BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1433—1438 (1972)

The Reaction and Reaction Products of μ-O_2-Dicobalt Ammine Complexes with Nitrites, Thiocyanates, *etc.*[1]

Takashi SHIBAHARA and Masayasu MORI
Faculty of Science, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka

(Received December 14, 1971)

In a neutral solution $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ was found to react with NO_2^- and SCN^- to give $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ and $[SCN(en)_2CoO_2Co(en)_2NCS]^{2+}$ respectively, without causing any cleavage of the O_2-bridge, while in an acid solution it was found to be oxidized by NO_2^- to a μ-superoxo (O_2^-) complex ion, $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{5+}$. The latter is not affected by NO_2^-, in contrast with $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$, in which the O_2^--bridge is replaced by an NO_2^--bridge. The $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ formed as described reacts with CN^- to give $[Co_2(CN)_6(en)_2O_2]^{2-}$. The EPR spectra of some new μ-superoxo complexes which were synthesized by oxidizing some of the above μ-peroxo complexes were measured and compared with those of similar complexes. Infrared and electronic spectra were also taken.

The reactions of binuclear complexes of cobalt, in which two cobalt atoms are connected by both NH_2 and O_2 ligands, have been studied by many investigators, and various specific features have been found, as is shown by the following examples:

$$[(NH_3)_4Co\genfrac{}{}{0pt}{}{NH_2}{O_2}Co(NH_3)_4]^{4+} \xrightarrow[H^+]{NO_2^-}$$

μ-superoxo, green

$$[(NH_3)_4Co\genfrac{}{}{0pt}{}{NH_2}{NO_2}Co(NH_3)_4]^{4+} \qquad (1)\,[2]$$

orange

$$[(NH_3)_4Co\genfrac{}{}{0pt}{}{NH_2}{O_2}Co(NH_3)_4]^{4+} \xrightarrow[H^+]{SO_3^{2-}}$$

μ-superoxo, green

$$[(NH_3)_4Co\genfrac{}{}{0pt}{}{NH_2}{SO_4}Co(NH_3)_4]^{3+} \qquad (2)\,[3]$$

reddish violet

The reactions of the $[(NH_3)_5CoO_2Co(NH_3)_5]^{n+}$ complexes ($n=4$, 5), containing an O_2 single bridge, were also studied; in this case, the cleavage of the O_2-bridge and the formation of a mononuclear cobalt(III) ammine complex and/or a cobalt(II) ion is the usual mode of reaction:

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{5+} \xrightarrow[H^+]{NO_2^-}$$

μ-superoxo, green

$$[CoOH_2(NH_3)_5]^{3+} + Co^{2+} \qquad (3)\,[4]$$

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{4+} \xrightarrow[H^+]{}$$

μ-peroxo, brown

$$2Co^{2+} + O_2 + 10NH_3 \qquad (4)\,[5]$$

However, the last two examples do not seem to depend solely on the nature of the O_2 bridge, since the starting material itself is comparatively unstable. In this respect, the reaction of the more stable single-O_2-bridged

---

[1] Presented at the 21st Conference on Coordination Chemistry of the Chemical Society of Japan, Nagoya, October (1971), Proceedings, p. 115.

[2] A. Werner, F. Salzer, and M. Pieper, *Ann.*, **375**, 54 (1910).

[3] A. G. Sykes and R. D. Mast, *J. Chem. Soc., A*, **1967**, 784.

[4] A. G. Sykes, *Trans. Faraday Soc.*, **59**, 1325 (1963).

[5] A. Werner and A. Mylius, *Z. Anorg. Chem.*, **16**, 245 (1898).

complex, $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{n+}$, was thought to reflect the nature of the O_2 bridge more clearly. Therefore, we started to study the reaction of this complex with nitrites, thiocyanates, sulfites, etc. As a result, several new compounds with a peroxo or a superoxo bridge were obtained; they were examined by various spectroscopic techniques, such as UV, IR, and EPR.

Experimental

Reaction and Preparation. 1. *μ-Peroxobis[amminebis(ethylenediamine)cobalt(III)] Triperchlorate Nitrate Dihydrate*: This compound was prepared by the method of Duffy *et al.*[6] Though they described the compound as a tetraperchlorate dihydrate, a definite amount of the nitrate ion has been detected in the sample even after multiple recrystallizations with sodium perchlorate. The nitrate ion was determined as follows: the anions were separated by passing a solution through cation-exchange resin in the Na-form (DIAION SK#1), the nitrate ion was reduced to ammonia using Devarda's alloy, and the ammonia which came over by distillation was titrated.

Found: Co, 14.18; C, 11.73; H, 4.89; N(total), 18.79; NO_3^-, 7.69%. Calcd for $[NH_3(en)_2CoO_2Co(en)_2NH_3](ClO_4)_3\cdot NO_3\cdot 2H_2O$: Co, 14.36; C, 11.71; H, 5.16; N(total), 18.78; NO_3^-, 7.56%.

2. *Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ with NO_2^- in an Acid Solution*: Brown μ-peroxobis[amminebis(ethylenediamine)cobalt(III)] triperchlorate nitrate dihydrate was added to an acid solution (0.05N HCl) of sodium nitrite. The solution immediately turned green. The electronic spectrum of the green solution was identical with that of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{5+}$, which had been prepared by oxidizing the same starting 4+ ion with chlorine gas.

3. *Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ with NO_2^- in a Neutral Solution at Room Temperature*: 3·1. *Preparation of μ-Peroxobis[nitrobis(ethylenediamine)cobalt(III)] Dinitrate Tetrahydrate*: Thirty-three grams of μ-peroxobis[amminebis(ethylenediamine)cobalt(III)] triperchlorate nitrate dihydrate (2 above) was added to 500 m*l* of water containing 27 g of potassium nitrite. After this solution had been cooled in an ice bath, it was filtered and the precipitate (mainly potassium perchlorate) was discarded. The brown solution was evaporated almost to dryness using a rotary evaporator, while the temperature was kept at approximately 30°C. The product was washed successively with 50% ethanol, 95% ethanol, and ethyl ether. Yield, 20 g. This product will be named A. On the dissolution of 5 g of A in 80 m*l* of water at 40°C, followed by filtration and cooling, black crystals were precipitated. These crystals were washed with 95% ethanol and ethyl ether. Yield, 2 g.

Found: C, 14.21; H, 5.87; N, 24.95%. Calcd for $[NO_2(en)_2CoO_2Co(en)_2NO_2](NO_3)_2\cdot 4H_2O$: C, 14.19; H, 5.94; N, 24.80%.

3·2. *Preparation of μ-Peroxobis[nitrobis(ethylenediamine)cobalt(III)] Dithionate Pentahydrate*: Ten grams of sodium dithionate dihydrate was added to 10 g of A in 1 *l* of water. The brown precipitate that deposited was collected by filtration and washed successively with cold water, 95% ethanol, and ethyl ether, and then air-dried. Yield, 9.4 g. The sample (1 g) was recrystallized by dissolving it in 2 *l* of water at 30°C and by then adding 10 g of sodium dithionate dihydrate to the cooled, filtered solution. The brown crystalline material that was thus deposited was collected, washed, and dried as above. Yield, 0.3 g.

Found: Co, 16.38; C, 13.71; H, 5.81; N, 19.45%. Calcd for $[NO_2(en)_2CoO_2Co(en)_2NO_2]S_2O_6\cdot 5H_2O$: Co, 16.09; C, 13.12; H, 5.78; N, 19.15%.

3·3. *Preparation of μ-Peroxobis[nitrobis(ethylenediamine)cobalt(III)] Dichloride Tetrahydrate*: The A product (1 g; *cf.* 3·1), dissolved in 80 m*l* of water, was added to the top of the anion-exchange resin, Cl-form (DIAION SA#100), which was then washed with water. The effluent was evaporated to dryness with a rotary evaporator. The brown product was washed with 95% ethanol and ethyl ether. Yield, 0.1 g. It is very soluble in water.

Found: C, 15.91; H, 6.74; N, 22.64%. Calcd for $[NO_2(en)_2CoO_2Co(en)_2NO_2]Cl_2\cdot 4H_2O$: C, 15.37; H, 6.45; N, 22.56%.

4. *The Oxidation Product of the μ-Peroxobis[nitrobis(ethylenediamine)cobalt(III)] Complex*: 4·1. *μ-Superoxobis[nitrobis(ethylenediamine)cobalt(III)] Triperchlorate Dihydrate*: Three grams of brown μ-peroxobis[nitrobis(ethylenediamine)cobalt(III)] dithionate pentahydrate (*cf.* 3·2) was stirred into 200 m*l* of a 0.2N hydrochloric acid solution, while a slow stream of chlorine gas was bubbled through the solution. As portions of the solid were added, the solution turned green. After about 5 min, the unreacted solid was filtered off and twenty grams of sodium perchlorate monohydrate was added to the ice-cooled filtrate. The green precipitate that deposited was collected by filtration and washed successively with water, 95% ethanol, and ethyl ether. Yield, 1.3 g. To recrystallize, as much of the sample as possible (1 g) was dissolved in 400 m*l* of water at 25°C, and then 5 g of sodium perchlorate monohydrate was added to the cooled filtered solution. The green crystalline material that was thus deposited was collected and washed as above. Yield, 0.8 g.

Found: Co, 14.25; C, 11.87; H, 4.42; N, 17.49%. Calcd for $[NO_2(en)_2CoO_2Co(en)_2NO_2](ClO_4)_3\cdot 2H_2O$: Co, 14.42; C, 11.78; H, 4.44; N, 17.17%.

4·2. *μ-Superoxobis[nitrobis(ethylenediamine)cobalt(III)] Trithiocyanate Dihydrate*: This complex was prepared similarly, using sodium thiocyanate instead of sodium perchlorate.

Found: Co, 17.04; C, 19.54; H, 5.25; N, 27.45; S, 14.66%. Calcd for $[NO_2(en)_2CoO_2Co(en)_2NO_2](SCN)_3\cdot 2H_2O$: Co, 17.03; C, 19.10; H, 5.24; N, 26.30; S, 13.88%.

4–3. *μ-Superoxobis[nitrobis(ethylenediamine)cobalt(III)] Sesquisulfate Tetrahydrate*: Five-tenths of a gram of the triperchlorate dihydrate (4·1 above) was dissolved in 60 m*l* of 6N sulfuric acid. Five hundred milliliters of ethanol was then stirred into the filtered solution. The green precipitate that was thus deposited was collected and washed successively with 95% ethanol and ethyl ether. Yield, 0.4 g. The sample (0.4 g) was recrystallized by dissolving it in 20 m*l* of a 0.5N sulfuric acid solution at room temperature and by then adding 50 m*l* of 95% ethanol to the filtered cooled solution. Yield, 0.2 g.

Found: Co, 16.58; C, 13.73; H, 5.29; N, 19.97%. Calcd for $[NO_2(en)_2CoO_2Co(en)_2NO_2]_2(SO_4)_3\cdot 8H_2O$: Co, 16.87; C, 13.75; H, 5.77; N, 20.05%.

5. *Reaction of $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ with NO_2^- in a Neutral Solution at a High Temperature. The formation of* trans-*$[Co(NO_2)_2(en)_2]NO_3$*: Twenty milliliters of water containing 0.7 g of μ-peroxobis[nitrobis(ethylenediamine)cobalt(III)] dinitrate tetrahydrate (*cf.* 3·1) and 1 g of sodium nitrite were warmed on a water bath at about 80°C for 2 hr. During the process, water was sometimes supplied. While hot, the solution was filtered, and a little 14N nitric acid was added to the filtered, cooled solution. The yellow crystals that

---

6) D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).

were thus deposited were filtered and washed with 95% ethanol and ethyl ether. Yield, 0.3 g.

Found: Co, 17.01; C, 14.38; H, 5.46; N, 29.13%. Calcd for $[Co(NO_2)_2(en)_2]NO_3$: Co, 17.68; C, 14.42; H, 4.84; N, 29.41%. The complex was concluded to be *trans* isomer by a comparison of its electronic spectrum with that of the known sample.

6. Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ *with* SCN^-: Sixteen and four-tenths grams of μ-peroxobis[amminebis(ethylenediamine)cobalt(III)] triperchlorate nitrate dihydrate was added to a stirred solution of 15.6 g of potassium thiocyanate in 250 m*l* of water. The crude product (14 g) was obtained by the vacuum evaporation of this mixture, as in the case of 3·1. This product was named B. Five grams of B was dissolved in 250 m*l* of water at 40°C, and 50 g of sodium perchlorate monohydrate was added to the cooled filtrate. The brown precipitate that was thus deposited was collected by filtration and washed with 95% ethanol and ethyl ether. Yield, 3.6 g. The sample (3.6 g) was recrystallized by dissolving it in 250 m*l* of water at 40°C and by adding $NaClO_4 \cdot H_2O$ (50 g) to the cooled, filtered solution. The brown crystalline material that was thus deposited was collected and washed as above. Yield, 1.7 g.

Found: Co, 15.18; C, 16.09; H, 5.21; N, 18.36; S, 7.98%. Calcd for $[SCN(en)_2CoO_2Co(en)_2NCS](ClO_4)_2 \cdot 4H_2O$: Co, 15.16; C, 15.46; H, 5.18; N, 18.02; S, 8.25%.

7. Oxidation Product of $[SCN(en)_2CoO_2Co(en)_2NCS]^{2+}$: Ten milliliters of 14N nitric acid was added to 1 g of B (Exp. 6). The green solution obtained by this procedure was cooled in a refrigerator. The green crystals that deposited were washed with a little cold water, methanol, and ethyl ether. Yield, 0.1 g.

Found: C, 11.96; H, 5.21; N, 27.17%. Calcd for $[NH_3(en)_2CoO_2Co(en)_2NH_3](NO_3)_5 \cdot 2H_2O$: C, 12,46; H, 5.46; N, 27.13%.

8. Reaction of $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ *with* CN^-*. Preparation of* $K_2[Co_2(CN)_6(en)_2O_2] \cdot 5H_2O$: Two hundred milliliters of a solution containing 14 g of μ-peroxobis[nitrobis(ethylenediamine)cobalt(III)] dinitrate tetrahydrate and 26 g of potassium cyanide were warmed in a water bath at 35°C for 5 hr. Six hundred milliliters of methanol was added to the cooled, filtered solution. The precipitate that was thus deposited was filtered and washed with ethanol and ethyl ether. Yield, 7 g. The sample (7 g) was recrystallized by dissolution in 15 m*l* of water and filtration; this was followed by the successive addition of 20 m*l* of water and 200 m*l* of methanol. The precipitate that was thus deposited was again filtered and washed as above. Yield, 4.6 g. Recrystallization was repeated by dissolving this recrystallized sample (4 g) in 10 m*l* of water at 40°C and by stirring 10 m*l* of methanol (50°C) into the filtered solution. This solution was cooled in a refrigerator. The fragile, crystalline, red-brown precipitate that was thus deposited was washed with 60% methanol, pure methanol, and ethyl ether. Yield, 0.35 g.

Found: Co, 19.71; C, 20.40; H, 4.77; N, 23.71; K, 13.60%. Calcd for $K_2[Co_2(CN)_6(en)_2O_2] \cdot 5H_2O$: Co, 19.83; C, 20.21; H, 4.41; N, 23.59; K, 13.16%.

9. Oxidation Product of $[Co_2(CN)_6(en)_2O_2]^{2-}$*. The Preparation of* $H[Co_2(CN)_6(en)_2O_2] \cdot 4H_2O$: Five tenths of a gram of red-brown $K_2[Co_2(CN)_6(en)_2O_2] \cdot 4H_2O$ was added to 5 m*l* of water while a stream of chlorine gas was bubbled in. The violet solution obtained by this procedure was added to the cation-exchange resin in the H-form (DIAION SK#1) which had been washed with water. The effluent was then stirred into acetone (150 m*l*). The violet precipitate was washed with acetone. Yield 0.3 g.

Found: Co 23.40; C 25.23; H 5.18; N 28.34; H^+ (neutralization titration) 0.200%. Calcd for $H[Co_2(CN)_6(en)_2O_2] \cdot 4H_2O$: Co 23.62; C, 24.08; H, 5.05; N, 28.10; H^+, 0.201%.

10. Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ *with* SO_3^{2-}: Sixteen and four-tenths grams of μ-peroxobis[amminebis(ethylenediamine)cobalt(III)] triperchlorate nitrate dihydrate was stirred into a solution of 25.2 g of potassium sulfite in 200 m*l* of water. A crude yellow product (25 g) was obtained by the vacuum evaporation of this mixture, as in the case of 3·1. The sample was recrystallized from a dilute sodium sulfite solution. The electronic spectrum was identical with that of *trans*-$[Co(SO_3)_2(en)_2]^-$, which was prepared from *trans*-$[CoCl_2(en)_2]^+$ by a known method.[7]

Apparatus. The visible and UV absorption measurements were carried out with a Hitachi EPS-3T spectrometer. IR spectra were recorded on a Jasco IR-E spectrometer, while the EPR spectra were recorded on a JEOL JES-3B spectrometer at room temperature. The pH measurements were carried out with a Hitachi-Horiba M-5 pH meter.

Results and Discussion

The reaction scheme elucidated in the present research is summarized in Chart 1. Some characteristic features will now be discussed in detail.

Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{n+}$ $(n=4, 5)$ *with* NO_2^-. As expected, $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{n+}$ is far more stable than $[(NH_3)_5CoO_2Co(NH_3)_5]^{n+}$; in fact, the Co-$O_2$-Co linkage in the former showed a remarkable stability to various reagents in a neutral solution. Thus, at room temperature, the μ-peroxo complex $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ in a neutral solution reacts with NO_2^- to give a new μ-peroxo complex $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$, without any cleavage of the O_2-bridge (Exp. 3). This is thought to be the first example in which the O_2-bridge remains intact in the reaction of the μ-O_2 complex with NO_2^- (Compare with the cases shown in Eqs. (1) and (3)). At about 80°C, $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ further reacts with NO_2^- to give *trans*-$[Co(NO_2)_2(en)_2]^+$ (Exp. 5), but it seems difficult to discuss the steric configuration of the starting material, since rearrangement may occur in the course of the reaction. Sasaki *et al.* reported that NH_3 in $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ is replaced comparatively easily, and that in water the complex is readily changed to $[(en)_2Co(\mu\text{-}OH, O_2)Co(en)_2]^{3+}$.[8] It thus seemed worthwhile to test if $[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2]^{3+}$ is the intermediate product in our reaction on the way from $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ to $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$. This possibility was eliminated, however, since $[(en)_2Co(\mu\text{-}OH,O_2)Co(en)_2]^{3+}$, which had been prepared by the method of Foong *et al.*,[9] did not react with NO_2^- to give $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$. However, it is still possible that an aquo-substituted complex, $[H_2O(en)_2CoO_2Co(en)_2OH_2]^{4+}$, is formed as an intermediate product.

---

[7] M. E. Baldwin, *J. Chem. Soc.*, **1961**, 3123.

[8] Y. Sasaki, J. Fujita, and K. Saito, the 20th Conference on Coordination Chemistry of the Chemical Society of Japan, Tokyo, November (1970), Proceedings, p. 17; This Bulletin, to be published.

[9] S. W. Foong, J. E. Miller, and F. D. Oliver, *J. Chem. Soc.*, *A*, **1969**, 2848.

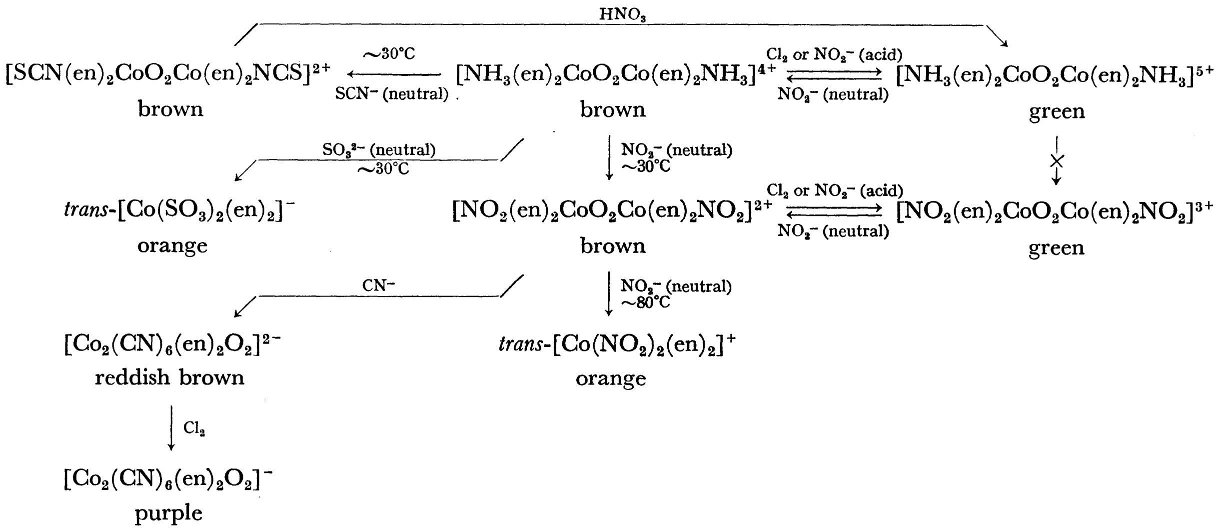

Chart 1. Reaction scheme of μ-O_2 dicobalt complexes

In an acid solution, the μ-peroxo complex $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ is easily oxidized by NO_2^- to the corresponding μ-superoxo complex $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{5+}$ (Exp. 2), and the latter does not further react with NO_2^- to give $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{3+}$. In other words, the NH_3 in the μ-superoxo complex $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{5+}$ is not replaced by NO_2^-, in contrast with the NH_3 in the corresponding μ-peroxo (4+) complex (see above). Nor is the O_2-bridge in $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{5+}$ replaced by NO_2^-. This is in contrast with the reaction of the double-bridged complex with NO_2^- cited in Eq. (1). Thus, the additional NH_2-bridge seems to play an important role in the transformation of the O_2-bridge to the NO_2-bridge. Davies *et al.* explained the easier reduction of $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$ by I^- by supposing that the presence of the NH_2-bridge places more strain on the O_2-bridge and places it more outside of the complex.[10] This idea may also explain the present situation.

The nitro-substituted μ-superoxo complex $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{3+}$ may be obtained by the oxidation of the corresponding μ-peroxo (2+) ion described above by Cl_2 or even by NO_2^- (Exp. 4).

Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ *with* SCN^-. In a neutral solution, $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ reacts with SCN^- to give $[SCN(en)_2CoO_2Co(en)_2NCS]^{2+}$ (Exp. 6) similarly to the case of $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$. The preparation of the corresponding μ-superoxo complex has not yet been successful, for the reagents that oxidize the peroxo bridge to superoxo bridge also oxidize SCN^- to NH_3 (Exp. 7). The latter oxidation reaction is known to occur in mononuclear thiocyanato cobalt complexes as well. The above reaction shows that SCN^- coordinates to Co through the nitrogen atom.

Reaction of $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ *with* CN^-. $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ has been found to react with CN^- to give another new μ-peroxo complex $[Co_2(CN)_6(en)_2O_2]^{2-}$ (Exp. 8), which is then oxidized by chlorine gas to the corresponding μ-superoxo (1−) complex ion. The titration curve (Fig. 1) of $H[Co_2(CN)_6(en)_2O_2]\cdot 4H_2O$ (Exp. 9) showed it to be a strong acid. Analysis by the decomposition of $K_2[Co_2(CN)_6(en)_2O_2]\cdot 5H_2O$ with 12N hydrochloric acid, followed by the use of cation-exchange resin, showed that $[(CN)_5CoO_2Co(en)_2CN]^{2-}$ was the major component, accom-

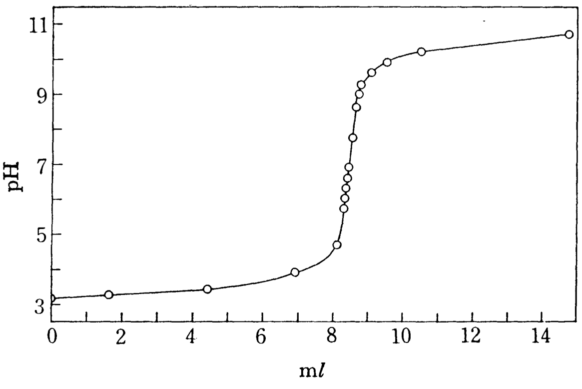

Fig. 1. Titration curve of $H[CO_2(CN)_6(en)_2O_2]\cdot 4H_2O$ solution (0.08890 mmol of complex in 30 ml of water) with 0.1043 N NaOH

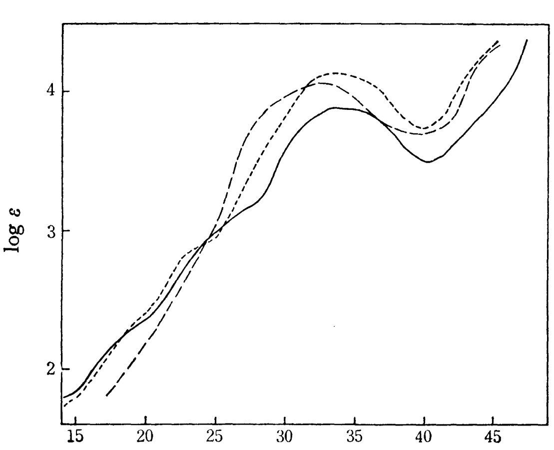

Fig. 2. Electronic spectra of several μ-peroxo dicobalt complexes in water.

——: $[NH_3(en)_2CoO_2Co(en)_2NH_3](ClO_4)_3\cdot NO_3\cdot 2H_2O$
----: $[NO_2(en)_2CoO_2Co(en)_2NO_2]S_2O_6\cdot 5H_2O$
------: $[SCN(en)_2CoO_2Co(en)_2NCS](ClO_4)_2\cdot 4H_2O$

---

[10] R. Davies and A. G. Sykes, *J. Chem. Soc., A*, **1968**, 2237.

TABLE 1. EPR PARAMETERS OF SEVERAL μ-SUPEROXO Co(III) COMPLEXES AT ROOM TEMPERATURES

Complex	Form	g	A_{Co}(Oe)
$[NO_2(en)_2CoO_2Co(en)_2NO_2](SO_4)_{3/2}\cdot 4H_2O$	40% H_3PO_4	2.026	10.5
$H[Co_2(CN)_6(en)_2O_2]\cdot 4H_2O$	H_2O	2.021	9.00
$[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$	50% H_2SO_4	2.025	11.4[11]
$[NH_3(en)_2CoO_2Co(en)_2NH_3](ClO_4)_4\cdot NO_3\cdot 3H_2O$	H_2O (slightly acid)	2.028	11.0[6]
$K_5[(CN)_5CoO_2Co(CN)_5]\cdot H_2O$	50% H_2SO_4	2.020	8.50[11]

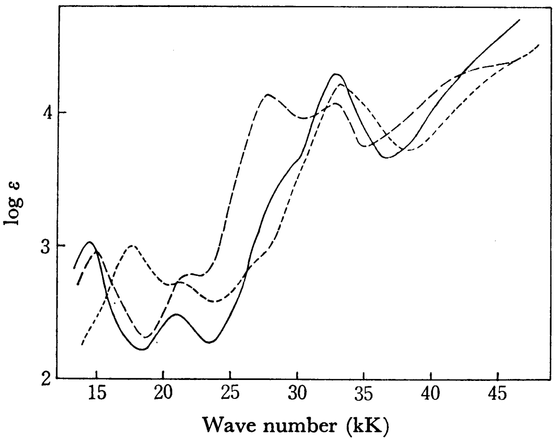

Fig. 3. Electronic spectra of several μ-superoxo dicobalt complexes in water
——: $[NH_3(en)_2CoO_2Co(en)_2NH_3](ClO_4)_4\cdot NO_3\cdot 3H_2O$ (in 0.3 N $HClO_4$)
----: $[NO_2(en)_2CoO_2Co(en)_2NO_2](ClO_4)_3\cdot 2H_2O$ (in 0.3 N $HClO_4$)
------: $H[Co_2(CN)_6(en)_2O_2]\cdot 4H_2O$ (in water)

panied by a small quantity of isomeric $[(CN)_3enCoO_2$-$Coen(CN)_3]^{2-}$ (*cf.* Ref. 11).

Reaction of $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ *with* SO_3^{2-}. In a neutral solution at room temperature, $[NH_3(en)_2$-$CoO_2Co(en)_2NH_3]^{4+}$ reacts with SO_3^{2-} to give *trans*-$[Co(SO_3)_2(en)_2]^-$ with a cleavage of the O_2-bridge; this is in contrast with the reaction of $[NH_3(en)_2CoO_2$-$Co(en)_2NH_3]^{4+}$ with NO_2^-. Further experiments are in progress.

Electronic, IR, and EPR Spectra. The electronic spectra of the μ-peroxo and μ-superoxo complexes, obtained mainly in the present research, are shown in Figs. 2 and 3 respectively. The spectra of the μ-peroxo complexes (Fig. 2) have similar broad absorption peaks at about 33 kK; they have no clear peaks in the visible region, and the complexes are generally brown. On the other hand, every spectrum of the μ-superoxo complexes (Fig. 3) has characteristic absorption peaks in the visible and ultraviolet regions. The one lying in the 14—18 kK range has a log ε value of about 3, and its position change appreciably with the ligands in the order of the spectrochemical series. The positions of the peaks appearing at about 21 and 33 kK are not much affected by the change in ligands. Some assignments of the absorption bands of μ-superoxo complexes have been offered by several investigators,[12–15] but none of these seems to be conclusive, and further works will be required to explain the spectra satisfactorily. The strong absorption at 28 kK in the spectrum of $[NO_2$-$(en)_2CoO_2Co(en)_2NO_2](ClO_4)_3\cdot 2H_2O$ (Fig. 3) is considered to be the specific absorption band due to NO_2^- ligands. The IR spectra in the NaCl region proved the existence of NO_2, SCN, and CN in related complexes.

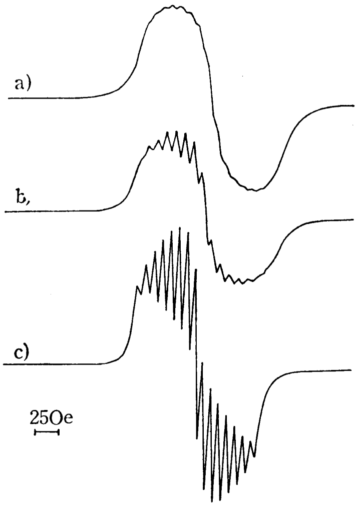

Fig. 4. EPR spectra of several μ-superoxo Co(III) complexes at room temperatures.
a): $[NO_2(en)_2CoO_2Co(en)_2NO_2](SO_4)_{312}\cdot 4H_2O$ in H_2O (slightly acid)
b): $[NO_2(en)_2CoO_2Co(en)_2NO_2](SO_4)_{312}\cdot 4H_2O$ in 40% H_3PO_4
c): $H[Co_2(CN)_6(en)_2O_2]\cdot 4H_3O$ in H_2O

The room-temperature EPR spectra are shown in Fig. 4 for the paramagnetic μ-superoxo complexes. The appearance of the hyperfine structure depends upon the experimental conditions, and, in the case of aqueous solutions, considerably concentrated solutions are required. Some of these results, together with those of other workers relevant to the following discussion, are collected in Table 1. It may be seen from the table that the change in ligands does not affect the Zeeman splitting factor, g, very sensitively, but that

---

[11] M. Mori, J. A. Weil, and J. K. Kinnaird, *J. Phys. Chem.*, **71**, 103 (1967).

[12] S. Yamada, Y. Shimura, and R. Tsuchida, This Bulletin, **26**, 72 (1953).

[13] M. Linhard and M. Weigel, *Z. Anorg. Chem.*, **308**, 254 (1961).

[14] J. Barrett, *Chem. Commun.*, **1968**, 874.

[15] Y. Sasaki, J. Fujita, and K. Saito, This Bulletin, **42**, 146 (1969).

it does affect the cobalt hyperfine coupling consant, A_{Co}. The low A_{Co} values in cyano- and nitro-substituted complexes suggest that there is less spin density on the ^{59}Co nuclei in these complexes.[11] This may be explained in terms of the lowering of the t_{2g} orbitals caused by π-bonding, and by the subsequent decrease of the hole density therein.

The authors wish to thank Mr. Y. Miura for the EPR measurements and Mr. J. Goda for the elemental analyses.