Bridges in Polynuclear Complexes. I. The Reaction and Reaction Products of $\mu(NH_2,O_2)$ Dicobalt Complexes with Nitrites†

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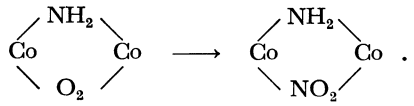
The IR spectroscopy of the μ-amido-μ-nitro complex, $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4\cdot 2H_2O$ obtained from normal and ^{18}O-labeled $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$ has revealed that the O atom in the Co-N-O-Co chain comes from the O_2 bridge of the starting complex, whereas the O atom attached to the N atom from outside the chain comes from the nitrite used in the bridge conversion, $\mu O_2 \rightarrow \mu NO_2$. A reaction mechanism involving N_2O_3 as the reacting species is proposed. The reaction of $[(NH_2,O_2)\{Co(NH_3)_4\}_2]X_3$ with the nitrite in neutral solution gave a non-electrolytic μ-hyperoxo dicobalt complex, $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$ (I). Treatment of I with perchloric acid gave a triple-bridged complex, $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]^+$, which reproduces I when treated with sodium nitrite.

Dioxygen-bridged dicobalt complexes may be classified into two series, one of which includes brown μ-peroxo complexes, and the other green μ-hyperoxo complexes. Both react with nitrite ion but the reaction features are quite diverse depending on the nature of the starting complex and the condition of the reaction. In the case of $[O_2\{Co(NH_3)_5\}_2]^{n+}$, in an acidic solution there occurs reduction of the μ-hyperoxo complex ($n=5$) to the μ-peroxo complex ($n=4$) followed by cleavage of the O_2 bridge and formation of the mononuclear complex.[1] In the case of the ethylenediamine analog $[O_2\{Co(en)_2NH_3\}_2]^{n+}$, oxidation of the μ-peroxo complex ($n=4$) to the μ-hyperoxo complex ($n=5$) occurs in an acidic solution, whereas in a neutral solution substitution of the ammine ligands by nitro groups takes place.[2]

The double-bridged complex also reacts with the nitrite ion, and in an acidic solution, conversion of the O_2 bridge into the NO_2 bridge occurs without any change on the NH_2 bridge:[3]



The kinetic study of the reaction of the μ-amido-μ-hyperoxo complex, $[(NH_2,O_2)\{Co(en)_2\}_2]^{4+}$, by Edwards *et al.* suggested that reduction ($\mu O_2^- \rightarrow \mu O_2^{2-}$) and bridge conversion ($\mu O_2 \rightarrow \mu NO_2$) should occur successively.[4] The first part of the present paper is concerned with the investigation into the reaction mechanism of such bridge conversion ($\mu O_2 \rightarrow \mu NO_2$) by the combined use of ^{18}O-labeling and the IR study of the reaction product.

The work on the reaction of the μ-NH_2-μ-O_2 complex with the nitrite ion in a neutral or a basic solution still seems to be meager[2] especially with the ammine complex. The remaining part of the present paper describes the study of such a reaction and some new dicobalt complexes obtained as the reaction product, one of which is a non-electrolytic μ-amido-μ-hyperoxo complex.

Experimental

Materials. $^{18}O_2$ (^{18}O atom % = 92) gas was obtained commercialy from International Chemistry and Nuclear Corp.

Analyses. Ammoniacal N was determined by titration of ammonia after distillation from aqueous sodium hydroxide with arsenic(III) oxide;[5] total N was determined similarly except for use of Devarda's alloy in place of arsenic(III) oxide; Cl in perchlorate was determined as silver chloride after decomposition of the sample with melted sodium nitrite in a nickel crucible.[6] Other elements were analysed by the standard methods.

Reaction and Preparation. *1. Preparation of ^{18}O-Substituted $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$:* This ^{18}O-labeled dicobalt complex was prepared by the adaption of the usual method[7] by using a closed system: A 100-ml flask containing 2.5 g of cobalt(II) nitrate hexahydrate, 15 ml of water previously boiled and cooled under nitrogen, and a magnetic bar coated with Teflon was connected to a vacuum line. The flask was degassed by three freeze-pump cycles, then filled with *ca.* 1 atm ammonia gas from cylinder connected to the line. The content was stirred with a magnetic stirrer until the blue precipitate which had once appeared redissolved and the solution turned red. Although some temperature rise was observed during the absorption of ammonia, it was allowed to be, because absorption of too large excess of ammonia by cooling is unfavorable for the succeeding dioxygen-bridging reaction. After the supply of ammonia gas was stopped the reaction flask was cooled in an ice bath, and 100 ml (N. T. P.) of $^{18}O_2$ gas was introduced into it *via* a Toeplar pump, and was allowed to be absorbed by the solution for 3 h. The mercury of the pump was previously covered with liquid paraffine because it is easily oxidised in the presence of ammonia. At this stage, black crystals of $[O_2\{Co(NH_3)_5\}_2](NO_3)_4$ were precipitated. The reaction mixture was exposed again to 1 atm ammonia gas, and kept at 35 °C for 2 h to introduce the NH_2 bridge; addition of potassium hydroxide was omitted in this experiment to minimize the contamination by normal oxygen. After the reaction mixture was freezed, the flask was removed from the vacuum line, and succeeding procedures were carried out under air. Upon the freezed mixture, 3.5 g of ammonium cerium(IV) nitrate, 30 ml of nitric acid, and 50 g of ice was placed. The whole mixture was melted and stirred. The precipitate was separated from the solution,

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and purification *via* practically insoluble sulfate gave 380 mg of ^{18}O-substituted $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$; in addition, 160 mg of ^{18}O-labeled $[O_2\{Co(NH_3)_5\}_2](NO_3)_5$ was obtained as a co-product in the course of the purification of the former. The complexes were examined by the IR spectroscopy.

2. Reaction of $[(NH_2, {}^{18}O_2)\{Co(NH_3)_4\}_2](NO_3)_4$ with NO_2^- in an Acidic Solution and Isolation of Product: The procedure was modified from the method of Werner[3] owing to the scantiness of the reactant complex available for the experiment.

To a solution of 500 mg of sodium nitrite in 10 ml of water, 100 mg of the complex was added, and then 1.5 ml of 14 M nitric acid was added dropwise with stirring. The mixture was cooled in an ice bath, and the precipitated orange μ-amido-μ-nitro dicobalt complex nitrate was filtered with suction, washed with methanol, and dissolved in 1.5 ml of 12 M hydrochloric acid. After filtration, 3 ml of ethanol was added to it, and the mixture was cooled in an ice bath. The precipitate (complex chloride) was filtered, and recrystallized in the same manner. The product was washed with ethanol, and dried by aeration; yield 70 mg.

The product with normal oxygen prepared by the same procedure was submitted to chemical analysis; each product obtained in the experiments with $^{18}O_2$ and with normal oxygen respectively gave the identical X-ray diffraction pattern and IR spectrum except for the isotopic shift. Found: Co, 23.81; N(total), 28.08; N(ammoniacal), 25.23; Cl, 28.54; H, 6.02%. Calcd for $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4\cdot 2H_2O$: Co, 23.86; N(total), 28.35; N(ammoniacal), 25.52; Cl, 28.71; H, 6.21%.

3. Reaction of $\mu(NH_2,O_2)$ Complex with NH_4NO_2 in a Neutral Solution (Preparation of $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$): To 750 ml of 10% ammonium nitrite, 20 g of $[(NH_2,O_2)\{Co(NH_3)_4\}_2]Na(ClO_4)_4$ (prepared by the method in Ref. 7) was added with stirring, and the mixture was allowed to stand at *ca.* 5 °C in a refrigerator. From the next day, 1 g of ammonium persulfate was added every day until the solution assumed a reddish orange color and no more precipitate increased (It took *ca.* 20 days). The green precipitate was filtered, washed with water and then with acetone, and dried by aeration; yield 8 g.

The product obtained was insoluble in any solvents so far examined, and could not be recrystallized by the usual method. For the purification, the crude product was once changed to $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]ClO_4\cdot 0.5H_2O$ by the process described in the next section, and brought back to the original compound by the following procedure: To a solution of 1 g of the perchlorate dissolved in 130 ml of water was added 10 ml of 10% aqueous sodium nitrite. The mixture was allowed to stand in a refrigerator overnight. The precipitate was filtered, washed with water and then with acetone, dried by aeration, and kept over calcium chloride. Green powder; yield 0.6 g. Found: Co, 27.92; N(total), 29.66; N(ammoniacal), 16.31%. Calcd for $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$: Co, 28.20; N(total), 30.16; N(ammoniacal), 16.75%.

4. Preparation of $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]ClO_4\cdot 0.5H_2O$: Six grams of the crude $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$ (described above) were added to 150 ml of ice-cold perchloric acid (60%) and the mixture was stirred under reduced pressure of aspirator for 2 h for dissolution. (Without reduced pressure it took longer time for dissolution and decomposition to form by-products was more pronounced.) The cold green solution was filtered with a sintered-glass filter and added in small portions to 900 ml of ether wihch had been cooled in an ice bath, care being taken to minimize the temperature rise. The flocky precipitate was filtered and washed with ether. After the ether was eliminated with aeration, the product was washed with two small portions of cold water and air dried. The green material was dissolved in 150 ml of acetone and an equal volume of ether was added to it. The mixture was allowed to stand in an ice bath for *ca.* 1 h and the precipitate was filtered, washed with ether, and air-dried. Green thin plates; yield 1.9 g. Found: Co, 24.85; N(total), 23.16; N(ammoniacal), 14.60; Cl, 7.45; H, 3.16%. Calcd for $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]ClO_4\cdot 0.5H_2O$: Co, 24.53; N(total), 23.32; N(ammoniacal), 14.58; Cl, 7.38; H, 3.14%.

5. Preparation of $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]Cl$: To a solution of 3 g of the perchlorate (described above) dissolved in 400 ml of water, 80 ml of 6 M hydrochloric acid was added, and the mixture was cooled in an ice bath. The precipitate was filtered, and washed with cold 2 M hydrochloric acid and then with acetone. The product was dissolved in 700 ml of cold water, and 70 ml of 6 M hydrochloric acid was added. The precipitate was filtered, washed with 0.5 M hydrochloric acid and then with acetone, and dried by aeration. Green thin prisms; yield 1.6 g. Found: Co, 29.02; N(total), 26.96; N(ammoniacal), 17.02; Cl, 8.81%. Calcd for $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]Cl$: Co, 28.93, N(total), 27.50; N(ammoniacal), 17.19; Cl, 8.70%.

6. Preparation of $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]Br$: To a solution of 2 g of the perchlorate (described above) dissolved in 400 ml of water, 50 ml of 24% hydrobromic acid was added, and the mixture was allowed to stand in an ice bath. The precipitate was filtered, and washed with cold water and then with acetone. The product was recrystallized from the aqueous solution by addition of hydrobromic acid and dried by aeration after filtration and washing. Green needles; yield 1.7 g. Found: Co, 26.20; N(total), 24.30; N(ammoniacal), 15.37; Br, 17.69%. Calcd for $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]Br$: Co, 26.08; N(total), 24.79; N(ammoniacal), 15.50; Br, 17.68%.

Apparatus. IR spectra were recorded with samples in Nujol on a JASCO IR-E or IR-G spectrometer. Recording of absorption spectra was carried out with a Hitachi 124 spectrometer, and that of reflectance spectra with the same apparatus by use of an integration sphere attachment. ESR spectra were recorded on a JEOL JES-3B spectrometer at room temperature. Magnetic susceptibilities were determined by the Faraday technique with a Shimadzu MB-2 balance. Powder X-ray diffraction patterns were recorded on a Rigaku 2171 diffractometer with the Ni $K\alpha$ radiation.

Results and Discussion

IR Spectroscopy of ^{18}O-Labeled Complexes. 1. μ-(NH_2,O_2) Complex: The IR spectra of normal and isotopically labeled $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$ in the region of *ca.* 700—1200 cm^{-1} are shown in Fig. 1. The fact that the labeled complex shows no peak corresponding to $^{16}O_2$ stretching vibration proves that there has been no shuffling of oxygen between O_2 and H_2O or NO_3^- in the formation process of the single-bridged complex $[O_2\{Co(NH_3)_5\}_2]^{4+}$, as well as in the transformation process to the double-bridged complex. The possibility of scrambling of oxygen atoms among the oxygen molecules and the O_2-moieties of complex ions also was excluded because a sample prepared by using a mixture of $^{18}O_2$ and $^{16}O_2$ showed no peak of ^{18}O-^{16}O stretching vibration.

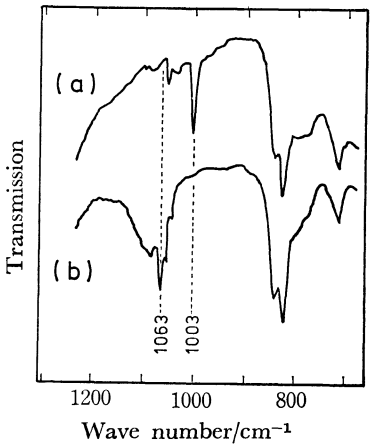
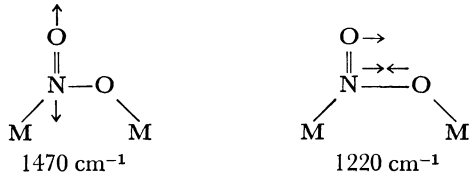


Fig. 1. IR spectra of $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$ (a) with ^{18}O-labeled O_2-bridge and (b) with normal O_2-bridge.

2. $\mu(NH_2,NO_2)$ Complexes: Werner[3] reported two hydrates of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4$, one of which was monohydrate crystallized from dilute hydrochloric acid and the other tetrahydrate crystallized from aqueous solution containing some pyridine. The IR spectrum and the X-ray powder pattern of the ^{18}O-labeled complex chloride prepared as described showed that it was a third form; the chemical analysis of the corresponding normal complex conformed to the formula of dihydrate. The authors later knew that this dihydrate was reported in 1975 by Huang *et al.*[8] who crystallized it from 6 M hydrochloric acid. Not only the IR peaks due to water of crystallization the content of which is different in these three forms, but also the IR peaks due to nitro bridge and ammonia ligand showed slight differences in their frequency and intensity, such differences in some cases being of comparable magnitude to those due to isotopic effect. The variation in the IR spectrum owing to the difference in the crystal form was noticed in this laboratory, with $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$.[9] Thus in the detailed examination of IR spectra and especially in the discussion of their isotopic shifts, one must make sure of the identity of the number of crystal water or the crystal form of the complexes compared.

The IR spectrum of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4$ was reported by Gatehouse[10] although it is not clear which type of the above three hydrates was examined. He assumed an asymmetric structure of the nitro bridge and assigned two strong IR peaks as shown below:



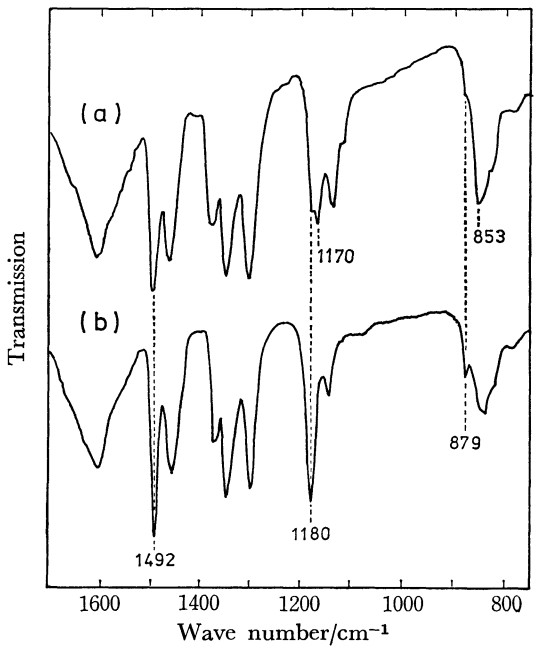


Fig. 2. IR spectra of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4 \cdot 2H_2O$ prepared (a) from ^{18}O-labeled $\mu(NH_2,O_2)$ complex and (b) from normal complex.

Nakamoto *et al.*[11] examined a similar nitro-bridged compound $[(NO_2,OH,OH)\{Co(NH_3)_3\}_2]Cl_3$ and made the same sort of assignment.

The X-ray structural study of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4 \cdot 4H_2O$ by Thewalt and Marsh[12] and that of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4 \cdot 2H_2O$ by Huang *et al.*[8] both proved the correctness of the formula postulated by Gatehouse, and his assignment of the two IR bands also seems to be a sound one.

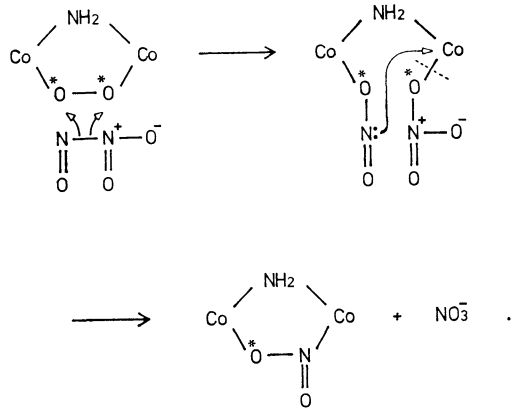
The IR spectra of two samples of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4 \cdot 2H_2O$, one derived from ^{18}O-substituted $[(NH_2,O_2)\{Co(NH_3)_4\}_2](NO_3)_4$ and the other from the same complex with natural isotopic abundunce are shown in Fig. 2, and relevant frequencies are listed in Table 1. As the band in the normal $\mu(NH_2, NO_2)$ complex at 1180 cm^{-1} which is assigned to the vibration mainly consisting of the stretching of NO bond in the Co–N–O–Co chain shifts to 1170 cm^{-1} in the ^{18}O-labeled complex, the O atom in the Co–N–O–Co chain is concluded to have come from the O_2 bridge of the starting complex. On the other hand, the O atom attached to the N atom from outside the chain must have come from the nitrite ion since the band at 1492 cm^{-1} mainly attributable to the stretching of NO bond that makes the branch does not show appreciable shift.

The above results bear some resemblance to the case of nitrosation of aquapentaammine complex, and seems to be equally explained by assuming N_2O_3 as the

Table 1. IR frequencies of $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4 \cdot 2H_2O$ in cm^{-1}

	$\nu_{as}(NO_2)$	$\delta_s(NH_3)$		$\nu_s(NO_2)$		$\delta(NO_2)$	$\rho_r(NH_3)$
^{18}O-enriched	1493 s	1350 m	1304 m	1170 s	1138 w	853 m	843 sh
				1180 sh		879 sh	
Normal oxygen	1492 s	1351 m	1305 m	1180 s	1146 w	879 w	843 m

reacting species as[13]



The new situation here is that the reaction seems to occur more homolytically, and that the remaining nitrite group is oxidized to a nitrate ion.

Although the $\mu(NH_2,OH)$ complex which is formed by reduction of $\mu(NH_2,O_2)$ complex is also known to react with the nitrite to form the $\mu(NH_2,NO_2)$ complex, such a reaction is reported to be very slow[14] and bridge conversion $\mu O_2 \rightarrow \mu NO_2$ through this path may be excluded.

The IR spectra of the $[(NH_2,NO_2)\{Co(en)_2\}_2]Br_4 \cdot 5H_2O$ is somewhat more complicated, but the positions and intensities of peaks assignable to NO_2 stretching vibration (1492 and 1151 cm^{-1}) are very similar to those of the corresponding ammine complex and this IR feature again is explicable only on the assumption of a nitro bridge as shown by Gatehouse and by Nakamoto *et al.* for ammine complexes. One of the reasons which led Garbett and Gillard[15] to assume a *nitrito* bridge instead of a *nitro* bridge was the high resistivity to acids, but our ^{18}O-labeled μ-amido-μ-nitro-octaammine complex also showed high stability, retaining ^{18}O in the Co–N–O–Co chain even after two cycles of recrystallization from hydrochloric acid. The other reason on which they based their conclusion was the formation of hydroxo complex ions on base hydrolysis, but nitro complexes also are known to form hydroxo complexes on base hydrolysis.

Thus the general similarity of the behavior of the ammine and the corresponding ethylenediamine complex seems to be present also in the present case of the reaction of the $\mu(NH_2,O_2)$ complex to form the $\mu(NH_2, NO_2)$ complex.

The IR absorption band due to the bending mode of the coordinated nitro group and that due to the rocking mode of ammonia ligand appears in the region of 900—750 cm^{-1}, and when both are present it is difficult to discriminate them. On the basis of ^{18}O isotope shift, the absorption at 879 cm^{-1} could be assigned to $\delta(NO_2)$ for $[(NH_2,NO_2)\{Co(NH_3)_4\}_2]Cl_4 \cdot 2H_2O$.

Reaction in Neutral or Basic Solutions. Treatment of $[(NH_2,O_2)\{Co(NH_3)_4\}_2]X_3$ with an aqueous solution of ammonium nitrite followed by oxidation with ammonium persulfate gave green powder of composition, $Co_2O_2NH_2(NH_3)_4(NO_2)_4$ (I). The ammonium nitrite was replaceable by an equimolar mixture of sodium nitrite and ammonium salt, but not by sodium nitrite alone, in which case the mixture turned red showing decomposition.

The IR spectrum of the green product (Table 2) indicated the existence of nitro ligands as well as ammine ligands and a peroxo bridge,[9] but no peaks corresponding to a nitro bridge nor those corresponding to a free nitrite ion were observable (*cf.* the preceding section). The compound is thus considered to be $[(NH_2,O_2)\{Co(NH_3)_2(NO_2)_2\}_2]$ or $[(NH_2,O_2)\{CoNH_3(NO_2)_3\}\{Co(NH_3)_3NO_2\}]$, and is the first example of non-electrolytic μ-hyperoxo dicobalt complex.

Table 2. IR absorption frequencies of $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$ (I) and $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]X$ (II-X) in cm^{-1}

I	II-$ClO_4 \cdot 0.5H_2O$	II-Cl	II-Br	Assignment
	3550 w			ν(OH)
3320, 3260, 3210 s	3310, 3240, 3170 s	3340, 3330, 3180 s	3290, 3240, 3160 s	ν(NH)
1630 m	1630 m	1630 m	1627 m	$\delta_{as}(NH_3)$
	1495 s	1495 s	1485 s	$\nu_{as}(\mu\text{-}NO_2)$
1410 s	1410 s	1410 s	1409 s	$\nu_{as}(NO_2)$
1328 s	1335 s	1340 s	1334 s	$\nu_s(NO_2)$
1275 s	1305 s	1317 s	1308 s	$\delta_s(NH_3)$
		1280 m		
	1180 m	1190 s	1170 s	$\nu_s(\mu\text{-}NO_2)$
1078 w		1078 m	1095 w	$\nu(\mu\text{-}O_2)$
	1089 s			$\nu(ClO_4)$
		996 w	1013 vw	
	853 w	857 w	849 w	$\delta(\mu\text{-}NO_2)$
822 m	820 s	825 s	822 m	
		807 w		$\rho_r(NH_3)$
783 vw	780 w	773, 759 w	788 w	$\delta(NO_2)$

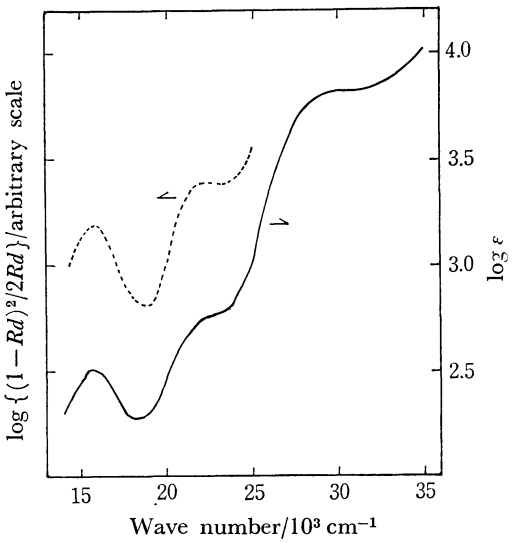
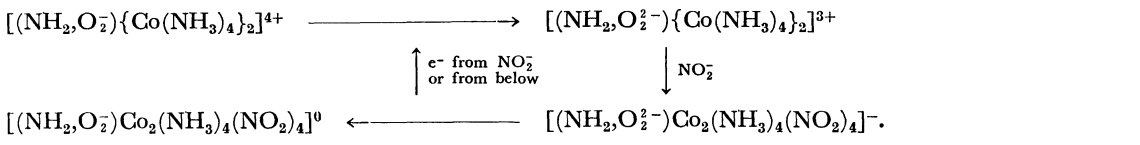


Fig. 3. Absorption spectrum of $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]ClO_4$ (in 0.5 M acetic acid, ——) and diffuse reflectance spectrum of $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$ (in K_2SO_4, ----).

The presence of the amido bridge was inferred from the consideration of the composition, balance of charge, and the high stability of $\mu(NH_2,O_2)$ dicobalt moiety usually observed. The possibility of the formula $[(NH_2,O_2)\{Co(NO_2)_4\}\{Co(NH_3)_4\}]$ seems to be excluded from the consideration of the reaction with perchloric acid (*cf.* next section).

The electronic spectrum obtained from diffuse reflectance measurement (Fig. 3) showed peaks of comparable intensities at $15.8\times10^3\,cm^{-1}$ ($d\pi Co^{3+}$-$\pi^*(\mu O_2^-)$) and at $22.3\times10^3\,cm^{-1}$ ("$^1A_{1g}$-$^1T_{2g}$").[16] Such intensity relation is usually encountered when the ammine complex has a second bridge such as NH_2 in addition to the hyperoxo bridge; in single-bridged μ-hyperoxo dicobalt ammine complexes the band at *ca.* $15\times10^3\,cm^{-1}$ is distinctly more intense than that at *ca.* $20\times10^3\,cm^{-1}$.

Compound I can also be obtained in a somewhat lower yield by the treatment of μ-hyperoxo complexes such as $[(NH_2,O_2)\{Co(NH_3)_4\}_2]X_4$ or $[(NH_2,OH,O_2)\{Co(NH_3)_3\}_2]X_3$ with ammonium nitrite solution. In this case oxidizing agent is unnecessary: Probably the starting μ-hyperoxo complex itself acts as an oxidizing agent as represented by the following scheme;



That only the terminal ammine ligands are replaced by nitro ligand and the O_2 bridge remains unattacked in the reaction of $[(NH_2,O_2)\{Co(NH_3)_4\}_2]X_3$ with the nitrite in neutral solution is in the same line as the similar reaction of $[O_2\{CoNH_3(en)_2\}_2]X_4$ which gave $[O_2\{CoNO_2(en)_2\}_2]X_2$.[2] It indicates that the bridge conversion, $\mu O_2\rightarrow\mu NO_2$ does not proceed through the reaction of the peroxo bridge with the nitrite ion but with some other chemical species present only in acidic solutions of nitrites, such as N_2O_3 as suggested in the preceding section.

Reaction of $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$ with Perchloric Acid. It has not been successful to find a proper solvent of I which dissolves it without decomposition. Sixty-percent perchloric acid dissolves it with a loss of one nitrite group, the species in solution being $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]^+$ (II), which can be isolated as the perchlorate by treatment with ether.

The aqueous solution of II reacts with sodium nitrite to reproduce I with a capture of one nitrite group. These reactions are very peculiar and seem to deserve closer studies. The structure of II was inferred from the chemical analysis and IR spectra (Table 2) which showed peaks assignable to a hyperoxo bridge, a nitro bridge, terminal nitro ligands, and ammine ligands. The amido bridge is considered to be present because it is usually very resistant to acids, and also because II reproduces I on treatment with sodium nitrite. The formation of nitro bridge in 60% perchloric acid in the reaction I→II again proves the stability of the nitro bridge in acids.

The absorption spectrum of II-ClO_4 solution (Fig. 3) showed peaks at $15.8\times10^3\,cm^{-1}$ ($\varepsilon=320$) ($d\pi Co^{3+}$-$\pi^*(\mu O_2^-)$), $22.8\times10^3\,cm^{-1}$ ("$^1A_{1g}$-$^1T_{2g}$"), and $29.8\times10^3\,cm^{-1}$ (specific band of nitro ligand).

Magnetic Properties. The magnetic susceptibility measurements of I, II-$ClO_4\cdot0.5H_2O$, II-Cl, and II-Br proved the existence of one unpaired electron in each complex (Table 3).

The ESR spectrum of I in powder gave $g=2.035$, and that of II-ClO_4 in solution exhibited a symmetrical pattern at $g=2.027$ with well-resolved fifteen hyperfine lines ($A_{Co}=11.8$) such as is observed with many μ-amido-μ-hyperoxo dicobalt ammine complexes.[17]

Table 3. Magnetic susceptibilities of $[(NH_2,O_2)Co_2(NH_3)_4(NO_2)_4]$ (I) and $[(NH_2,NO_2,O_2)Co_2(NH_3)_4(NO_2)_2]X$ (II-X)

Complex	μ_{eff}[a]/B. M.
I	1.60 (24.5 °C)
II-Cl	1.88 (22.6 °C)
II-Br	1.83 (24.9 °C)
II-$ClO_4\cdot0.5H_2O$	1.91 (24.5 °C)

a) Corrected for diamagnetic susceptibilities of terminal ligand, anion, and crystal water.

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References

1) M. Green and A. G. Sykes, *J. Chem. Soc., A*, **1970**, 3209.
2) T. Shibahara and M. Mori, *Bull. Chem. Soc. Jpn.*, **45**, 1433 (1972).
3) A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910).
4) J. D. Edwards, C.-H. Yang, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1974**, 1561.
5) H. A. Horan and H. J. Eppig, *J. Am. Chem. Soc.*, **71**, 581 (1949).
6) M. Dittrich and H. Bollenbach, *Ber. Deut. Chem. Ges.*, **38**, 751 (1905).
7) M. Mori, J. A. Weil, and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).
8) C. Y. Huang, J. A. Weil, and B. E. Robertson, *Acta Crystallogr., Sect. B*, **31**, 914 (1975).
9) T. Shibahara and M. Mori, *Bull. Chem. Soc. Jpn.*, **51**, 1374 (1978).
10) B. M. Gatehouse, *J. Inorg. Nucl. Chem.*, **8**, 79 (1958).
11) K. Nakamoto, J. Fujita, and H. Murata, *J. Am.*

Chem. Soc., **80**, 4817 (1958).
12) U. Thewalt and R. E. Marsh, *Inorg. Chem.*, **9**, 1604 (1970).
13) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, **76**, 5920 (1954); R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, **78**, 4886 (1956).
14) A. G. Sykes and R. D. Mast, *J. Chem. Soc., A*, **1967**, 784.
15) K. Garbett and R. D. Gillard, *J. Chem. Soc., A*, **1968**, 1725.
16) V. M. Miskowski, J. L. Robbins, I. M. Treitel, and H. B. Gray, *Inorg. Chem.*, **14**, 2318 (1975).
17) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).