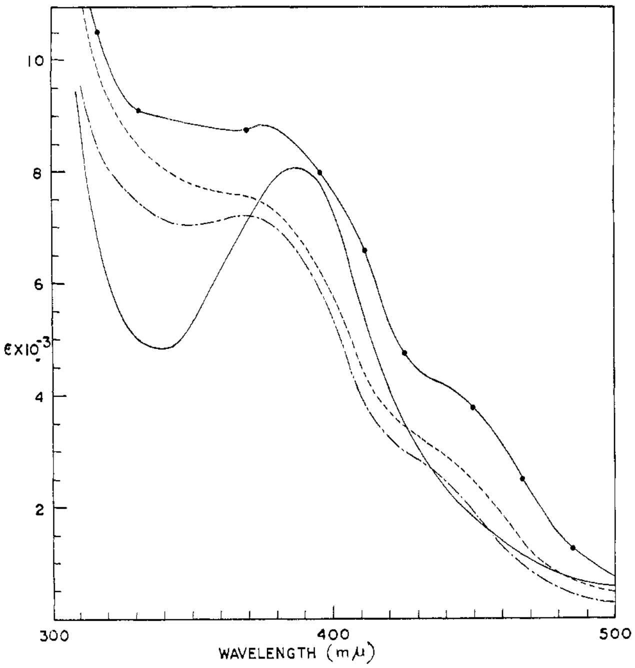

Figure 3.—Near-ultraviolet spectra of: ———, tris(N-methylsalicylaldimine)cobalt(III); — — —, tris(N-methyl-2-hydroxyacetophenimine)cobalt(III); - - - -, tris(N-methyl-2-hydroxypropiophenimine)cobalt(III)-dichloromethane; -●—●-, tris(5-methyl-N-methyl-2-hydroxypropiophenimine)cobalt(III). All spectra were taken in benzene.

ful examination now reveals a shoulder around 24,000 cm^{-1} for both **3** and **4** complexes; for **2** it is very ill defined (Figure 3). The $^1A_{1g} \rightarrow {}^1T_{2g}$ transition should be at higher energy than the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition, the difference being $16B$ where B is an interelectronic repulsion parameter. B remains practically constant for a wide variety of complexes.[5,15] For tris(acetylacetonato)cobalt(III), the crystal field spectrum is consistent[5] with $B = 500$ $cm.^{-1}$ Complexes **2**, **3**, and **4** are of lower symmetry than O_h. However, since the rhombic component is small, the chelates may be roughly described as O_h particularly in cases where ν_1 and ν_3 overlap very seriously. Considering the energy of $^1A_{1g} \rightarrow {}^1T_{1g}$ to be ~16,000 cm^{-1}, one calculates $^1A_{1g} \rightarrow {}^1T_{2g}$ to be at ~24,000 cm^{-1} ($B = 500$ cm^{-1}). Thus the energy of the shoulder of **3** and **4** in the near-ultraviolet region is consistent with $^1A_{1g} \rightarrow {}^1T_{2g}$. In C_{2v} symmetry $^1T_{2g}$ splits into $^1A_1 + {}^1B_1 + {}^1B_2$. However the splitting is expected to be smaller[12,13] for $^1T_{2g}$ than for $^1T_{1g}$. This together with the fact that the ~24,000-cm^{-1} band is observed only as a shoulder on a steeply rising ultraviolet tail will explain the absence of any observable splitting for the band. Our assignment of the ~24,000-cm^{-1} band can only be tentative since the possibility that this band represents a metal–ligand rather than a crystal field transition cannot be ruled out.

Acknowledgment.—Thanks are due to Mr. K. C. Kalia and Mr. K. C. Patil for assistance and to Professor C. N. R. Rao for making available the facilities for thermogravimetric measurements.

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An Infrared and Chemical Investigation of the Two Isomers of the Pentaamminenitrosylcobalt Ion[1a]

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An infrared and chemical investigation of the two series of isomers known for the compounds having the empirical formula $[CoNO(NH_3)_5]X_2$ was undertaken. The infrared spectra were recorded from 4000 to 33 cm^{-1}. Previous vibrational assignments for bands above 700 cm^{-1} have been corrected by the use of ^{15}NO and deuterium isotopic substitutions. Assignments for the bands below 700 cm^{-1} which have not previously been observed are reported. On the basis of all the evidence accumulated a monomeric structure is assigned to the "black" isomers and a dimeric structure containing the hyponitrite moiety has been definitely established for the "red" isomers.

Introduction

The existence of two series of isomeric salts (hereafter referred to as red and black) having the empirical formula $[CoNO(NH_3)_5]X_2$ has been known for many years.[2] There has been a great deal of controversy over the assignment of structures to these salts for several years[3-10] which resulted from conflicting interpretations of the experimental evidence. Recently,

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(1) (a) Taken from the thesis submitted by W. A. McAllister to the University of South Carolina in partial fulfillment of the Ph.D. degree. Presented in preliminary form at the ACS Southeast–Southwest Regional Meeting, Memphis, Tenn., Dec. 2-4, 1965. (b) NDEA Fellow, 1963–1966.

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Hall and Taggart[11] and Dale and Hodgkin[12] have determined the crystal structure of $CoNO(NH_3)_5Cl_2$, a black isomer, and showed that it is monomeric. Feltham[13] has presented conductance data supporting a dimeric structure for the red isomer.

While these works have resolved the uncertainty concerning the gross features of the two isomers, the detailed structure of the dimer, as well as the interpretation of the infrared spectra of these compounds, is still open to question.

Griffith, *et al.*,[8,9] have assigned the N–O stretching vibration to the band at 1045 cm^{-1} in the red isomer by using ^{15}NO substitution. They assumed that this isomer was monomeric on the basis of chemical evidence. Quagliano, *et al.*,[10] on the other hand, was unable to assign this vibration in his studies. For the black isomers the same sets of authors assigned the N–O stretching vibration to bands occurring at 1171 and 1620 cm^{-1}, respectively. It is generally agreed that the nitrosyl complexes of cobalt contain the NO group as a negatively charged ligand. The very low frequency range for the NO stretching vibration when this group carries a negative charge has been widely accepted and rests mainly on the assignments made by Griffith, *et al.*, for these cobalt complexes. In recent investigations by Feltham and Nyholm[14] on compounds of the general formula $[CoXNOL_2]^+$, where X is a halogen and L is a bidentate ligand, the Co has been shown to be in the +3 oxidation state and the NO stretching frequency is assigned to bands between 1550 and 1650 cm^{-1}. These assignments are in agreement with those given by Quagliano, *et al.*, but in direct contrast to those of Griffith, *et al.* Because of the importance of the assignment of the N–O stretching frequency and other uncertainties in the molecular structures of these complexes, we have reinvestigated some chemical reactions of both isomers and extended the infrared spectra to lower frequencies.

Experimental Section

The compounds were prepared using the procedure reported by Moeller and King.[15] The deuterium-substituted compounds were obtained by the same method using completely deuterated ammonia with D_2O as a solvent, the deuterated ammonia having been made by the addition of magnesium nitride to D_2O. The ^{15}NO (95% isotopic purity) was introduced into the complexes by contacting the gas for approximately 12 hr with aqueous ammoniacal solutions of the appropriate cobaltous salt. It was necessary to maintain the reaction mixture at about 0° when preparing the black chloride. Samples were recrystallized from dilute ammonia solutions, washed with absolute ethanol and ether, and dried in a vacuum desiccator.

Two initial decomposition products of the "red" nitrate were prepared by dissolving the red salt in cold 6 *M* HCl and fractionally precipitating the products immediately by successive additions of ethanol. These could be separated in reasonably large fractions, although the more soluble product could never be prepared in high purity regardless of the size of the fractions taken. The fractions were washed with ethanol and ether and dried in a vacuum desiccator.

The charge per cobalt atom was determined by adsorbing a known amount of the compound from aqueous solution on a cation column in the hydrogen ion form. The column was then washed with distilled water and the hydrogen ion in the eluent was titrated with base of known concentration. By dividing the number of moles of hydrogen ion liberated from the resin by the moles of Co adsorbed, the charge per Co atom was determined.

The infrared spectra were recorded from 4000 to 250 cm^{-1} on a Perkin-Elmer Model 521 spectrophotometer. In the higher frequency range the instrument was calibrated in the usual manner[16] while in the lower frequency region it was calibrated by using the atmospheric water vapor and the assignments of Randall, *et al.*[17] Samples were examined as Nujol mulls and hexachlorobutadiene mulls on cesium bromide plates and in potassium bromide and cesium iodide disks. The far-infrared spectra from 350 to 33 cm^{-1} were recorded on a Beckman Model-IR 11 spectrophotometer which was calibrated with water vapor.[17] Both instruments were purged with dry nitrogen. In the low-frequency region all samples were examined as Nujol mulls supported between $^1/_{32}$-in. polyethylene plates or were suspended in polyethylene matrices. All frequencies reported are expected to be accurate within 2 cm^{-1} for sharp bands.

Analyses were performed on the solid compounds by Alfred Bernhardt Mikroanalytisches Laboratorium in Max Plank Institute für Kohlenforschung. *Anal.* Black salt: Calcd for $[CoNO(NH_3)_5]Cl_2$: Co, 24.06; Cl, 28.95. Found: Co, 24.26; Cl, 28.71. Red salts: Calcd for $[CoNO(NH_3)_5]_2(NO_3)_4$: Co, 19.77. Found: Co, 19.69. Calcd for $[Co(NO(NH_3)_5]_2Br_4$: Co, 17.65; Br, 47.88. Found: Co, 17.45; Br, 47.48. Decomposition products: Found for product I: Co, 21.97; Cl, 28.80; N, 28.40; H, 6.15. Routine cobalt analyses on solutions were performed by the use of a Perkin-Elmer Model 202 atomic absorption spectrometer. The range of analysis extended up to 40 ppm of cobalt. The "red" nitrate was used as a standard since its analysis was consistent, and it was stable and not hygroscopic.

Results and Discussion

The infrared spectra of three pentaamminenitrosylcobalt salts and four of their decomposition products have been recorded from 4000 to 50 cm^{-1}. These particular compounds are believed to contain the NO^- ligand and are therefore of interest for comparison with complexes containing the more common NO^+ ligand.[18] From an investigation of the decomposition products along with the infrared spectral data, it was possible to assign the "red" isomer to a dimeric species containing an O–N–N–O grouping and the "black" isomer to a monomeric species. Certain other facts about the configuration of the "red" isomer do seem obvious and these are reported.

Decomposition Studies.—In the decomposition studies the only "black" salt that was used was the chloride. This was decomposed rapidly by the addition of either 6 *M* HCl or 6 *M* H_2SO_4. In both decompositions the major product arising from the NO group was nitric oxide (see Table I). This is contrary to the acid decompositions reported by Griffith, *et al.*, in which they presented evidence that the major nitrogen-containing product was nitrous oxide (N_2O). In our

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[11] D. Hall and A. A. Taggart, *J. Chem. Soc.*, 1359 (1965).

[12] D. Dale and D. C. Hodgkin, *ibid.*, 1364 (1965).

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Table I

Products from the Acid Decomposition of Pentaamminenitrosylcobalt Ions

	Compound	Acid	Products[a]
Black	$[CoNO(NH_3)_5]Cl_2$	H_2SO_4	NO (98%), N_2O (2%), Co(II)
Black	$[CoNO(NH_3)_5]Cl_2$	HCl	NO (96%), N_2O (2%), NOCl (2%), Co(II)
Red	$[CoNO(NH_3)_5]_2Br_4$	H_2SO_4	N_2O (100%), Co(III)
Red	$[CoNO(NH_3)_5]_2(NO_3)_4$	H_2SO_4	N_2O (100%), Co(III)
Red	$[CoNO(NH_3)_5]_2Br_4$	HCl	N_2O (100%), Co(III)
Red	$[CoNO(NH_3)_5]_2(NO_3)_4$	HCl	N_2O (100%), Co(III)[b]

[a] Percentage of products is based on extinction coefficients reported previously: E. L. Saier and A. Pozefsky, *Anal. Chem.*, **26**, 1079 (1954). [b] After 12 hr the cobalt-containing product was definitely identified by X-ray powder patterns as $[Co(NH_3)_5Cl]Cl_2$.

experiments the small quantity (2% or less) of N_2O produced was reduced upon recrystallization and probably arose from a small amount of the red isomer which was present as an impurity.

The decomposition of the red isomers to give N_2O (see Table I) by either acid occurred much more slowly, requiring several hours to produce sufficient gas for infrared analysis. The only gaseous product formed in this case was nitrous oxide. The final cobalt present in the aqueous solution was all in the +3 oxidation state.

Since the analysis of the gaseous products indicated that a hyponitrite structure was present in the "red" isomer, we attempted to prepare this complex from a reaction of cobalt(II) chloride with sodium hyponitrite in an ammoniacal solution in the presence of air. A very small amount of dark solid was formed similar to that reported by Griffith, *et al.*,[8] in the same experiment. The formation of this solid was the principal experimental evidence presented by them that the "black" isomer was dimeric. We were able to isolate a sufficient amount of this material to observe its infrared spectrum. The spectrum clearly showed that the product obtained was neither isomer.

Two intermediate products were formed which will be referred to as I and II. Decomposition product I is easily obtained in reasonable quantity by addition of ethanol to a freshly prepared solution of the "red" nitrate in cold 6 *M* HCl. It is pink-orange and seems to be crystalline. There is a considerable difference in the solubilities of I and II in the $C_2H_5OH-HCl-H_2O$ solution which permitted the isolation of pure I. The charge per cobalt atom was found to be +2 by determining the equivalents of hydrogen ion liberated from ion-exchange resin when the Co compound is absorbed. Upon redissolving I in 6 *M* H_2SO_4 or HCl, it liberates N_2O slowly as does the "red" salt. The conductance study on this compound indicates a dimeric structure for this material.

Chemical analysis gave a Co:N:Cl atom ratio of 1:5:2, which is inconsistent with a hyponitrite-bridged structure assuming none of the ammine ligands have been displaced. Such an assumption appears valid since the final cobalt-containing product was clearly shown to be chloropentaamminecobalt(III) chloride from its infrared spectrum and X-ray powder pattern. The apparent molecular weights for both the "red" nitrate and compound I were highly concentration dependent and no conclusion could be reached from this data. The accumulated experimental evidence on product I is only consistent with a dimeric structure for this material.

Samples of product II were of dubious purity and obtained in very small quantities. The ultraviolet and visible spectra in solution contained peaks at 479 and 300 mμ. The wavelengths of these bands are the same as found in the spectrum of $[Co(NH_3)_5(H_2O)]^{3+}$, but the 330-mμ band has a considerably higher intensity. The chemical analysis on our purest samples of product II give a Co:N:Cl ratio of 2:10:5. This analysis is consistent with the ion-exchange results. A reasonable structure that fits this analysis is $[(NH_3)_5CoOHCo(NH_3)_5]Cl_5$. In any event the cobalt to chloride ratio suggests a dimer structure for decomposition product II.

Infrared Band Assignments.—The infrared frequencies of the observed bands for the "black" chloride in the various forms studied are summarized in Table II, along with the band assignments. The spectrum of the normal compound is shown in Figure 1. In the infrared spectrum of the "black" chloride, the nitrogen-15 substitution caused a shift of 25 cm^{-1} in the broad band observed at 1613 cm^{-1}, which is in good agreement with the 28.9-cm^{-1} shift calculated for an isolated NO motion. This conclusively shows the N–O stretching vibration is contributing significantly to the intensity of the 1600-cm^{-1} band as was suggested by Quagliano.[10] Also contributing to this band is the absorption resulting from the antisymmetric NH_3 deformation. The band at 1172 cm^{-1} (not reported in Table II), assigned by Griffith, *et al.*, as the NO stretching vibration, was found to decrease in intensity upon recrystallization and must arise from an impurity.

Table II

Infrared Spectra of the Black Pentaamminenitrosylcobalt Ion in Some of Its Isotopically Substituted Forms[a]

$[Co^{14}NO(NH_3)_5]Cl_2$		$[Co^{15}NO(NH_3)_5]Cl_2$		$[Co^{14}NO(ND_3)_5]Cl_2$		
Cm^{-1}	Rel intens	Cm^{-1}	Rel intens	Cm^{-1}	Rel intens	Assignment
3280 b	vs	3280 b	vs	2450	vs	N–H str
3185 sh	s	3195 sh	s	2340 sh	s	N–H str
1613	vs	1610	vs	1200	m	NH_3 antisym def
1610	vs	1588	vs	1610	vs	NO str
1292	vs	1293	vs	990	s	NH_3 sym def
812	s	811	s	697	m	NH_3 rock
644 sh	m	630 sh	m	640	m	Co–NO str
578	m	580	m	580	w	Co–NO bend
469 sh	w	466 sh	w	452	w	Co–NH_3 str
442	w	443	w	416	w	Co–NH_3 str
290	s	290	s	262	s	$H_3N-Co-NH_3$ bend
128	m	129	m	127	m	Lattice vibration

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad.

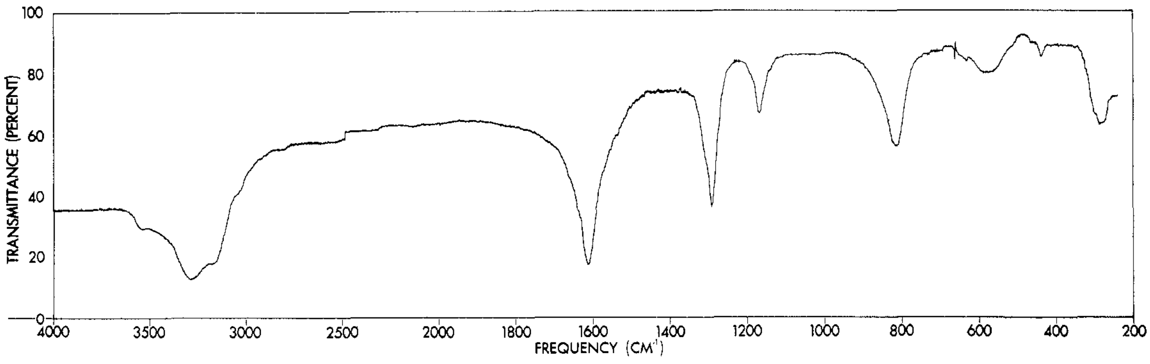

Figure 1.—Infrared spectrum of the black $[CoNO(NH_3)_5]Cl_2$.

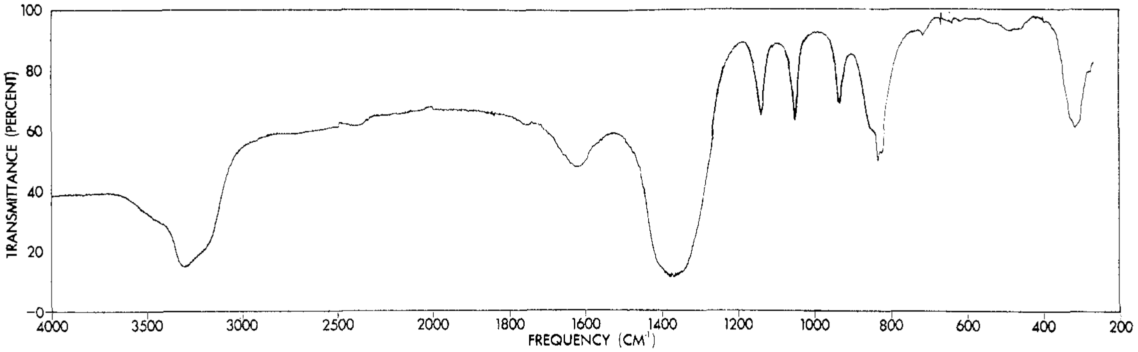

Figure 2.—Infrared spectrum of the red $[CoNO(NH_3)_5]_2(NO_3)_4$.

Since this band and the band observed at 630 cm^{-1} appeared to change in intensity and contour in the same manner, we believe the impurity is hexaamminecobalt(II) chloride. In none of our samples were we able to eliminate completely this impurity, which probably explains the variable magnetic moments[4,5,7] that have been reported for this compound.

The only other band which shifted with ^{15}NO substitution was the shoulder at 644 cm^{-1} which indicates it is the Co–NO stretching frequency. The bending mode of the Co–NO was assigned to the band at 578 cm^{-1} even though this frequency is higher than was expected. However, the Co–NO bond appears to be very strong so this assignment is not unreasonable. Because of the breadth and shape of the band, the expected isotopic shift was not observed. The bands at 467, 438, and 288 cm^{-1} are in accord with other known Co–NH_3 stretching and bending frequencies and are shifted appropriately upon deuterium substitution. The band at 129 cm^{-1} is presumed to be the lattice vibration.

The infrared spectrum of the "red" isomer was considerably more complicated than anticipated (see Figure 2). The discussion of band assignments will be directed toward the "red" nitrate since the isotopic substitution studies were all made on this compound. The bands and their assignment are summarized in Table III. There is no need to discuss the well-known assignments for the nitrate ion. Above 1200 cm^{-1} no band could be attributed to the N–O stretching vibration on the basis of ^{15}NO substitution or deuteration of the complex. However, the bands at 1136, 1046, and 932 cm^{-1} all shifted to lower frequency on ^{15}NO substitution indicating they were in some way concerned with the motion of the nitrogen in the NO group. The 1136-cm^{-1} band shifted by 24 cm^{-1} which was greater than the 21 cm^{-1} calculated for a simple N–O stretching mode. This result indicated that this band is best described as an N–N stretching vibration. The 1046-cm^{-1} band shifted 19 cm^{-1} upon isotopic substitution which was about 0.5 cm^{-1} less than that calculated for an NO stretching motion. On the basis of previous work[19,20] on the $N_2O_2^{2-}$ ion, the N–N and antisymmetric N–O stretching frequencies agree closely with the above, justifying the assignment of the 1046-cm^{-1} band to the antisymmetric stretching mode. The band at 932 cm^{-1} shifted 14 cm^{-1}, nearly the same as the 16-cm^{-1} shift calculated for a N–O stretching motion. On this basis it was assigned to the NO symmetric stretching vibration. Both the isotopic shifts and the band positions indicate that a considerable mixing of these modes is present, and therefore the band descriptions are highly idealized.

In the far-infrared region the only band showing a significant shift upon ^{15}NO substitution is the band at 577 cm^{-1}. This is assigned to the Co–NO stretching frequency. On the basis of the frequency shift on deuterium substitution, the Co–NH_3 stretching mode was assigned to the two bands at 485 and 455 cm^{-1}. The only other band shifting with deuterium substitution was the strong band at 315 cm^{-1} which was in the

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TABLE III

INFRARED SPECTRA OF THE RED PENTAAMMINENITROSYLCOBALT ION IN SOME OF ITS ISOTOPICALLY SUBSTITUTED FORMS[a]

$[Co^{14}NO(NH_3)_5]_2[NO_3]_4$		$[Co^{15}NO(NH_3)_5]_2[NO_3]_4$		$[Co^{14}NO(ND_3)_5]_2[NO_3]_4$		$[Co^{14}NO(NH_3)_5]_2Br_4$		
Cm^{-1}	Intens	Cm^{-1}	Intens	Cm^{-1}	Intens	Cm^{-1}	Intens	Assignment
3460 sh	s	3460 sh	s	2460	s	3440 sh	m	N–H str
3250 b	vs	3240 b	vs	2380 sh	s	3260	vs	N–H str
						3140 sh	s	N–H str
2400	w	2390	w	2390	vw			NO_3^- combination
1748	vw	1749	vw	1750	w			Combination
1615	s	1610	s	1280 sh	s	1610	s	NH_3 def
1360 b	vs	1350 b	vs	1360 b	vs	1360 sh[b]	m	NO_3^- str
								NH_3 def
				1003	s	1300	vs	NH_3 def
1136	s	1112	s	1137	m	1165	s	N–N str
1046	s	1027	s	1045 sh	m	1045	s	N–O antisym str
932	s	918	s	925	s	940	s	N–O sym str
832	vs	832	vs	824	s			NO_3^- out-of-plane bend
830 sh	s	830 sh	s	710	m	835	vs	NH_3 rock
712	w	713	w	715 sh	w			NO_3^- def
616	w	615	w	613	w	608	w	N–NO bend
577 sh	vw	566 sh	vw	575 sh	vw	573	vw	Co–NO str
536 sh	w	535 sh	w	537 sh	w	535	vw	ONNO out-of-plane bend
485	m	487	m	465	m	490	w	Co–NH_3 str
455 sh	w	452 sh	w	430 sh	w	446	m	Co–NH_3 str
419	vvw							?
374 sh	nw	366 sh	vw	365 sh	vw	380 sh	w	N–NO bend
310	s	311	s	275	s	315	s	H_3N–Co–NH_3 bend
247 b	m	245 b	m	230 b	m	243 b	m	O_2N_2–Co–NH_3 bend
137 b	m	135	m	140	m	119 sh	m	Lattice vibration
						108	s	Lattice vibration

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad. [b] We suspect this band is the result of a small amount of nitrate impurity.

expected region for and was therefore assigned to the H_3N–Co–NH_3 bending motion.

Other bands were located at 616, 536, and the very weak shoulder at 374 cm^{-1} and these are assigned on the basis of the vibrational analysis made by Hisatsune and McGraw[21] for the $N_2O_2^{2-}$ ion. They attribute a band at 696 cm^{-1} to the N–NO bend. It is felt that the corresponding band in the complex could reasonably occur at 616 cm^{-1}, considering the change in bonding and additional mass. The out-of-plane bending for the $N_2O_2^{2-}$ ion was found at 492 cm^{-1} which is in reasonable agreement with the band at 536 cm^{-1} in the complex. The very weak shoulder at 374 cm^{-1} in the spectrum of the complex is comparable to the N–NO bending frequency at 371 cm^{-1} in the hyponitrite ion. The band of lowest frequency had an apparent isotopic shift upon ^{15}NO substitution. However, because of the band contour the uncertainty in the assigned frequency is quite large, and the shift may not be meaningful. In the lowest region the band at 247 cm^{-1} was assigned to the ON_2–Co–NH_3 bending motion, and the band at 137 cm^{-1} probably arises from a lattice vibration.

In brief, the infrared spectrum of decomposition product I is essentially identical with that of the "red" bromide, with two notable exceptions. Neither the band at 932 nor that at 247 cm^{-1} is present. The possible reasons for the disappearance of these bands are (1) the removal of an impurity or (2) a chemical transformation which produces either an isomer of the original material or a compound having a very closely related structure. Repeated recrystallizations of the starting material from very weakly acidic, neutral, and ammoniacal solutions gave no noticeable changes in the relative intensity of the 932-cm^{-1} band. For this reason we have rejected the possibility of an impurity. The chemical analysis of decomposition product I appears to be inconsistent with the reaction being an isomerization; however, the analysis is also inconsistent with the slow evolution of N_2O upon further treatment with aqueous acid.

Summary and Conclusions

As previously stated, this work on the "black" chloride is in agreement with the X-ray crystal studies of Taggart and Hall[11] and Dale and Hodgkin,[12] who found the "black" isomer to be monomeric. The infrared band assignments are in agreement with those of Quagliano[10] down to his instrumentation limits and are in opposition to those of Griffith, *et al.*,[8,9] who believed this to be a dimer. Owing to the extensive use of isotopic substitution and agreement with previous workers, there is little question about most of the assignments. However, it probably should be mentioned that the Co–NO stretching frequency was assigned on the basis of the ^{15}NO shift and thus to the higher of the two bands in this region. It was satisfying that the 644- and 578-cm^{-1} bands apparently did not shift on deuterium substitution, clearly indicating they were not attributable to $Co(NH_3)$ motions. The band at 578 cm^{-1} did change shape when the intensities of the

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(21) I. C. Hisatsune and G. E. McGraw, Fifth National Meeting of the Society for Applied Spectroscopy, June 1966, Chicago, Ill., Paper No. 8.

impurity bands at 1172 and 630 cm^{-1} (not reported in Table II) were varied by repeated recrystallizations, as would be expected if a band of $[Co(NH_3)_6]Cl_2$ were partially obscuring a real band. These assignments do seem reasonable and when compared to previous work on the nitrosylruthenium complexes definitely indicate the isomer to be monomeric.

From the location of the NO stretching frequency, it seems appropriate to assign a negative charge to this group. A comparison of the NO stretch at 1610 cm^{-1} in this compound to the range observed in the ruthenium nitrosyls (1830–1900 cm^{-1}) shows the great weakening of the N–O bond. This is most easily interpreted in terms of the change in bond order expected when the charge on the group is changed from -1 to $+1$. During decomposition the NO^- in acid solution reduces the Co(III) to Co(II), explaining the observed decomposition products. The only other case where an NO^- ligand is believed to be present in a monomeric ion is in $K_3[Co(NO)CN)_5]$[8,9] and the complexes prepared by Feltham and Nyholm.[12] All of the ammine frequencies in the complex were located at normal frequencies. However, one might note the large splitting of the Co–NH_3 stretching frequency perhaps due to some *trans* bond weakening effect as we observed earlier in the ruthenium nitrosyl complexes.[18]

Our assignment for the NO stretching frequency for the "red" isomer is in disagreement with the assignments of Griffith, *et al.*[8,9] The observed shifts with ^{15}NO substitution compare so favorably with the calculated values for the three peaks found between 900 and 1200 cm^{-1} that there can be little question of the presence of a nitrogen–nitrogen bond in these isomers. Undoubtedly, the idealized descriptions of the normal modes are only rough approximations and a considerable amount of mixing is present. The interpretation of the spectrum below 700 cm^{-1} is considerably more speculative. The isotopic shifts do indicate the presence of at least one Co–NO bond. The final decomposition products and chemical analyses also strongly support a hyponitrite-bridged dimer.

While the infrared activity of the N–N stretching vibration would be consistent with a *cis*-hyponitrite in which the cobalt atoms are bonded to the nitrogen atoms, steric requirements seem almost certainly to prohibit this configuration. However, this *cis* configuration in which the cobalt is bonded to the oxygen atoms is entirely possible. On the other hand, the related *trans*-hyponitrite seems inconsistent with the infrared activity of the 1136-cm^{-1} band. However, the activity of this band could arise from a lowering of the site symmetry by the crystal lattice. A third alternative that has not been previously considered is an unsymmetrical structure in which one cobalt atom is bonded to the oxygen atom of the hyponitrite and the other to a nitrogen atom. While such a structure is quite uncommon, it is most consistent with our experimental data.

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Five-Coordinated High-Spin Complexes of Cobalt(II) and Nickel(II) with Bis(2-dimethylaminoethyl) Sulfide

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The tridentate ligand bis(2-dimethylaminoethyl) sulfide (Me_4daes) forms 1:1 complexes with the chlorides, bromides, and thiocyanates of cobalt(II) and nickel(II). These complexes have been studied with spectral, conductivity, and molecular weight measurements. The complexes are five-coordinated in the solid state while in solution at room temperature they give rise to an equilibrium between monomeric five-coordinated and associated species. Tetrahedral species are also present at elevated temperatures.

Introduction

In this laboratory systematic research is in progress to determine the preparative conditions and characteristics of high-spin five-coordinated complexes of the metals of the first transition group.[1-4] With regard to the influence of donor atoms on the magnetic properties of five-coordinated compounds, it would appear that oxygen and nitrogen lead to a high-spin configuration, in contrast to phosphorus and arsenic which lead to a low-spin configuration. The behavior of sulfur is however uncertain because in the known

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