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New Red Pentaamminenitrosylcobalt(III) Complexes Obtained by the Reaction of a Cobalt(II)-ammoniacal Solution with Nitrogen Oxide

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New Red Pentaamminenitrosylcobalt(III) chloride and nitrate, $[Co_2(N_2O_2)(NH_3)_{10}]Cl_4 \cdot 4H_2O$ and $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot 2H_2O$ were prepared by the reaction of NO at *ca.* 0 °C with a cobalt(II)-ammoniacal solution which had been exposed to air for 20 h at *ca.* 20 °C. Data of the new red salts were compared with those of the red salt $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot H_2O$ prepared by Sand and Genssler. The new red salt may be considered to be a linkage isomer of the red salt, a binuclear complex in which two of the $Co(NH_3)_5$ groups are bridged through a dimer of nitrosyl group, N–O–O–N^{2-} ion.

Extensively studies have been carried out on the black and red series of compounds with the composition $Co(NH_3)_5(NO)X_2$ (X=Cl, Br, I, and NO_3) since they were first prepared by Sand and Genssler by the reaction of a cobalt(II)-ammoniacal solution with NO gas.[1] Recent X-ray diffraction studies have shown that the black salt $[Co(NO)(NH_3)_5]Cl_2$ is a monomer,[2] and the red one $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot H_2O$ (Red salt I) is a binuclear complex in which two cobalt atoms are bridged through a *cis*-hyponitrite ion, one cobalt atom being bound to the oxygen atom and the other to the nitrogen atom.[3]

We prepared new red-pentaamminenitrosylcobalt(III) chloride and nitrate (Red salt II), $[Co_2(N_2O_2)(NH_3)_{10}]Cl_4 \cdot 4H_2O$ and $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot 2H_2O$ by the reaction of a ammoniacal cobalt(II)-solution with NO gas.[4] Molar conductivities, UV spectra, ^{15}N-isotopic effects on IR spectra upon ^{15}NO-substitution, and ^{15}N-NMR spectra were measured for Red salt I and II. Red salt II is considered to be a new type of compound containing a dimer of nitrosyl, N–O–O–N^{2-} ion.

Experimental

Preparations. *Red Salt I (Nitrate)*: The compound was prepared according to the method of Moeller and King,[5] and could be recrystallized from a dilute ammoniacal solution and dimethyl sulfoxide (DMSO). Found: Co, 19.2; N, 36.1; H, 4.93; NH_3, 28.4%. Calcd for $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot H_2O$: Co, 19.19; N, 36.49; H, 5.09; NH_3, 27.73%. The ^{15}NO-complexes (^{15}N atom %=50 and 99) were synthesized in a vacuum line; 4 ml of concentrated ammonia was added to a solution of cobalt (II) salt (2 g of $Co(NO_3)_2 \cdot 6H_2O$/9 ml of H_2O) at room temperature. The fresh filtrate was degassed with nitrogen, evacuated, and kept at 20 °C in a reaction vessel. 5 mmol of ^{15}NO was introduced at 20 °C into the ammoniacal solution and allowed to stand for 4 hr. Resulting red precipitates were collected by filtration, washed with concentrated ammonia, methyl alcohol, and ether, succesively, and dried in air. Yield, 50—200 mg.

Red Salt I (Chloride): The compound was prepared from Red salt I (nitrate) by stirring its aqueous solution with anion exchange resins of a chloride-ion form, and then adding a large excess of ammonium chloride to the filtrate. Found: Co, 22.4; N, 31.2; H, 5.71; Cl, 24.3%. Calcd for $[Co_2(N_2O_2)(NH_3)_{10}]Cl_4 \cdot 2H_2O$: Co, 22.4; N, 31.9; H, 6.52; Cl, 27.0%.

Red Salt II (Chloride and Nitrate): Red salt II was prepared by the following procedure; 15 ml of ice-cooled concentrated ammonia was added to a cobalt(II) chloride or nitrate solution (5 g of the cobalt(II) salts/20 ml of H_2O) at *ca.* 0 °C. The solution was then exposed to air for 20 h at *ca.* 20 °C. The filtrate thus obtained was poured into a reaction vessel and degassed with nitrogen. Nitrogen oxide was passed into the solution cooled with an ice-water bath to obtain red precipitates. Yield, *ca.* 1 g. Red salt II (chloride) could be recrystallized only from an ice-cooled aqueous solution, and not from an ammoniacal solution. Red salt II (nitrate) could be recrystallized from an ice-cooled aqueous solution and from DMSO. The ^{15}NO-complexes (^{15}N atom %=50 and 99) were synthesized in a vacuum line; by cooling with liquid nitrogen, 5 mmol portion of ^{15}NO was trapped in a reaction vessel containing the ammoniacal cobalt (II) solution (*ca.* 4 g of the chloride or the nitrate/*ca.* 5M ammonia) which had been exposed to air for 20 hr at *ca.* 20 °C. The reaction vessel was shaken under running water until the frozen solution thawed, and was kept at *ca.* 0 °C for 1 hr to obtain the ^{15}NO-complex. Yield, 300—400 mg. The ^{2}H-complex was prepared by use of deuterated ammonia which was obtained by the reaction of magnesium nitride with heavy water. Found: Co, 21.5; N, 30.8; H, 5.4 (±1.0)[6]; NH_3, 32.0; Cl, 25.2%. Calcd for $[Co_2(N_2O_2)(NH_3)_{10}]Cl_4 \cdot 4H_2O$: Co, 20.97; N, 29.90; H, 6.81; NH_3, 30.30; Cl, 25.23%. $\chi_g = -0.170 \times 10^{-6}$ (at 117 K), -0.193×10^{-6} (at 157 K), -0.262×10^{-6} (at 244 K), and -0.276×10^{-6} (at 288 K) (c. g. s.). Preparation of the $N^{18}O$-complex of Red salt II (chloride) was attempted by the use of $N^{18}O$ prepared by a reduction of $N^{18}O_2$ (^{18}O atom %=*ca.* 50) using selenium metal. However, the isotopic labeling of the nitrosyl group with ^{18}O was unsuccessful. Found: Co, 18.9; N, 33.63; H, 4.6 (±1.0)[6]; NH_3, 27.2%. Calcd for $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4 \cdot 2H_2O$: Co, 18.64; N, 35.44; H, 5.42; NH_3, 26.94%.

Measurements. The UV spectra in an aqueous solution and in DMSO (Dotite Spectrosol) were measured with a Hitachi 124 spectrometer and the diffuse reflection spectra with a Hitachi EPS-3T spectrometer. The molar conductivities in an aqueous solution (at 2.5 °C) and in DMSO (at 25 °C) were measured with a universal bridge (Model 4225A of Yokogawa-Hewlett-Packard Ltd.). The IR spectra of Red salt I and II were measured in the region 200—4000 cm^{-1} with JASCO DS-402G and JASCO model IR-F spectrometers as Nujol and hexachlorobutadiene mulls. The wave numbers of the observed IR bands were calibrated with polystyrene

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film, 1,2,4-trichlorobenzene, and water vapor. The differential thermal analyses were performed with a DTA standard-type apparatus of Rigaku Denki Co. Ltd., Gaseous products obtained by the decomposition of Red salt I and II were trapped in a calcium difluoride gas cell with the aid of liquid nitrogen, and were identified from their IR bands.[7] Solid products obtained by dissolving Red salt II in ammonia or water and adding ammonium chloride or acetone to the solution were identified on the basis of their IR spectra[7] and elementary analyses. The Raman spectra for Red salt I (nitrate) and Red salt II (chloride) of the powdered samples and of the rotating potassium bromide disk were measured in the region 650—1700 cm^{-1} on a JASCO R-800 spectrometer equipped with an Ar ion laser, and on a Narumi 750Z-1200 double monochrometer equipped with a He-Ne laser. The magnetic susceptibility was measured by the Gouy method in the temperature range 120—290 K. ^{15}N-NMR spectra of the ^{15}NO-complex (^{15}N atom %=99) or Red salt II (nitrate) in DMSO-d^6 (*ca.* 0.2 g/2 ml) were measured on JEOL JNM-PS-100/PFT-100 FT-NMR system.

Results and Discussion

Red salt II could be prepared at *ca.* 0 °C by the reaction of nitrogen oxide with ammoniacal cobalt(II) solution which had been exposed to the air for 20 h at *ca.* 20 °C. It has been reported that when an ammonical cobalt(II) solution is exposed to the air, some binuclear cobalt(III) ammine complexes containing peroxo, superoxo, or amide groups are likely to be formed,[8] and reactions of these complexes with nitrogen oxide give μ-nitro or μ-nitrato complexes.[9] However, there was no spectroscopic evidence that the μ-nitro or μ-nitrato complexes were formed under the conditions for preparation of Red salt II. A mixture of $[Co(NO)(NH_3)_5]X_2$ and Red salt II was formed but not Red salt I when the time of exposure was less than 20 h and the temperature of the solution was kept below *ca.* 20 °C. No precipitate was obtained nor did the yield of Red salt II decrease when the time of exposure exceeded 20 h and the temperature of the ammoniacal solution was above 20 °C. A mixture of Red salt I and II was obtained when nitrogen oxide, without being fully cooled in an ice-water bath, was passed in the ammoniacal solution which had been exposed to air at 20 °C for 20 h. Red salt I seems to be prepared through the black isomer.[10] It might be possible that the black isomers dimerise to give Red salt II. Another possibility that Red salt II is formed by the reaction of nitrogen oxide with the peroxo complex formed when the cobalt(II)-ammoniacal solution has been exposed to air cannot be excluded. The temperature in the reaction of the ammoniacal cobalt solution with nitrogen oxide might control the formation of Red salt I or Red salt II.

The failure to label the nitrosyl group in Red salt II with ^{18}O is considered to be due to the fact that oxygen of the nitrosyl group is rapidly exchanged with oxygen in the ammoniacal solution.

UV Spectra and Molar Conductivities. The UV spectra for Red salts I and II in an aqueous solution were nearly the same as those in DMSO, and their spectral figures were also similar to those of the diffuse reflection spectra as shown in Table 1.

Table 1. UV spectra of red salts I and II in the solid state and in solution

	in H_2O		in DMSO		in solid state	
Complexes	position of band (in cm^{-1})	log ε	position of band (in cm^{-1})	log ε	position of band (in cm^{-1})	log $f(R)$
Red salt I (nitrate)	20700	1.50	20800	1.28	20700	2.03
	35100	4.05	a)			
	38300	4.15	a)			
Red salt II (chloride)	20300	1.28			20200	1.99
	31000	2.82				
	38000	3.48	insoluble			
	42000	4.08				
Red salt II (nitrate)	20600	1.38	20600	1.18	20500	1.51
	31200	2.91	31000	2.91		
	39000	3.74	a)			
	42000	4.30	a)			

a) These bands could not be measured due to the strong absorption of DMSO.

The molar conductivities of Red salts I and II were compared with those of 4: 1-, 3: 1-, and 2: 1-type electrolytes by the method of Feltham and Hayter.[11] In an aqueous solution at 2.5 °C, the molar conductivities at infinite dilution of Red salt I(nitrate), Red salt II(nitrate), and Red salt II(chloride) were 333, 358, and 366 $ohm^{-1}cm^2$, respectively, while those of $K_4[Fe(CN)_6]$, $[Cr(NH_3)_6](ClO_4)_3$, and $K_2[RuBr_5(NO)]$ were 386, 283, and 164 $ohm^{-1}cm^2$, respectively. The result for Red salt I supports that obtained by Feltham.[12] In DMSO at 25 °C, the molar conductivities at infinite dilution of Red salt I(nitrate) and Red salt II(nitrate) were 142 and 169 $ohm^{-1}cm^2$, and those of $[(CH_3)_4N]_4[RuCl(SnCl_3)_5]$, $[Co(phen)_3](ClO_4)_3$, and $[Ru(phen)_3](ClO_4)_2$ were 140, 115, and 77 $ohm^{-1}cm^2$, respectively.

Studies based on the UV spectra and molar conductivities show that Red salt II is a 4: 1-type electrolyte as well as Red salt I, and that the structure of the cationic ions in the solid states of Red salts I and II can be kept in aqueous and DMSO solutions.

Products Obtained by the Decomposition of Red Salts I and II. Gaseous Products Obtained by Thermal and Acid Decompositions of Red Salts I and II: Differential thermal analyses in atmosphere showed that for Red salt I(nitrate) an endothermic peak was observed at 143 °C, a violent exothermic reaction following at 180 °C. For Red salt II (chloride) an endothermic reaction began at 220 °C and a violent exothermic one followed at 260 °C, and for Red salt II(nitrate) an endothermic reaction at 150 °C and a violet exothermic one at 180 °C. These endothermic reactions are considered to correspond to the liberation of water of crystallization. Red salts I and II darkened at *ca.* 180 °C in a vacuum. Red salt II(chloride) was completely decomposed at 210 °C in a vacuum to give a blue powder, $CoCl_2$. Gaseous analyses by the IR spectra showed that NH_3, N_2O, and water vapor were liberated when Red salts I and II were heated in a vacuum up to 350 °C at a rate of *ca.* 10 °C/min in an electric furnace. A small amount of NO was also detected. However, $^{15}NH_3$ could not be identified in the gaseous decomposition

Table 2. Nitrosyl chloride and dinitrogen oxide from acid and thermal decompositions of red salts I and II

Compounds		Acid		Thermal[a]
Red salt I (nitrate)	^{14}NO-complex	6M H_2SO_4	^{14}N^{14}NO	^{14}N^{14}NO
		6M HCl	^{14}N^{14}NO ^{14}NOCl	
	^{15}NO-complex (^{15}N atom%=99)	6M H_2SO_4	^{15}N^{15}NO	^{14}N^{14}NO(1) ^{15}N^{15}NO(1.5)
	^{15}NO-complex (^{15}N atom%=50)			^{14}N^{14}NO(1.6) ^{15}N^{14}NO(1.5) ^{14}N^{15}NO(1.2) ^{15}N^{15}NO(1)
	Mixture of ^{14}NO-complex and ^{15}NO-one (^{15}N atom%=99) (1: 1)			^{14}N^{14}NO(1.4) ^{15}N^{15}NO(1)
Red salt II (nitrate)	^{14}NO-complex	6M H_2SO_4	^{14}N^{14}NO	^{14}N^{14}NO
		6M HCl	^{14}NOCl, ^{14}N^{14}NO	
	^{15}NO-complex (^{15}N atom%=98)			^{14}N^{14}NO(2.3) ^{14}N^{15}NO(1)
Red salt II (chloride)	^{14}NO-complex	6M H_2SO_4	^{14}NOCl ^{14}N^{14}NO	^{14}N^{14}NO
		6M HCl	^{14}NOCl ^{14}N^{14}NO	
	^{15}NO-complex (^{15}N atom%=99)	6M H_2SO_4	^{15}NOCl ^{15}N^{15}NO	^{14}N^{14}NO(0.3) ^{14}N^{15}NO(1)
	^{15}NO-complex (^{15}N atom%=50)			^{14}N^{14}NO(1.5) ^{14}N^{15}NO(1)
	Mixture of ^{14}NO-complex and ^{15}NO-one (^{15}N atom%=99) (1: 1)			^{14}N^{14}NO(1.4) ^{14}N^{15}NO(1)

a) The values in parentheses indicate the relative ratio of the amount of dinitrogen oxide.

product of the ^{15}NO-complexes of Red salts I and II. The results obtained are summarized in Table 2. ^{14}N^{14}NO and ^{14}N^{15}NO were derived from the ^{15}NO-complexes(^{15}N atom%=50 and 99) of Red salt II and from a mixture of the ^{14}NO- and ^{15}NO-complexes-(^{15}N atom%=99)(1: 1) of Red salt II. On the other hand, ^{14}N^{14}NO and ^{15}N^{15}NO were derived from the ^{15}NO-complex(^{15}N atom%=99) of Red salt I and from a mixture of the ^{14}NO- and ^{15}NO-complexes(^{15}N atom%=99)(1: 1) of Red salt I. ^{14}N^{14}NO, ^{15}N^{14}NO, ^{14}N^{15}NO, and ^{15}N^{15}NO were observed in the ^{15}NO-complex (^{15}N atom%=50) of Red salt I.

Studies on a catalytic reaction of ^{15}NO with a large excess of $^{14}NH_3$ at 200—250 °C on platinum supported on alumina have shown that the reaction products and their relative ratios are ^{15}N^{15}NO: $^{15}N_2$:^{14}N^{15}N:^{14}N^{15}NO =32: 6: 50: 13, and that a considerable amount of ^{14}N^{15}NO was obtained but no ^{15}N^{14}NO was detected.[13]

The thermal decomposition of ^{15}NO-complex(^{15}N atom%=99) of Red salt I(nitrate) gave ^{14}N^{14}NO and ^{15}N^{15}NO, but not ^{14}N^{15}NO. The ^{14}N^{14}NO from the ^{15}NO-complex of Red salt I(nitrate)(^{15}N atom%=99) probably arise as a by-product in the thermal decomposition; the ^{14}N^{14}NO contains two nitrogen atoms which come from the nitrogen of ammines and nitrate ions in this complex. The ^{14}N^{14}NO thus obtained occupied *ca.* 40% in all of the N_2O. The relative ratios of ^{14}N^{14}NO : ^{15}N^{14}NO: ^{14}N^{15}NO: ^{15}N^{15}NO from the hyponitrite ion in the ^{15}NO-complex (^{15}N atom%=50) of Red salt I(nitrate) became 1: 1.4: 1.2: 1, and those of ^{14}N^{14}NO: ^{15}N^{15}NO from the mixture of the ^{14}NO- and ^{15}NO-complexes(^{15}N atom%=99)(1: 1) became 1: 1.2. If the dinitrogen oxide exclusively comes from the hyponitrite ion in Red salt I without the N–N bond cleavage, the relative ratios of the mixture of ^{14}N^{14}NO, ^{15}N^{14}NO, ^{14}N^{15}NO, and ^{15}N^{15}NO derived from the ^{15}NO-complex(^{15}N atom%=50) will be 1: 1: 1: 1, and those of ^{14}N^{14}NO and ^{15}N^{15}NO from the mixture of ^{14}NO- and ^{15}NO-complexes(^{15}N atom%=99)(1: 1) will be 1: 1. It is hardly conceivable that the hyponitrite ion in Red salt I(nitrate) is decomposed to give nitrogen oxide, and the nitrogen oxide thus obtained reacts with NH_3.

The ^{14}N^{15}NO from the ^{15}NO-complex(^{15}N atom%=99) of Red salt II(chloride and nitrate) suggests the presence of the reaction of ^{15}NO with an excess of coordinated ammonia in these compounds. The ^{14}N^{14}NO from the ^{15}NO-complex(^{15}N atom%=99) of Red salt II(chloride) seems to arise from oxidation of the $^{14}NH_3$. The ^{14}N^{14}NO as a by-product occupied *ca.* 20% of the total N_2O. The relative ratio of ^{14}N^{14}NO and ^{14}N^{15}NO from the nitrosyl group in the ^{15}NO-complex(^{15}N atom%=50) of Red salt II(chloride) became 1.2: 1, and that of ^{14}N^{14}NO and ^{14}N^{15}NO from the mixture of the ^{14}NO- and ^{15}NO-complexes(^{15}N atom%=99)(1: 1) became 1: 1. These isotopic studies suggest that the coordinated nitrosyl groups react with the NH_3 groups to give the dinitrogen oxide. The ratio, the dinitrogen oxide as the by-product to all the dinitrogen oxide derived from Red salt II(nitrate) was about 40%, showing that a considerable amount of the dinitrogen oxide is derived from the reaction of the coordinated NH_3 groups with the nitrate ions.

Table 2 also shows the gaseous products obtained by acid decomposition which is milder than the thermal one. The ^{15}NO-complex (^{15}N atom%=99) of Red salt II(chloride) was decomposed by addition of 6M sulfuric acid to give ^{15}NOCl and a very small amount of ^{15}N^{15}NO, while only ^{15}N^{15}NO was derived from the ^{15}NO-complex(^{15}N atom%=99) of Red salt I(nitrate). The result from the addition of 6M sulfuric acid to the ^{14}NO-complex of Red salt I(nitrate) was in agreement with that obtained by Mercer *et al.*[14] The ratio of N_2O to NOCl derived from Red salt II(nitrate) was much smaller than that derived from Red salt I(nitrate) when 6M hydrochloric acid was added.

The thermal and acid decompositions of Red salts I and II suggest the following. If the hyponitrite ion were present in Red salt II, the N–N bond strength of the hyponitrite group would be smaller than that for Red salt I. However, another possibility that a small amount of ^{15}N^{15}NO from Red salt II is due to the contamination of Red salt II by Red salt I cannot be excluded (see IR spectra of Red salts I and II). In this case, it may be considered that the hyponitrite group is absent in Red salt II.

Solid Products Obtained by Treating Red Salt II with Ammoniacal Solution and Water: Red salt II(chloride) was completely decomposed in boiling water to give a mixture of cobalt(III) hydroxide and cobalt(III) ammine-complex with coordinated nitro group. The IR spectra of solid products precipitated by the addition of ammonium chloride or acetone to a 3M ammoniacal solution of Red salt II(0.5 g/40 ml) at *ca.* 0°C showed that Red salt II(chloride) was completely decomposed within 4 h to give an orange-yellow compound, the nitro-complex, while, in an aqueous solution of Red salt II at *ca.* 0 °C, Red salt II was stable for 9 days. The pink precipitate obtained by the addition of acetone to the aqueous solution was identified to be Red salt II with a small amount of the nitro-complex. Thus, Red salt II is considered to be stable in water at *ca.* 0 °C.

A yellow product was obtained when the ammoniacal solution of Red salt II was boiled and then cooled at *ca.* −15 °C. The IR spectra of this compound show the characteristic absorption bands of nitro-complex and of nitrate ion[7] and the corresponding bands of the ^{15}*N*-compound shifted downwards, but no characteristic ones of Red salt II could be observed. The IR spectra of the yellow product obtained from Red salt II(nitrate) was almost equal to that from Red salt II(chloride). Elementary analyses of the yellow salt from Red salt II(chloride) gave a Co: N: H: Cl atom ratio of 1: 7.7: 15.4: 0.2, and those from Red salt II(nitrate) gave a Co: N: H atom ratio of 1: 8.5: 16.9. The results obtained from the IR spectra and the elementary analyses show that a main component of the yellow salts is $[Co(NO_2)(NH_3)_5](NO_3)_2$.

Red salt I(nitrate) is very stable in a boiling 3M ammoniacal solution, and can be recrystallized by cooling the solution to −15 °C, and reprecipitated by addition of a large excess of ammonium nitrate to the ammoniacal solution. In boiling water, however, a part of Red salt I(nitrate) was decomposed to give cobalt(III) hydroxide.

The complex cation of Red salt II might be generally unstable with respect to the nitrosyl groups. No intermediates clearly reflecting structure for the complex cation of Red salt II could be isolated. All of the nitrosyl group in Red salt II might change into the nitro and nitrate ions.

IR Spectra of Red Salts I and II. *Red Salt I(Nitrate)*: No isotopic shifts for the bands in the region 200—700 cm^{-1} could be observed because of the broadness of the bands. Of the bands in the region 700—4000 cm^{-1}, three bands at 1137, 1048, and 930 cm^{-1} shifted to 1112, 1027, and 917 cm^{-1}, respectively, upon ^{15}NO-substitution(^{15}N atom%=99). These bands have been previously assigned to the N–N, the antisymmetric N–O, and the symmetric N–O stretching vibrations, respectively, on the basis of the oxtent of the isotopic shifts upon ^{15}NO-substitution[14] and IR studies on $M_2N_2O_2$ (M=Na and K) containing *cis*-$N_2O_2^{2-}$ ion.[15]

However, our assignments of these three bands differ from those by Mercer *et al.*[14] Five absorption bands for the ^{15}NO-complex(^{15}N atom%=50) were observed at 1137, 1112, 1048, 1027, and 924 cm^{-1}, and six absorption bands for the mixture of the ^{14}NO-complex and the ^{15}NO-complex(^{15}N atom%=99)(1: 1) at 1137, 1112, 1048, 1027, 929, and 920 cm^{-1}.

For the ^{15}NO-complex(^{15}N atom%=50), the N–N stretching vibration can be expected to split into three absorption bands, the ^{14}N–^{14}N, the ^{14}N–^{15}N, and the ^{15}N–^{15}N stretching vibrations(their intensity ratio 1: 2: 1).[16] For the mixture of the ^{14}NO- and the ^{15}NO-complexes(^{15}N atom%=99)(1: 1), the ratio of the absorption intensity for the ^{14}N–^{14}N and ^{15}N–^{15}N stretching vibrations can be expected to be 1: 1. Both the 1137 cm^{-1} and the 1048 cm^{-1} bands clearly splitted into two bands upon ^{15}NO-substitution(^{15}N atom%=50), so they may not be due to the N–N stretching vibration. On the other hand, the 930 cm^{-1} band shifted to 924 cm^{-1} (this wave number lies midway between 930 cm^{-1} of the ^{14}NO-complex and 917 cm^{-1} of the ^{15}NO-complex) upon ^{15}NO-substitution(^{15}N atom%=50). The 924 cm^{-1} band is seemingly a single band, the half width of this band being larger than that of the 930 cm^{-1} band and of the 917 cm^{-1} one. The 924 cm^{-1} band might therefore consist of three absorption bands, the ^{14}N–^{14}N, the ^{14}N–^{15}N, and the ^{15}N–^{15}N stretching vibrations. The 1137 cm^{-1} and the 1048 cm^{-1} bands could be assigned to the antisymmetric and the symmetric N–O stretching vibrations, respectively, since the wave numbers of antisymmetric stretching vibration are generally larger than those of symmetric one.[7]

If the 930 cm^{-1} band corresponds to the N–N stretching vibration, the bond order of the N–N would be about one[7] and the bond distance about 1.4 Å.[17] X-Ray diffraction study on Red salt I has shown that the N–N bond distance is 1.25 Å,[3] and the bond order about two,[17] suggesting that the N–N stretching vibration can be observed in the region *ca.* 1300 cm^{-1}. There was a possibility that the N–N stretching vibration could not be observed due to overlapping with very strong broad bands of the nitrate ions at 1360 cm^{-1}. However, this was eliminated by measurement of the IR spectra for the chloride of Red salt I; no absorption band was observed in the 1360 cm^{-1} region except for the band due to the NH_3 symmetric deformation vibration. Three bands at 1154, 1060, and 940 cm^{-1} were observed in the region 900—1200 cm^{-1}. They can be assigned to the antisymmetric N–O stretching vibration, the symmetric N–O one, and the N–N one, respectively.

The N–N stretching vibration for the *cis*-$N_2O_2^{2-}$ ion has been observed in the region 1300—1390 cm^{-1},[15] while the N–N stretching vibration due to the hyponitrite ion bridged with the $Co(NH_3)_5$ groups was observed at 930 cm^{-1}. Lowering of the wave numbers is considered to be due to the coordination of two cobalt atoms to the hyponitrite ion.

Red Salt II(Chloride and Nitrate): The IR spectra and their assignments for Red salt II(chloride) in the region 200—4000 cm^{-1} are shown in Table 3 and Fig. 1.

The absorption bands due to the water of crystallization may be overlapped with the broad bands due to the N–H stretching and the NH_3 degenerate deformation vibrations as observed on Red salt I(nitrate).

Table 3. Wave numbers and assignments of IR bands for red salt II (chloride and nitrate)[a]

Red salt II (chloride)	Red salt II (nitrate)	Assignments
3250 vs, b	3280 vs	O–H str and
3110 vs, b	3200 vs, sh	N–H str
1608 m, b	1625 m, b	H_2O bend and NH_3 deg def
1481(31)[b] vs	1491(32) s	N–O str
	1370 vs, b	N–O asym str of NO_3^{1-}
1318 vs	1320 sh	NH_3 sym def
1278(19) vs	1269(20) vs	N–O str
	1050 vw	N–O sym str of NO_3^{1-}
1020(1) m	1011(3) s	O–O str
859 s	852 s	NH_3 rock
	831 s	out-of-plane def of NO_3^{1-}
804(21) w	806(26) w	N–O–O bend
595(14) s	586(17) w	N–O–O bend or Co–N–O bend
501 s	493 w	Co–NH_3 str
478 m	475 sh	
334 vs	325 vs, b	H_3N–Co–NH_3 bend
278 vs	270 m, b	
223 vs		

a) The bands due to Red salt I contained as impurity are excluded. b) The values in parentheses indicate the observed isotopic shift. Abbreviations: str=stretching, bend=bending, deg=degenerate, sym=symmetric, asym=asymmetric, rock=rocking, def=deformation, vs=very strong, s=strong, m=medium, w=weak, vw=very weak, b=broad, sh=shoulder.

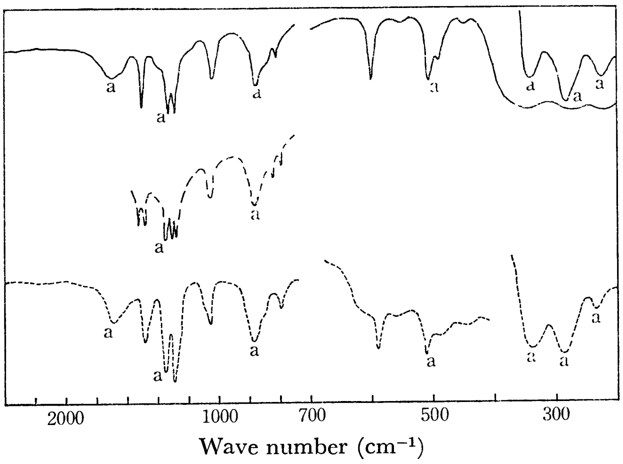

Fig. 1. IR spectra of Red salt II(chloride); —, ^{14}NO-complex; –·–, ^{15}NO-complex (^{15}N atom %=50); ---, ^{15}NO-complex (^{15}N atom %=99.3); a, characteristic bands of cobalt(III)-ammine complex.

IR studies on ammine-complexes show that the NH_3 rocking vibration is sensitive to the oxidation state of the metal atom.[18,19] The wave numbers of these bands of Red salt II seem to support the view that the oxidation state of the cobalt atom for Red salt II is III as for Red salt I. Red salt II was diamagnetic as expected from the oxidation state of the cobalt atom of Red salt II.

Upon ^{15}NO-substitution(^{15}N atom%=99.3), the bands at 1481(vs),[20] 1278(vs), 804(w), and 595(s) cm^{-1} for the chloride shifted, and the bands at 1481, 1278, and 804 cm^{-1} split into two peaks upon ^{15}NO-substitution(^{15}N atom%=50). The band at 1020 cm^{-1}(m) did not shift or split, but shifted downwards by *ca.* 6 cm^{-1} upon ^2H-substitution. The spectral features for the nitrate were similar to those for the chloride except for the absorption band, *ca.* 1360 cm^{-1} due to the nitrate ions. The 1011 cm^{-1}(s) band hardly shifted upon ^{15}NO-substitution as observed on the 1020 cm^{-1} band of the chloride.

From a comparison of the IR spectra of Red salts I and II, II seems to be contaminated with a very small amount of I. I could not be removed from II by crystallization.

If the same N–N bond as in Red salt I and in $K_6[Co_2(CN)_{10}(N_2O_2)]\cdot nH_2O$,[16] is present in Red salt II, the N–N stretching and the N–N–O bending vibrations should be observed on IR and/or Raman spectra and shift and split into three peaks upon ^{15}NO-substitution (^{15}N atom%=50). However no such phenomena were observed. Such a N–N bond might not be present in the complex cation of Red salt II.

IR studies with the use of nitrogen-15 will exclude the possibility that the nitrosyl group terminally coordinates to the cobalt atom, and that two cobalt atoms are bridged through two nitrogen atoms of the two nitrosyl groups; in the former case, the stretching vibration of the terminal NO group is generally observed in the region 1530—1980 cm^{-1},[21] and in the latter case, the coordination number of the cobalt(III) ion becomes seven and the IR bands cannot be explained in terms of this skeleton. Elementary analyses and IR studies show that the number of the nitrogen atoms labeled with nitrogen-15 is two, and two of the nitrosyl groups are present in Red salt II.

The possibility that two of the $Co(NH_3)_5$ groups are bridged through an ion consist of a dimer of nitrosyl, $N–O–O–N^{2-}$ can not be excluded. If the N–O–O–N anion is contained in the complex cation of Red salt II, the five IR bands in the region 580—1490 cm^{-1} could be explained on the basis of this anion; the 1481 and 1278 cm^{-1} bands of the chloride and the 1490 and 1269 cm^{-1} bands of the nitrate can be assigned to the N–O stretching vibrations, the 1020 cm^{-1} band of the chloride and the 1011 cm^{-1} band of the nitrate to the O–O stretching vibrations. The 804 cm^{-1} band of the chloride and the 806 cm^{-1} band of the nitrate may be assigned to the N–O–O bending vibrations. The 595 cm^{-1} band of the chloride and the 586 cm^{-1} band of the nitrate may be assigned to another N–O–O bending or the Co–N–O bending vibrations. The wave numbers of the N–O stretching vibrations for Red salt II are larger than those for the complexes with the hyponitrite ions. This seems to reflect the fact that the bond order of the N–O for Red salt II is larger than that for the complexes with the bridged hyponitrito ion. The O–O stretching vibrations of O_2^{2-} and O_2^{1-} anions are in the region 1050—1090 cm^{-1}, and 1070—1150 cm^{-1} [22] and those of μ-oxo cobalt(III)-ammine complexes and μ-superoxo ones are in the region *ca.* 830 cm^{-1} [23] and 1070—1150 cm^{-1}, respectively.[24] The band in the region 1010—1020 cm^{-1} for Red salt II may be reasonably assigned to the O–O stretching vibration. The N–N–O bending vibration of the hyponitrite ion are also observed in the region 600—860 cm^{-1}.[15,25] Thus, the bridged $N–O–O–N^{2-}$ ion would most likely explain the results obtained.

Raman Spectra of Red Salts I and II. Since the nitrates of Red salts I and II decomposed in DMSO on irradiation with laser, their spectra could not be measured. Satisfactory Raman spectra of the powdered samples and the rotating potassium bromide disk could not be obtained because of a partial decomposition of the compounds. The bands due to nitro group and an unassignable band at 1653 cm^{-1} overlapped with the original bands for Red salt I(nitrate) and Red salt II(chloride). For Red salt II(chloride), the bands due to nitrate ion were also observed. However, all of the bands observed on IR spectra could be observed on Raman spectra for both Red salts I and II.

Nitrogen-15 NMR Spectra of Red Salt II. A preliminary ^{15}N-NMR study of the ^{15}NO-complex(^{15}N atom%=99) of Red salt II(nitrate) in DMSO-d_6 showed one peak, which is considered to support the view that two of the nitrosyl groups are in an equivalent chemical circumstance. The possibility that one cobalt atom is bound to the oxygen atom and the other to the nitrogen one in $N–O–O–N^{2-}$ ion may be excluded.

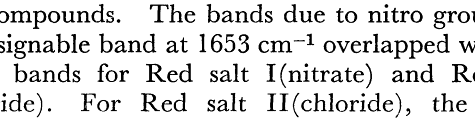

Fig. 2. Probable structure of the complex cation of Red salt II.

From the results, the structure as shown in Fig. 2 can be predicted for the complex cation of Red salt II. The coordination ability of the nitrogen of the $N–O–O–N^{2-}$ ion to the cobalt atom may be stronger than that of the oxygen.

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