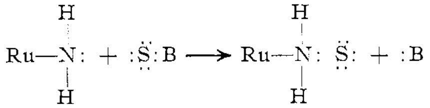
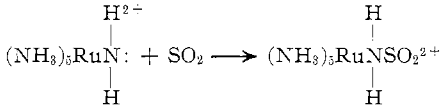
The most significant observation made in this connection is that thiophosphate as well as thiosulfate produces the complex in good yield. The high pH may be necessary if for no other reason than that a proton needs to be dissociated from coordinated ammonia so that displacement on S can occur



$$\mathrm{Ru{-}\overset{H}{\underset{H}{N}}{:}} + {:}\ddot{\mathrm{S}}{:}\mathrm{B} \longrightarrow \mathrm{Ru{-}\overset{H}{\underset{H}{N}}{:}\ \ddot{S}{:}} + {:}\mathrm{B}$$

the sulfur then being oxidized by O_2. It is possible that proton dissociation is promoted by a valence change on Ru. Ru(IV) is expected to be very acidic; it can arise by disproportionation of Ru(III)[12] enhanced by O_2 oxidation of Ru(II). The oxidation of the coordinated S may also be assisted by the Ru center.

The fact that SO_3^{2-} also leads to the sulfamate complex, though slowly, is compatible with the ideas advanced. Sulfur dioxide can be expected to add to coordinated NH_2^-



$$\mathrm{(NH_3)_5Ru\overset{H^{2+}}{\underset{H}{N}}{:}} + SO_2 \longrightarrow \mathrm{(NH_3)_5Ru\overset{H}{\underset{H}{N}}SO_2{}^{2+}}$$

The slowness of the reaction with sulfite as source of sulfur can be attributed to the fact that amide, a strongly basic species, and SO_2 cannot coexist at high concentrations. Thus, when the solutions are alkaline enough to produce amide, SO_3^{2-} rather than SO_2 is present and SO_3^{2-} is a very poor SO_2 donor.

The observations made on the direct replacement of NH_3 from $Ru(NH_3)_6^{3+}$ by $S_2O_3^{2-}$ deserve further attention. In other work[13] it has been shown that $t_{1/2}$ at 25° for the spontaneous loss of NH_3 from $Ru(NH_3)_6^{3+}$ in slightly acidic solution is about 3 years. The formation of the $Ru(III)–S_2O_3^{2-}$ bond takes place much more rapidly than this. The higher rate, in the absence of a detailed kinetic study, can be attributed to (a) an OH^--promoted path for release of NH_3, (b) an SN2 process for entry of $S_2O_3^{2-}$, or (c) formation of $Ru(NH_3)_6^{2+}$ which is known to be more labile than $Ru(NH_3)_6^{3+}$. It is clearly of interest to resolve the questions of mechanism raised.

Acknowledgment.—Financial support for this research by the National Institutes of Health, Grant No. GM 13638-04, and by predoctoral fellowships for J. N. A., 1967–1970, is gratefully acknowledged.

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[12] D. P. Rudd has shown that $Ru(NH_3)_5py^{3+}$ in mildly alkaline solutions rapidly forms Ru(II) and Ru(IV).

[13] Continuation of experiments described in footnote 4 of J. N. Armor, H. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 5928 (1968).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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The Synthesis and Properties of Diamminedinitratocobalt(II) and Related Diammine Complexes[1]

BY G. L. McPHERSON, J. A. WEIL,* AND J. K. KINNAIRD

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Thermal decomposition of both hexaamminecobalt(II) dinitrate and μ-peroxo-bis[pentaamminecobalt(III)] tetranitrate under vacuum leads to formation of diamminedinitratocobalt(II). Similarly, the complex diamminedinitratozinc(II) was prepared from the tetraamminezinc(II) salt. Magnetic susceptibility and infrared and electronic spectral measurements suggest that the cobalt ion in the diamminecobalt complex is hexacoordinated, with two bidentate nitrato groups. This complex in organic solvents reacts with iodide ion to give first diammine(iodo)(nitrato)cobalt(II) and eventually diammine(diiodo)cobalt(II). Both complexes were isolated. Infrared and optical spectra suggest that the nitrate ions in the former are bound in bidentate fashion; the latter is known to be a tetrahedral complex.

Introduction

As part of a study of oxygen-bridged binuclear complexes, μ-peroxo-bis[pentaamminecobalt(III)] tetranitrate was found to yield an intensely rose-violet solid when heated under vacuum. This material was shown to be diamminedinitratocobalt(II) by chemical analysis. This paper describes the preparation and characterization of this and other related diammine complexes.

Experimental Section

Preparation and Purification of Diamminedinitratocobalt(II).—The μ-peroxo-bis[pentaamminecobalt(III)] tetranitrate was prepared as described elsewhere.[2] This material is easily synthesized but difficult to purify; it was used immediately without attempts at recrystallization. Approximately 3 g of the tetranitrate salt was heated to *ca.* 85° under vacuum for 36 hr. During this time, the color of the material changes from greenish brown to rose-violet. Because of the product's extreme sensitivity to moisure, it was transferred to a nitrogen-flushed drybag without exposure to the atmosphere. Reagent grade acetonitrile and benzene were dried by distillation from calcium hydride under a flow of dry nitrogen. The compound was stirred with 20 ml of acetonitrile and allowed to stand for a few minutes. The resulting solution was then carefully filtered off. This extraction process was repeated with additional solvent until it seemed that most of the rose-violet material had been separated from the remaining insoluble solid. Benzene was added slowly to the acetonitrile solution until the volume was approximately doubled. The solution was allowed to stand quietly for several hours. During this time, a rose-violet solid crystallized out of solution. This material was recrystallized by dissolving it in dry acetonitrile, filtering, and adding benzene; it was then washed several times with benzene and dried under vacuum. The material

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. Mori, J. A. Weil, and M. Ishiguro, *J. Amer. Chem. Soc.*, **90**, 615 (1968).

melted at 174–179°, when heated in a sealed capillary. One sample exploded on heating it above 200°.

$Co(NH_3)_2(NO_3)_2$ was also prepared from $Co(NH_3)_6(NO_3)_2$ by heating approximately 4 g of the hexaammine salt under vacuum at *ca.* 100° for 24 hr. Purification of the resulting $Co(NH_3)_2(NO_3)_2$ was carried out as described above.

Anal. Calcd for $Co(NH_3)_2(NO_3)_2$: Co, 27.16; N (total), 25.82; N (ammine), 12.91; H, 2.79. Found: Co, 26.93; N (total), 25.76; N (ammine), 12.86; H, 2.79.

Preparation of Diammine(iodo)(nitrato)cobalt(II).—Diamminediiodocobalt(II) was prepared by thermal decomposition of $Co(NH_3)_6I_2$ at approximately 100° under vacuum. This material was treated under dry nitrogen with dry tetrahydrofuran and the resulting solution was carefully decanted from the undissolved solid. Benzene was added and the solution was allowed to stand for a few hours, during which the diamminediiodo salt crystallized from solution. The salt was added to an acetonitrile solution containing a stoichiometric amount of diamminedinitratocobalt(II) and the resulting blue solution was decanted from the insoluble material. Benzene was added and the solution was allowed to stand overnight. The blue-violet diammine(iodo)(nitrato)cobalt(II) crystallized from solution. The solid was washed with benzene and dried under vacuum. The material in a sealed capillary melted with rapid decomposition at 195–197°.

Anal. Calcd for $Co(NH_3)_2INO_3$: Co, 20.90; NH_3, 12.08; I, 45.02; NO_3, 22.00. Found: Co, 21.12; NH_3, 11.97; I, 44.4; NO_3, 22.9.

Preparation of Diamminedinitratozinc.—A 3-g sample of $Zn(NH_3)_4(NO_3)_2$, prepared by crystallization of hydrated $Zn(NO_3)_2$ from concentrated aqueous ammonia, was heated to *ca.* 100° under vacuum for 24 hr. The crude diamminedinitrato salt was transferred to a nitrogen-flushed drybag and was recrystallized from hot, dry acetonitrile. The material melted at 221–223°.

Anal. Calcd for $Zn(NH_3)_2(NO_3)_2$: Zn, 29.27; NH_3, 15.23; NO_3, 55.50. Found: Zn, 29.59; NH_3, 15.37; NO_3, 55.10.

Spectroscopic Measurements.—Infrared measurements from 600 to 4000 cm^{-1} with a Perkin-Elmer 421 grating spectrometer were made using both Nujol and halocarbon oil mulls between sodium chloride plates. The instrument was calibrated using polystyrene as a standard. Measurements from 70 to 600 cm^{-1} were made with a Beckman IR-11 spectrometer using Nujol mulls between polyethylene plates. Spectra in the visible and near-infrared regions were taken with a Cary 14-R recording spectrophotometer. The absorptions of solid samples were taken as Kel-F mull held between glass plates; a calcium carbonate mull was used as a reference. The low-temperature measurements were made using a dewar with glass windows. All samples were prepared in a dry atmosphere.

Susceptibility Studies.—The static magnetic susceptibility of the powdered $Co(NH_3)_2(NO_3)_2$ was determined at room temperature (27°) on a Faraday balance. This apparatus was calibrated with $HgCo(SCN)_4$.[3]

Mass Spectral Measurements.—Analyses of the gas evolved during the thermal decomposition of the μ-peroxo-bis[pentaamminecobalt(III)] tetranitrate were carried out by use of a CEC 21-620 Cycloidal mass spectrometer.

Results and Discussion

The formation of the diamminedinitratocobalt(II) from μ-peroxo-bis[pentaamminecobalt(III)](4+) nitrate presumably proceeds *via* an internal redox reaction between the cobalt(III) and peroxo bridge of the binuclear complex[4]

$$[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4 \xrightarrow{\Delta} 2Co(NH_3)_2(NO_3)_2 + 6NH_3\uparrow + O_2\uparrow$$

Mass spectroscopic measurements showed that the evolved gas contained molecular oxygen and ammonia in approximately stoichiometric amounts. The literature contains one previous report of this reaction which, though limited in detail, gives the correct stoichiometry for the product.[5]

Hexaamminecobalt(II) nitrate would appear to be a more logical starting material for the preparation of the diammine complex. However, a previous study of the thermal decomposition of the hexaammine salt reported $Co(NH_3)_4(NO_3)_2$ as the product.[6] In contrast, the results of the present study show that the diamminedinitrato complex is prepared quite easily from hexaamminecobalt(II) nitrate by heating the hexaammine under vacuum. The tetraammine salt appears only as a minor impurity and, in fact, the weight loss for the thermal decomposition corresponds nearly quantitatively to the loss of 4 mol of ammonia per mole of cobalt.

Diamminedinitratocobalt(II) is a deeply colored rose-violet solid. It is stable in dry air but reacts readily with water vapor, losing ammonia and changing color from rose-violet to blue. Extreme care must be taken to exclude moisture when handling this material. It appears to decompose only slowly at its melting temperature (174–179°). It is soluble in acetonitrile (*ca.* 1.5 g/100 ml), acetone, in nitromethane, and to a lesser extent in tetrahydrofuran and dioxane; it is insoluble in benzene and nitrobenzene. Conductance studies (see Table I) indicate that the compound partially ionizes in acetonitrile. Typical 1:1 electrolytes in acetonitrile have conductances in the 140–160 $ohm^{-1}\ M^{-1}\ cm^{-1}$ range.[7] The complex does not appear to dissociate in tetrahydrofuran, as may be seen from its low conductivity in this solvent.

TABLE I

ELECTRICAL CONDUCTIVITY OF DIAMMINEDINITRATOCOBALT(II) IN SOLUTION AT 25.0 ± 0.1°

	Concn, *M*	Molar conductance, Λ_m, $ohm^{-1}\ M^{-1}\ cm^{-1}$
Acetonitrile[a]	1.6×10^{-2}	30
	1.2×10^{-2}	34
	5.2×10^{-3}	45
	2.9×10^{-3}	57
Tetrahydrofuran[a]	1.3×10^{-3}	0.3

[a] Observed conductivity for pure acetonitrile is 5×10^{-7} $ohm^{-1}\ cm^{-1}$; for pure tetrahydrofuran, $<10^{-8}$.

The infrared spectrum of solid diamminedinitratocobalt(II) has been investigated in the 70–4000-cm^{-1} region. The band frequencies and assignments are given in Table II. Assignments were made on the basis of deuteration studies and comparison with published data for similar compounds.[8–13]

The appearance of a strong band at 295 cm^{-1} which can be assigned to the Co–O stretch is direct evidence that the nitrate ions are bonded to the metal. Coordination reduces the symmetry of the nitrate ion from

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[3] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[4] A. G. Sykes and J. A. Weil, "Inorganic Reaction Mechanisms," J. O. Edwards, Ed., Wiley, New York, N. Y., 1970.

[5] W. Gluud, K. Keller, and H. Nordt, *Ber. Ges. Kohlentech.*, **4**, 210 (1933).

[6] W. W. Wendlandt and J. P. Smith, *J. Inorg. Nucl. Chem.*, **25**, 985 (1963).

[7] R. Parsons, "Handbook of Electrochemical Constants," Academic Press, New York, N. Y., 1959.

[8] C. C. Addison and W. B. Simpson, *J. Chem. Soc.*, 598 (1965).

[9] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

[10] J. R. Ferraro and A. Walker, *J. Chem. Phys.*, **42**, 1273 (1965).

[11] J. R. Ferraro and A. Walker, *ibid.*, **42**, 1278 (1965).

[12] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

[13] R. J. H. Clark and C. S. Williams, *J. Chem. Soc. A*, 1425 (1966).

TABLE II

INFRARED SPECTRA OF AMMINENITRATO COMPLEXES[a]

Vibration	Freq, cm^{-1}			
	$Co(NH_3)_2(NO_3)_2$	$Co(ND_3)_2(NO_3)_2$[b]	$Zn(NH_3)_2(NO_3)_2$	$Co(NH_3)_2INO_3$
NH_3 str	3350 s, 3275 s, 3210 w, 3184 w	2506 s, 2416 w, 2388 m, 2328 w	3352 s, 3280 m, 3222 w, 3194 w	3328 s, 3257 m, 3193 w, 3165 w
$\nu_2 + \nu_1$	2490 w		2504 w	2505 w
$\nu_2 + \nu_4$	2340 sh, 2310 w		2330 w	
$2\nu_2$	2030 w	2040 vw	2072 vw	
$\nu_2 + \nu_3$	1762 vw	1761 vw	1776 vw	
$\nu_2 + \nu_6$	1745 w	1736 w	1730 w	1715 vw
NH_3 def (deg)	1610 w, b	1170 m	1618 w	1607 m
ν_1	1515 sh, 1475 vs, b	1525 s, 1480 vs, b	1470 vs, b	1494 s
NH_3 def (sym)	1329 s, 1267 vs, 1244 sh, 1232 vs	1056 m, 977 s, 960 s	1326 s, 1270 s, 1248 s	1310 sh, 1255 m, 1238 s
ν_4	1347 s, 1292 vs	1340 s, 1294 vs	1300 vs	1282 s
ν_2	1024 s	1023 v	1031 s	1014 s, sp
ν_5	812 s, sp	811 s, sp	814 m, sp	802 m, sp
ν_3	744 m, sp	744 m, sp	744 w, sp	751 m, sp
ν_6	713 m, sp	713 m, sp		710 w, sp
NH_3 rock	675 s, b, 620 sh		695 s, b	660 s, b
M–N str	460 m		475 m	450 m, sp, 422 m, sp
N–O str	295 s		265 s	295 s
NO_3 lib N–M–N bend	185 m, 165 sh		175 m, 140 sh	185 s, 155 w[c]
Lattice modes	105 w, 88 w		92 w, 76 w	80 m

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; sp, sharp; sh, shoulder; str, stretch; def, deformation; lib, libration. [b] The low-frequency spectrum was not obtained. [c] The Co–I stretches would also be expected in this region.

D_{3h} to C_{2v}, with resulting splitting of the degenerate modes as shown by the correlation diagram in Figure 1.

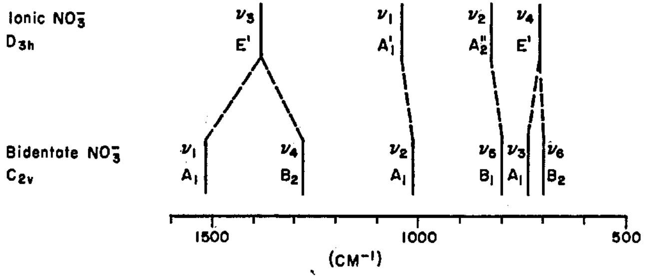

Figure 1.—The correlation of the vibrational modes of free and bidentate nitrate ions.

The observation of a strong band at 1024 cm^{-1}, which can be assigned to the symmetric N–O stretch (ν_2), is indicative of this change, since this vibration is allowed in C_{2v} but inactive in D_{3h} symmetry.[14] The splitting of the asymmetric N–O stretching mode in the 1200–1600-cm^{-1} region into two bands (ν_1 and ν_4) is further evidence for the loss of symmetry. Therefore, the infrared evidence definitely indicates that the nitrate ions act as ligands.

Nitrate ions are capable of functioning as either monodentate or bidentate ligands. In either case, the symmetry of the coordinated ion is C_{2v}. As others have pointed out,[15-18] determination of the mode of bonding from the infrared data alone may be difficult, especially when other ligands are also involved. The observed nitrate ion frequencies for diamminedinitratocobalt(II) are very similar to those found for bis(trimethylphosphine oxide)dinitratocobalt(II),[16] which has been shown from an X-ray crystal structure determination to contain bidentate nitrate ions.[15] However, this should not be considered as conclusive proof of bidentate coordination in the ammine complex.

The electronic spectrum of the complex has been studied from 6000 to 27,000 cm^{-1} in mulls and in several solvents. The results are reported in Table III.

TABLE III

ELECTRONIC SPECTRA OF COBALT AMMINENITRATO COMPLEXES

Medium	λ, nm	ν, cm^{-1}	ϵ_{max}, $M^{-1} cm^{-1}$
	$Co(NH_3)_2(NO_3)_2$		
Kel-F mull (77°K)[a]	1280	7,800	. . .
	1020	9,800	. . .
	603 sh	16,600 sh	. . .
	552	18,100	. . .
	518 sh	19,300 sh	. . .
	463 sh	21,600 sh	. . .
	425 sh	23,500 sh	. . .
Tetrahydrofuran (300°K)	1300	7,700	14
	1120	8,900	14
	544	18,400	120
Acetonitrile (300°K)	1260	7,900	11
	1120	8,900	11
	538	18,600	80
	$Co(NH_3)_2INO_3$		
Kel-F mull (77°K)[a]	1500	6,700	. . .
	1040	9,600	. . .
	610 sh	16,400 sh	. . .
	580	17,300	. . .
	550 sh	18,200 sh	. . .
	460	21,700	. . .

[a] The room-temperature spectrum was similar to the low-temperature spectrum except for poorer resolution of minor spectral features.

The solid and solution spectra are all similar. The band intensities observed in acetonitrile are somewhat lower than those found in tetrahydrofuran. This may be due to the partial dissociation of the complex in acetonitrile.

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(14) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(15) F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, **85**, 2402 (1963).

(16) F. A. Cotton, D. M. L. Goodgame, and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).

(17) A. B. P. Lever, *ibid.*, **4**, 1042 (1965).

(18) J. I. Bullock and F. W. Parrett, *Chem. Commun.*, 157 (1969).

The main features of the spectrum are two broad, low-intensity ($\epsilon \sim 10$–15 M^{-1} cm^{-1}) bands in the near-infrared region and a single broad and asymmetric band of higher intensity ($\epsilon \sim 80$–120) in the visible region (Figure 2). The spectrum of the solid at liquid nitrogen temperature shows several weak shoulders which are probably due to spin-forbidden transitions.

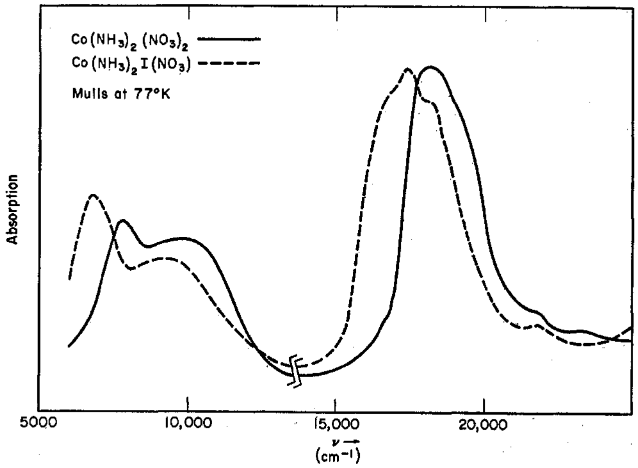

Figure 2.—The electronic spectra of the diamminenitratocobalt complexes. The amplitude scale of the lower frequency half is twice that of the upper frequency part.

The spectrum is very similar to those observed for the bis(phosphine oxide and arsine oxide)dinitratocobalt(II) complexes studied by Cotton, *et al.*,[16] and the bis(amine)dinitrato compounds investigated by Lever.[17] The trimethylphosphine oxide complex has a six-coordinate structure with bidentate nitrate coordination. Similar hexacoordinate structures have been postulated for the other complexes.

The magnetic measurements at 27° using powdered diamminedinitratocobalt(II) gave a value $\chi_{\text{molar}} = 8085 \times 10^{-6}$ cgsu for the static susceptibility. After correction for diamagnetic contributions (75×10^{-6} cgsu), assumption of Curie law behavior leads to an effective magnetic moment of 4.44 BM for the complex. Since the Weiss constants of the analogous bis-(phosphine oxide and arsine oxide) complexes were all small ($|\theta| < 5°$),[16] use of Curie's law appears reasonable. The observed moment is comparable to the values 4.47–4.55[17] and 4.59–4.65 BM[16] reported for the bis-amine and bis-(phosphine oxide and arsine oxide) complexes, respectively. (A search for epr absorption at 9500 MHz in the concentrated powder failed to disclose any signals at 20, 77, and 300°K.)

The spectral and magnetic data strongly indicate that diamminedinitratocobalt(II) must be similar in structure to the previously reported dinitratocobalt complexes. Thus, a six-coordinate structure with bidentate nitrate coordination is postulated. The diammine is the simplest member of the $CoL_2(NO_3)_2$ series.

The theoretical explanation of the spectral and magnetic properties of the dinitrato complexes is not yet clear. The band intensities in the electronic spectra are much higher than would be expected for octahedral cobalt(II) complexes but are lower than those observed for tetrahedral complexes. However, the magnetic moments are typical of tetrahedral cobalt(II). Lever[17] has suggested that the anomalous behavior can be ascribed to the low symmetry of the $CoL_2(NO_3)_2$ complexes. Strong deviations from octahedral geometry would be expected to relax the Laporte selection rule to some extent, resulting in increased band intensities for the ligand field transitions. Such distortions would also cause a reduction in magnetic moment due to the quenching of orbital angular momentum. Lever's explanation seems reasonable, since the crystal structure analysis of the bis-(triphenylphosphine oxide) complex shows the coordination about the cobalt ion to be quite unsymmetrical.

Since nitrate is a weakly coordinated ligand, the main feature of the chemical behavior of diamminedinitratocobalt(II) is the tendency of other ligands to replace the nitrate ions. Reaction with gaseous ammonia causes formation of hexaamminecobalt(II) nitrate. Acetonitrile solutions of the complex react with thiocyanate or halide ions to give blue or green solutions, probably containing tetrahedral complexes of the type $Co(NH_3)_2X_2$.

The reaction of $Co(NH_3)_2(NO_3)_2$ with KI was studied in some detail and was found to proceed in two steps, yielding first $Co(NH_3)_2INO_3$ and eventually $Co(NH_3)_2I_2$. The diiodide salt has been previously prepared[19] and characterized as a tetrahedral complex;[13,20] however, the iodonitrato salt has not been referred to in the literature.

The iodonitrato complex has a rather novel stoichiometry. This material is blue-violet and, like the dinitrato complex, is very sensitive to moisture. It is soluble in acetonitrile and tetrahydrofuran and melts with rapid decomposition at 195–197°. Its X-ray powder pattern differs from that of the dinitrato and the diiodo complexes. The iodonitrato complex can also be prepared by treating equimolar amounts of $Co(NH_3)_2(NO_3)_2$ and $Co(NH_3)_2I_2$ in acetonitrile solution, which suggests that the equilibrium $Co(NH_3)_2(NO_3)_2 + Co(NH_3)_2I_2 \rightleftarrows 2Co(NH_3)_2INO_3$ is established. The electronic spectrum of the iodonitrato complex in acetonitrile and in tetrahydrofuran shows bands characteristic of both $Co(NH_3)_2(NO_3)_2$ and $Co(NH_3)_2I_2$. The electronic spectrum of the solid complex, however, does not show the intense bands characteristic of a tetrahedral complex. The spectrum is similar to that of the diamminedinitrato complex and consists of a broad asymmetric band in the visible and two weaker bands in the near-infrared region (see Figure 2 and Table III). The infrared spectrum of the complex shows the nitrate ion frequencies to be approximately the same as those of the diamminedinitrato complex (see Table II) indicating bidentate nitrate coordination. A six-coordinate structure containing bridging iodide ions would seem reasonable; however, the spectroscopic data are certainly not sufficient for a structural proof.

The thermal decomposition of $Zn(NH_3)_4(NO_3)_2$ under vacuum was investigated to determine if diamminedinitrato complexes of other metals could be produced by decomposition of the ammine nitrate salts. As with cobalt, the zinc salt when heated under vacuum yielded a diamminedinitrato complex. This complex has been prepared previously by a different procedure.[21]

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[19] W. Biltz and B. Fetkenheuer, *Z. Anorg. Allg. Chem.*, **89**, 97 (1914).

[20] W. Klemm and W. Schüth, *ibid.*, **210**, 33 (1933).

[21] R. A. Edge, *J. Inorg. Nucl. Chem.*, **19**, 370 (1961).

Its infrared spectrum is quite similar to that of the cobalt complex (see Table II) indicating that the two have similar structures. The zinc compound is not as soluble in acetonitrile or tetrahydrofuran as the cobalt analog, suggesting that the zinc complex is more ionic. This conclusion is supported by the fact that the metal–oxygen stretching frequency is lower in the zinc compound than in the cobalt complex. The thermal decomposition of $Ni(NH_3)_6(NO_3)_2$ was also investigated. The product appears to be diamminedinitratonickel(II) on the basis of weight loss measurements; however, this complex was not characterized further.

In conclusion, the thermal decomposition under vacuum of μ-peroxo-bis[pentaamminecobalt(III)] tetranitrate has been shown to produce diamminedinitratocobalt(II) with loss of oxygen and ammonia. A similar decomposition of hexaamminecobalt(II) nitrate was found to yield the same diamminedinitrato complex. Spectroscopic and magnetic data strongly indicate that this complex is six-coordinate containing nitrate ions bound as bidentate ligands. It was found that diammine(iodo)(nitrato)cobalt(II) could be prepared from the dinitrato complex suggesting that diamminedinitratocobalt(II) might be useful in synthesizing new coordination compounds. Finally, the diamminedinitrato(zinc and nickel) complexes were prepared by the thermal decomposition of the ammine nitrate salts of these metals. In general, it appears that complexes of the type $M(NH_3)_2(NO_3)_2$ can be produced in this fashion.

Acknowledgment.—We particularly wish to thank Mr. K. J. Jensen for his advice and assistance and also Mr. A. Venters and other members of the analytical chemistry staffs of Argonne National Laboratory and of the University of Illinois for their help. G. L. M. wishes to acknowledge receipt of a predoctoral fellowship from the National Science Foundation.

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Acid-Promoted Redox Decomposition and Cerium(IV) Oxidation of Tris(oxalato)cobaltate(III) Ion in Aqueous Sulfuric Acid[1]

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In aqueous 1 *M* sulfuric acid, cerium(IV) reacts directly with $Co(C_2O_4)_3^{3-}$ as well as with oxalate species produced by acid-promoted decomposition of the tris-oxalato complex. The one-electron redox reaction between $Co(C_2O_4)_3^{3-}$ and cerium(IV) proceeds with a second-order rate constant of $1.2 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$ at 25°. An induction period exhibited in the acid-promoted decomposition of $Co(C_2O_4)_3^{3-}$ is ascribed to slow formation of a monodentate oxalato species which then provides the major path for decomposition.

For some time we have been interested in the factors which influence the redox reactivities of metal–oxalato complexes.[2] In this connection we have undertaken studies on the cerium(IV) oxidations of $Cr(C_2O_4)_3^{3-}$, $Co(C_2O_4)_3^{3-}$, $Rh(C_2O_4)_3^{3-}$, and $Ir(C_2O_4)_3^{3-}$. A summary of this work has been presented,[3] and more recently a full report on the $Cr(C_2O_4)_3^{3-}$–Ce(IV) and $Rh(C_2O_4)_3^{3-}$–Ce(IV) systems has been given.[4] The purpose of the present paper is to provide a detailed account of results obtained for the $Co(C_2O_4)_3^{3-}$–Ce(IV) system.

In acidic sulfate media, addition of cerium(IV) to $Cr(C_2O_4)_3^{3-}$ or $Rh(C_2O_4)_3^{3-}$ results in stepwise oxidation of coordinated oxalate. While oxalate remains attached to the chromium or rhodium, there is no evidence for the oxidation of these metal centers.[4] On the other hand, cerium(IV) rapidly and quantitatively oxidizes[3] $Ir(C_2O_4)_3^{3-}$ to the corresponding iridium(IV) complex, $Ir(C_2O_4)_3^{2-}$. A further contrast is found in the behavior of $Co(C_2O_4)_3^{3-}$ toward cerium(IV).

It is well known[5–10] that $Co(C_2O_4)_3^{3-}$ in aqueous acidic solution undergoes internal redox decomposition to produce cobalt(II), carbon dioxide, and oxalic acid.[11] In the 1 *M* sulfuric acid medium used for the present studies, this internal redox decomposition exhibits an induction period which appears to have gone unnoticed by others who have investigated this reaction. The significance of this induction period is examined herein.

Addition of the *oxidant* cerium(IV) to solutions containing $Co(C_2O_4)_3^{3-}$ results in an *accelerated reduction* of the cobalt(III) center. Such behavior toward cerium(IV) is in marked contrast to the reaction patterns exhibited by the tris-oxalato complexes of chromium(III), rhodium(III), and iridium(III). This reactivity of $Co(C_2O_4)_3^{3-}$ toward cerium(IV) is analogous, however, to the type of behavior often observed when a

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(2) J. E. Teggins, M. T. Wang, and R. M. Milburn, *Advan. Chem. Ser.*, **No. 37**, 226–242 (1963).

(3) H. G. Kruszyna, M. W. Hsu, and R. M. Milburn, *Proc. Int. Conf. Coord. Chem., 10th, 1967*, 302 (1967).

(4) M. W. Hsu, H. G. Kruszyna, and R. M. Milburn, *Inorg. Chem.*, **8**, 2201 (1969).

(5) T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, **228**, 252 (1955).

(6) A. W. Adamson, H. Ogata, J. Grossman, and R. Newbury, *J. Inorg. Nucl. Chem.*, **6**, 319 (1958).

(7) F. D. Graziano and G. M. Harris, *J. Phys. Chem.*, **63**, 330 (1959).

(8) I. G. Murgulescu and T. Oncescu, *Z. Phys. Chem. (Leipzig)*, **214**, 238 (1960).

(9) W. Schneider, *Helv. Chim. Acta*, **46**, 1863 (1963).

(10) (a) C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4622 (1964); (b) J. Aggett and A. L. Odell, *ibid.*, *A*, 1415 (1968).

(11) The rate-determining step is not necessarily a redox process. See Discussion.