical value; Dq values for the cobalt(III) complexes of these two ligands have been calculated to be 2530 cm^{-1} (ethylenediamine) and 3600 cm^{-1} (cyanide ion).[3] However, our calculated value is somewhat lower than those determined by Wentworth and Piper (ranging between 3120 and 3262 cm^{-1}).[3]

The distorted anions (present in the barium and sodium salts) are assumed to have D_{4h} symmetry; the equatorial nitrites are assigned the same value of Dq that they have in the O_h complex.[3] Calculating Dq' for the axial ligands we obtain values of 1860 cm^{-1} for the sodium salt and 2280 cm^{-1} for the barium salt.

Two explanations may be advanced to explain these data. The lowered Dq' values could be accounted for by the oxygen end of the NO_2^- ions interacting with the cations in the crystal lattice. This would result in the electron density being shifted away from the central cobalt(III), thereby reducing Dq'. However, unless all six nitrites are affected in this fashion (which would maintain O_h symmetry), one would expect a much more complicated spectrum than observed. In addition to Co–N modes, new vibrations for the nitrites of lowered symmetry should be present.

These spectra are much more compatible with a different interpretation. A splitting in the Co–N stretching mode indicates a distortion, probably induced by the crystal lattice, from O_h symmetry. The calculated Dq' values for the axial ligands show that this distortion is one of elongation along the z axis; compression should, of course, be indicated by higher Dq' values.

Electronic and vibrational spectra very nicely complement each other in this series of compounds. In the infrared spectrum the extent of splitting of the Co–N mode correlates qualitatively with the shift of the Dq' values from Dq; both probably correlate with the degree of distortion from O_h symmetry.

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Rare Earth Metal–Metal Halide Systems. IX. The Dysprosium–Dysprosium(III) Chloride System and the Preparation of Dysprosium(II) Chloride[1]

BY JOHN D. CORBETT AND BILL C. MCCOLLUM

Phase studies of many metal–metal halide systems for the lighter rare earth metals have revealed that solid, intermediate phases exist in a number of instances and that, in general, the stability of the dipositive states increases rather regularly from lanthanum to europium.[2–4] Similar studies of the heavy rare earth metal systems have been less extensive. The existence of ytterbium(II) salts has been long known, while a stable dipositive state for thulium, the preceding element, has been predicted by Brewer, *et al.*,[5] and more recently by Polyachenok and Novikov[6] for the chloride and actually

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1830.

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