Accurate calculation should also consider the antishielding factor, which for oxygen-17 is not known; nevertheless, from the above calculation it is obvious that the contribution to the oxygen-17 quadrupolar relaxation through interaction with intermolecular electric field gradients, originating from the electrical charge of the metal ion, can be ignored.

The Plausibility of Proton Resonance Studies. It is now possible to determine the conditions under which the rate of exchange of the protons between the aquo complex and the bulk may be measured by proton magnetic resonance. The rate constants for the hydrolysis of the aquo complex of the ion can be estimated from the equilibrium constant of hydrolysis and the number of collisions between the hydrogen ion and the complex.

$$[M(H_2O)_6]^{3+} \underset{K_{-1}}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_5OH]^{2+} + H^+$$

Assuming that the rate of collisions is of the order of magnitude of 10^{10} sec^{-1} and the equilibrium constants of hydrolysis are[27] $K_A(Al) = 1.12 \times 10^{-5}$ *M* and $K_A(Ga) = 2.5 \times 10^{-3}$ *M*, we obtain for the rate constant for hydrolysis $k(Al) = 10^5$ sec^{-1} and $k(Ga) = 2.5 \times 10^7$ sec^{-1}, exceeding the rate of exchange of the water molecules by few orders of magnitude.

The chemical shift of the protons in a molar solution of cobaltous perchlorate at 20° is 380 Hz at 60 MHz[28] and decreases with decrease of temperature due to approach of the conditions of slow exchange, and thus it is not possible to observe the hydration sphere of the aluminum ion by proton magnetic resonance, using Co^{2+} to shift the bulk water proton signal. It might be possible to observe it at very low temperatures using a paramagnetic ion whose coordinated water molecules exchange sufficiently fast at these low temperatures so that the rate of exchange of the water coordinated to the diamagnetic ion is lower than the chemical shift of the bulk water. Some of the rare earth metal ions might serve this purpose. The proton molal chemical shift of aqueous solutions of Dy^{3+} ions is −390 Hz; the rate of exchange and the enthalpy and entropy of activation are $k_{25°} = 6.3 \times 10^7$ sec^{-1}, $\Delta H^{\ddagger} = 12$ kcal/mole, and $\Delta S^{\ddagger} = 18$ eu, respectively.[29]

The rate of exchange will equal the chemical shift between the solvation shell and the bulk water at a temperature of ∼−22 and ∼−69° for Al^{3+} and Ga^{3+}, respectively. The rate of hydrolysis would be 4×10^{-4} sec assuming 12 kcal/mole for the free energy of activation for the hydrolysis reaction.

This calculation shows that it should be possible to observe the proton magnetic resonance signal of the hydrations phere of Al^{3+}, but not of Ga^{3+} ions, and to study the rate of exchange of protons between the solvation sphere of Al^{3+} and the bulk at temperatures lower than −22° in the presence of Dy^{3+}.

Acknowledgment. This work was performed under the auspices of the U. S. Atomic Energy Commission at the University of California, Chemistry Department and Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, Calif. The authors wish to acknowledge the interest and help of the Lawrence Radiation Laboratory Computer Center and especially of M. Horowitz and E. Beals.

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(27) F. A. Cotton and G. W. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1966, p 437.

(28) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, 43, 3750 (1965).

(29) J. Reuben and D. Fiat, to be published.

The Formation of and Interrelation between Some μ-Peroxo Binuclear Cobalt Complexes. II[1a]

Masayasu Mori,[1b] John A. Weil, and Mibuo Ishiguro

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received March 29, 1967*

Abstract: By means of isotopic labeling, the peroxo bridge in $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ has been shown to originate from the gaseous oxygen used in the preparation. The bridging reaction adding an amido bridge to this ion has been investigated. At 35° in ammoniacal aqueous solution, especially in the presence of a small quantity of alkali hydroxide, transformation (*ca.* 30% in 90 min) to the dibridged complex ion, $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4]^{3+}$, occurs as proved by isolation of both the nitrate and the perchlorate as brown diamagnetic powders. Isomeric transformation of the dibridged ion in acidic solution, similar to that reported earlier for the analogous en complex, has been observed. Infrared absorption spectra of some dibridged dicobalt–ammine complexes have been studied. New or improved preparations for a number of dicobalt–peroxo–ammine complexes are included.

In the very early stages of the history of cobalt ammines, it was established that the initial oxygenation product of the cobalt(II) salt in aqueous ammonia is $[(NH_3)_5CoO_2Co(NH_3)_5]X_4$.[2,3] The structural constitution of the compound, however, remained unknown until the days of Werner. As is well-known,

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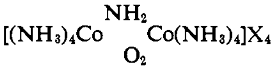
[1] (a) Based on work performed in part under the auspices of the U. S. Atomic Energy Commission; (b) Faculty of Science, Osaka City University, Osaka, Japan.

[2] (a) E. Fremy, *Ann. Chim. Phys.*, [3] 25, 257 (1852); *cf. Chem. Zentr.*, 161, 185 (1853). All the formulas given by Fremy in this literature can be transformed into the present system by doubling all the numbers of nitrogen and hydrogen atoms or else by halving all the numbers of oxygen, sulfur, and cobalt atoms. This is because the equivalence of atoms was not established correctly in his time. In spite of this, it seems remarkable that he at least gave the correct elemental constitution of the peroxo and other important cobalt ammines. (b) W. Gibbs, *Proc. Am. Acad. Arts Sci.*, 11, 38 (1876).

this diamagnetic complex can react further, by one-electron oxidation, and is converted to a paramagnetic form, $[(NH_3)_5CoO_2Co(NH_3)_5]X_5$, containing one odd electron equally distributed with respect to the two cobalt nuclei.[4-6]

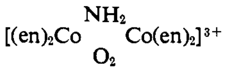
An analogous paramagnetic complex



$$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]X_4$$

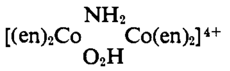
is known in which there is an amido (NH_2) bridge in addition to the peroxo bridge. It was first isolated by Werner, *et al.*,[7] from the mixture known as Vortmann's sulfate[3] and is an important starting material for many binuclear cobalt ammines. The preparation of Vortmann's sulfate was developed essentially from experience, and although the method has since been improved by several authors,[7,8a,9a] it has still been a mystery how such a dibridged binuclear complex ion is formed. The study reported in this paper was aimed mainly toward resolving this question.

In paper I of this series,[10] dealing with the analogous ethylenediamine complexes, the relation between two diamagnetic forms (A′, B′), two acid diamagnetic forms



$$[(en)_2Co\overset{NH_2}{\underset{O_2}{\quad}}Co(en)_2]^{3+}$$

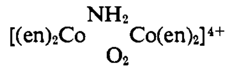
A′, B′



$$[(en)_2Co\overset{NH_2}{\underset{O_2H}{\quad}}Co(en)_2]^{4+}$$

AH′, BH′

(AH′, BH′), and a paramagnetic form (C′) has been discussed (see ref 10 for notation).



$$[(en)_2Co\overset{NH_2}{\underset{O_2}{\quad}}Co(en)_2]^{4+}$$

C′

No comparable diamagnetic and acid diamagnetic series of ammine (NH_3) complexes have been previously reported. Isolation of such series and elucidation of the interrelation between their members constitute another objective of the present study.

Results and Discussion

I. Formation of the Monobridged Peroxo–Dicobalt–Ammine Complexes. The formation of peroxo single-bridged binuclear cobalt ammines can be represented by the simple chemical equation

$$2[Co^{II}(NH_3)_5X]^{2+n} + O_2 \longrightarrow [(NH_3)_5CoO_2Co(NH_3)_5]^{4+} + 2X^n \tag{1}$$

where, because of the complex equilibria[11] and rapid interchange[12] between the various cobaltous aquoammines, it has not yet been definitely established whether X^n is H_2O or NH_3 ($n = 0$), OH^- ($n = -1$), or some other entity. However, some evidence has been presented that $[Co^{II}(NH_3)_5H_2O]^{2+}$ may be the actual precursor ion.[12] Reaction 1 appears to be reversible, although amido-bridge formation (discussed later) and also formation of mononuclear cobaltic ammine complexes interfere with this tendency.[12-14]

To clarify partially the above processes, it was deemed desirable to demonstrate that the bridging oxygen really does originate entirely from the gaseous oxygen and not from the water molecules. A scaled-down version of preparation 1 (Experimental Section) was used to synthesize the 4+ complex nitrate by passing ordinary dried oxygen gas through a solution of ordinary cobalt(II) nitrate (0.2 g, previously dehydrated under vacuum at 25°) in isotopically labeled aqueous ammonia (1.5 ml) prepared by bubbling ordinary dried ammonia through water containing 1.17% $H_2{}^{18}O$. The solid 4+ nitrate from this preparation was decomposed under vacuum at 100°, releasing its bridging oxygen quantitatively (plus *ca.* $4NH_3$ per molecule) with no evolution of nitrogen oxides or nitrogen gas. The oxygen gas was found to contain $0.20 \pm 0.01\%$ ^{18}O, as measured by mass spectrometry; this is exactly the natural abundance of this isotope. A similar experiment using the tetrabromide gave analogous results.

The above results, as well as the very high efficiency of the formation of the peroxo-bridged complex[2,3,12-14] (~90% even in preparative experiments, *cf.* also preparation 1, Experimental Section), seem to indicate that reaction 1 is a rather straightforward process involving a direct attack of the cobaltous complex by oxygen, although the process is likely to consist of two successive steps (1a and 1b). That only Co(II)

$$[Co^{II}(NH_3)_5X]^{2+n} + O_2 \longrightarrow [Co(NH_3)_5O_2\cdot]^{2+} + X^n \tag{1a}$$

$$[Co(NH_3)_5O_2\cdot]^{2+} + [Co^{II}(NH_3)_5X]^{2+n} \longrightarrow [(NH_3)_5Co^{III}O_2Co^{III}(NH_3)_5]^{4+} + X^n \tag{1b}$$

complex can participate in the reaction can be proved from the invariance of the optical spectra of ammoniacal aqueous solutions of aquopentaamminecobalt(III) nitrate and of hexaamminecobalt(III) nitrate before and after 1.5 hr of bubbling of oxygen. Similarly neither ozonized oxygen nor hydrogen peroxide was shown to produce any detectable amount of binuclear peroxo complexes from aquopentaamminecobalt(III) ion in aqueous ammonia.

Hydrogen peroxide does react with the *Co(II) salt* in aqueous ammonia to produce the μ-peroxo complex, but the yield is less than 50%. Moreover, excess hydrogen peroxide even decomposes the binuclear complex to a mononuclear one *via* eq 2. Thus in Gleu

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(3) G. Vortmann, *Monatsh.*, **6**, 404 (1885); G. Vortmann and O. Blasberg, *Ber.*, **22**, 2653 (1889).

(4) K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, **237**, 79 (1938).

(5) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

(6) J. A. Weil, G. L. Goodman, and H. G. Hecht, "Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem 1962," Academic Press, Ltd., New York, N. Y., 1963, p 880; also see *Bull. Am. Phys. Soc.*, [2] **6**, 152 (1961).

(7) (a) A. Werner and F. Beddow, *Z. Anorg. Chem.*, **16**, 129 (1898); (b) A. Werner, *Ber.*, 40, 4609 (1907); (c) A. Werner, *Ann.*, **375**, 61 (1910).

(8) (a) L. R. Thompson and W. K. Wilmarth, *J. Phys. Chem.*, **56**, 5 (1952); (b) H. Graff and W. K. Wilmarth, "Proceedings of the Symposium on Coordination Chemistry, Tihany 1964," Akademiai Kiado, Budapest, 1965, p 255; also see *Chem. Abstr.*, **64**, 18968*h* (1966).

(9) (a) G. L. Goodman, H. G. Hecht, and J. A. Weil, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 93; (b) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964).

(10) M. Mori and J. A. Weil, *J. Am. Chem. Soc.*, **89**, 3732 (1967); also see *Chem. Commun.*, 534 (1966). The following corrections should be made in the 1967 paper. In Table I, the charge on formula C′ should be 4+, and in formula BH′ $]^{a\,4+}$ should read $]_b{}^{4+}$. After eq 14, "exp" and both parentheses should be removed in the expression for *p*. On p 3740, line 5 of column 1, section IV should read section VI-B.

(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957, and references therein.

(12) R. Jouan, *J. Chim Phys.*, **56**, 277 (1959).

(13) W. Gluud, K. Keller, and H. Nordt, *Ber. Ges. Kohlentech.* (Halle), **4**, 210 (1933).

(14) L. Michaelis, *Arch. Biochem.*, **17**, 201 (1948).

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{4+} + H_2O_2 \longrightarrow 2[CoOH(NH_3)_5]^{2+} + O_2 \quad (2)$$

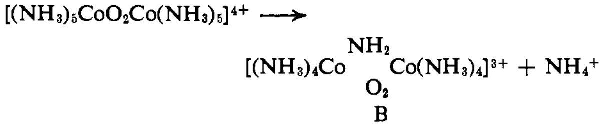
and Rehm's[4] method of preparing the oxidized 5+ complex, the yield is doubled if hydrogen peroxide is replaced by oxygen or air in the initial preparation of the 4+ complex; the succeeding oxidation to the 5+ complex (eq 3) proceeds very efficiently (~80%) with

$$[(NH_3)_5CoO_2Co(NH_3)_5]^{4+} \longrightarrow [(NH_3)_5CoO_2Co(NH_3)_5]^{5+} + e^- \quad (3)$$

ammonium persulfate, as reported by these investigators. The action of ozonized oxygen on cobalt(II) nitrate in aqueous ammonia in the presence of ammonium salts was reported to proceed as far as the formation of the 5+ peroxo complex, also in a good yield.[9a]

II. Formation of the Dibridged Peroxo–Dicobalt–Ammine Complexes. Vortmann's sulfate is generally prepared by aeration of ammoniacal cobalt(II) nitrate at about 35°, followed by very slow neutralization with dilute sulfuric acid. This sulfate was shown by Werner and co-workers[7] to be a mixture primarily of μ-amido-μ-hydroxo-bis(tetraamminecobalt)(4+) disulfate and μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) disulfate. Later, replacement of oxygen with ozone was tried, resulting in a better yield for the μ-amido-μ-peroxo complex isolated from the mixed sulfate,[9a] presumably because of more efficient oxidation during the acidification process.

While preparing Vortmann's sulfate, the present authors noticed that considerable deposition of dark brown crystals occurs at the first stage of aeration or ozonation at 35°, but that these gradually disappear toward the end of the process. These crystals were shown to be those of μ-peroxo-bis(pentaamminecobalt)(4+) tetranitrate dihydrate, the monobridged complex usually prepared by aeration of cold ammoniacal solutions of cobaltous salts, and which is the precursor of the green paramagnetic μ-peroxo-bis-(pentaamminecobalt)(5+) complex. It occurred to them, therefore, that even in the preparation of the dibridged complex, the first product might be this monobridged one (eq 1; *cf.* section I), which is then changed near 35° to the dibridged one (eq 4). Reaction 4 has been proved in the present research by starting with the monobridged complex and actually isolating brown crystalline salts of the previously unreported dibridged complex ion B (Experimental Section, preparations 2–5), which is the precursor of the green paramagnetic ion C (*cf.* eq 5). These compounds are stable as powders in air and for several hours in neutral or ammoniacal aqueous solution. Epr spectroscopy at room temperature disclosed only a weak absorption signal, of the strength of *ca.* 1% of the typical paramagnetic peroxo complexes, attributable to a small amount of the oxidized complex ion occurring as an impurity in the lattice.



$$[(NH_3)_5CoO_2Co(NH_3)_5]^{4+} \longrightarrow [(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]^{3+} + NH_4^+$$

(4)

B

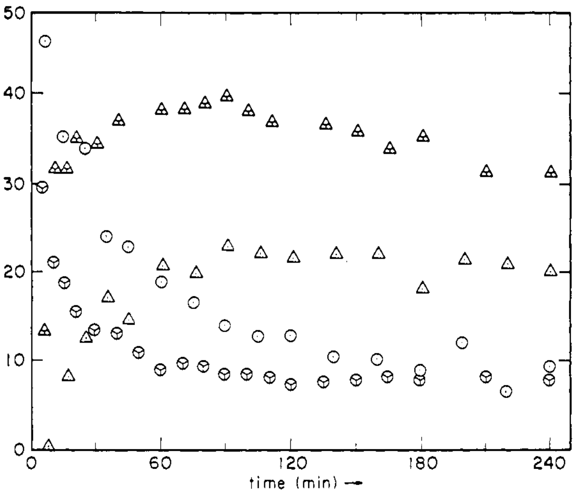
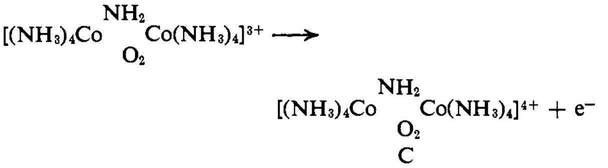


Figure 1. Formation of dibridged dicobalt complex from the monobridged complex (original concentration 0.071 *M*) in concentrated aqueous ammonia at 35°. Circles depict the amount of μ-peroxo-bis(pentaamminecobalt)(4+) complex, and triangles represent the amount of μ-amido-μ-peroxo-bis(tetraamminecobalt)(3+) complex. Simple circles and triangles denote experiments where no alkali was used, whereas tripartite ones represent runs in which 0.063 mole/l. of KOH was present.

When the solution of the nitrate or the perchlorate of the dibridged 3+ complex is treated with an acidic solution of cerium(IV) or permanganate ion, it immediately turns green and upon addition of nitric acid precipitates the paramagnetic green μ-amido-μ-peroxo-bis(tetraamminecobalt) tetranitrate, which can be identified by elemental analysis as well as by its characteristic optical and epr spectra.[5,6] Nitric acid itself, when sufficiently concentrated and at moderate temperature (20–30°), can also perform this oxidation.



$$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]^{3+} \longrightarrow [(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]^{4+} + e^-$$

(5)

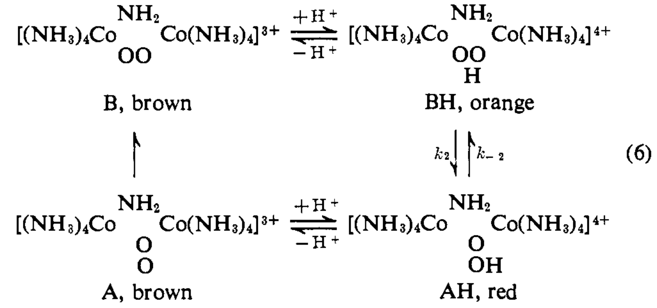
C

A semiquantitative rate study of formation of the dibridged complex from the monobridged one (eq 4) in aqueous ammonia was made under various conditions. Absorbance measurements were used for the analysis of both monobridged and dibridged complexes after they had been oxidized to the paramagnetic forms (*cf.* Experimental Section). The results of typical runs are illustrated in Figure 1. Thus, the amount of the dibridged complex is seen to reach a broad maximum (~40%) after about 90 min of digestion of the monobridged complex in aqueous ammonia at about 35°, in the presence of a little less than 1 mole of potassium hydroxide per mole of monobridged complex. These appear to be the optimal conditions of the digestion, found from some 18 such runs. However, it was very difficult to determine the exact optimal conditions because of side reactions, forming mononuclear ammines and hydrous cobalt(III) oxide. The beneficial effect of the base added in the digestion may be accounted for in terms of an enhanced removal of protons from ligand ammonia, which presumably facilitates amido-bridge formation.

The above findings form the basis of the new preparative method for the μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) salts described in the Experimental

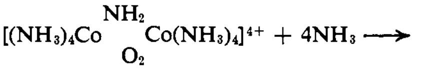
Section (preparation 8). Thus in this method the process is divided into four steps: preparation of the monobridged complex (eq 1), transformation to the diamagnetic dibridged complex (eq 4), oxidation to the paramagnetic dibridged complex (eq 5), and purification by utilizing the low solubility of the sulfate in water. By so doing it should become possible to let each reaction occur under optimal conditions, and, in fact, the new method has brought about an improvement of the yield by a factor of approximately 2 over the ozonation method and by a factor of about 10 over Werner's method *via* Vortmann's sulfate. The improvement of the yield is also partly due to the use of Ce^{4+} in the oxidation process: in the older methods in which the reactant mixture was simply neutralized with sulfuric acid, 60 + % of the crude product (Vortmann's sulfate) is known to be the complex $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}OH\text{-}Co(NH_3)_4]^{4+}$ formed presumably because of the decomposition of the μ-amido-μ-peroxo (3+) complex in acidic solution.

III. Diamagnetic Dibridged Dicobalt Ammines in Acids. The behavior of the diamagnetic ion B toward nonoxidizing acids has been found to be analogous to that of the corresponding ethylenediamine (en) compound reported in paper I.[10] In view of the recent X-ray crystallographic results on the en complexes by Thewalt and Marsh,[15] it is most probable that the reaction schemes in both the en and the ammine complexes are based on the isomerization of the peroxo bridge as illustrated by eq 6 for the ammine complexes. As in the case of the en complexes, only the starting complex B (preparations 2–5) and the isomerized protonated complex AH (perchlorate, preparation 6; nitrate, preparation 7) have been obtainable. In the present case of the ammine complexes, each ionic species is much less stable than the corresponding en complex, so that exact determination of the rate constants has not been carried out; the approximate values thus far obtained are $k_2 = \sim 0.003\ \text{sec}^{-1}$ at 10° and $\sim 0.01\ \text{sec}^{-1}$ at 20°; $k_{-2} = \sim 0.0006\ \text{sec}^{-1}$ at 20°. The k_{-2} value was actually evaluated from the oxidation rate of AH to the dibridged paramagnetic (+4) complex C in acidic solution with Ce^{4+}, on the assumption that AH → BH is the rate-determining step as in the en case;[10] the oxidation of B or BH to the same paramagnetic complex under the same conditions proceeds immeasurably fast, as described in section II.[15a]



IV. Paramagnetic Dibridged Dicobalt Ammines in Alkaline Solutions. When a green solution of complex C is treated with aqueous ammonia, gas is evolved and the solution turns brown. The reaction proceeds more smoothly with the chloride, and, when the resulting solution is treated with a small quantity of ammonium nitrate some hexaamminecobalt(III) complex (*ca.* 0.25 mole from 1 mole of the starting complex) and at times also a small quantity of unreacted green complex are recovered as the nitrate. Addition of a large quantity of ammonium nitrate (to the filtrate) then precipitates $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4]NH_4(NO_3)_4{\cdot}0.5H_2O$ (*ca.* 65%, preparation 4b), *i.e.*, the same diamagnetic dibridged complex also obtainable from the bridging reaction of the diamagnetic monobridged complex (*cf.* section II and preparation 4a).

Isotopic experiments starting with ordinary complex tetrachloride and ammoniacal ^{18}O-enriched water (1.29%) have indicated that the gas evolved during treatment of the 4+ ion with ammonia mainly consists of oxygen (*ca.* 0.15 mole from 1 mole of the starting complex) in the natural isotopic ratio (0.20% ^{18}O) admixed with small quantities of NO and N_2O (aside from NH_3 which may have come both from the complex and the solvent). This result demonstrates that the reduction of the paramagnetic complex to the diamagnetic form does not occur by the reducing action of OH^- ion. In this sense, the situation is similar to the case of the en complex.[8] The behavior here is, however, somewhat different since oxygen is evolved. From the present knowledge of the stoichiometry between the oxygen evolved and the hexaammine complex recovered, it seems probable that a part of the initial complex exerts a reducing power *via* eq 7. Here NH_2^- may also exert a further reducing ability; otherwise it should immediately be changed to NH_3 by H_2O (the latter changing to OH^-). Other paths may include oxidation of NH_3 either from the complex or the solvent; the behavior of the nitrogen would be made clearer by the use of either a base, which is not easily destroyed, or the ^{15}N-labeled complex.



$$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\ }}Co(NH_3)_4]^{4+} + 4NH_3 \longrightarrow 2[Co(NH_3)_6]^{3+} + O_2 + NH_2^- + e^- \quad (7)$$

V. Infrared Spectra of Dibridged Dicobalt Ammines. The main absorption peaks in the infrared spectra of dibridged dicobalt ammines, in the NaCl region, are listed in Table I. Most of them can be accounted for as due to the vibration of ammonia ligands,[16] peroxo bridges, or anions. Of these vibrations, symmetric deformation vibrations and rocking vibrations are known to be sensitive to the oxidation state[17] and the electronegativity[18] of the central metal ion. Thus whereas the symmetric deformation vibration and rocking vibrations of the hexaamminecobalt(II) ion appear at 1225 and 630 cm^{-1}, respectively, those of the hexaamminecobalt(III) ion are found at 1325 and 820 cm^{-1}. For both the diamagnetic and the paramagnetic forms of μ-amido-μ-peroxo dicobalt ammines, such frequencies fall well within the range of those for

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(15) U. Thewalt and R. E. Marsh, private communication of preliminary results.

(15a) Note Added in Proof. We note that A. G. Sykes and R. D. Mast [*J. Chem. Soc., Sect. A*, 784 (1967)] also invoke the tricovalent oxygen isomer A in their explanation of the rapid formation of μ-amido-μ-hydroxy-bis(tetraamminecobalt)(4+) ion on reduction of the μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) ion with iodide ion in acidic solution.

(16) I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955); S. Mizushima, I. Nakagawa, and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

(17) G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957).

(18) K. Wilmshurst, *Can. J. Chem.*, **38**, 467 (1960).

Table I. Infrared Absorption Peaks of Dibridged Dicobalt Ammines (cm^{-1}, NaCl Region)[a]

	$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]\cdot(ClO_4)_3\cdot H_2O$ Dark brown, diamagnetic	$[(NH_3)_4Co\overset{NH_2}{\underset{O_2H}{\quad}}Co(NH_3)_4]\cdot(ClO_4)_4\cdot 2H_2O$ Red, diamagnetic	$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]\cdot(ClO_4)_3\cdot NaClO_4$ Dark brown, diamagnetic	$[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\quad}}Co(NH_3)_4]\cdot(ClO_4)_4\cdot nH_2O$ Green, paramagnetic
$\nu(OH)$	3700–3550 m	3700–3550 s	3700 w (impurity?)	3800–3550 s
$\nu(NH)$	3300 vs	3300 vs	3340 vs	3300 vs
	3100 sh	3200 sh	3280 vs	
	1980 w	1985 w	2000 w	2000 w
$\delta_{as}(NH_3)$	1625 s	1620 s	1630 vs	1615 s
	1345 sh	1360 s	1360 m	1353 s
	1330 sh	1335 vs	1330 sh	1330 s
$\delta_s(NH_3)$	1305 s	1315 s	1310 s	
	1270 m	1300 sh		
	1245 sh			
$\nu_3(ClO_4)$	1050–1140 vs	1050–1140 vs	1050–1140 vs	1050–1140 vs
$\nu_1(ClO_4)$	938 w	938 w	940 w	938 w
$\nu(OO)$			830 m (sharp)	
	850 sh			
$\rho_r(NH_3)$	800 s	810 s	760 s	815 s
	760 sh	770 sh		775 sh

[a] ν, stretching vibration; δ_{as}, asymmetric deformation vibration; δ_s, symmetric deformation vibration; ρ_r, rocking vibration; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

regular cobalt(III) ammines. Thus the electron density around the cobalt nuclei does not appear to be much different from that in cobalt(III) ammines. This is consistent with the view that, during the oxidation, the electron is lost not from the pure cobalt orbital but from a molecular orbital formed by the two cobalt ions and the peroxo ligand, a view which was recently substantiated by Weil and Kinnaird[19] in their epr experiments made by using ^{17}O, and also by Schaefer and Marsh[20] in their X-ray study of $[(NH_3)_5CoO_2Co(NH_3)_5]SO_4(HSO_4)_3\cdot H_2O$ which disclosed that the O–O distance herein is close to that of the superoxide ion.

In the case of $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4]Na(ClO_4)_4$ (preparation 2a), the absorption at 830 cm^{-1} can probably be assigned to O–O stretching, for it is not shifted appreciably by deuteration and agrees in its position, intensity, and sharpness with the O–O stretching absorption in other peroxo metal compounds.[21] The peak at 760 cm^{-1} of this double perchlorate, on the other hand, is broad and is greatly shifted by deuteration and is assigned to the rocking frequency of the coordinated ammonia. It is not yet clear, however, why the O–O stretching frequency appears only in the spectrum of this double perchlorate; none of the previous reports described the appearance of such frequencies in peroxo dicobalt series, nor have any such peaks been found for the other three compounds examined in the present research. It is also to be noted that the rocking frequency of this double perchlorate is somewhat lower than those of the other three. Thus the compound seems to offer an interesting problem which requires further investigation.

Experimental Section

Preparation of Compounds. The literature describing the synthesis of dicobalt complexes hitherto reported is well summarized in Gmelin's Handbuch,[22] and in Werner's 1910 paper;[7c] more recent literature is also summarized.[9] Some peroxo dicobalt ammine perchlorates and permanganates (and possibly nitrates also) are explosive and caution should therefore be exercised in handling them.

I. **Diamagnetic μ-Peroxo Complexes. 1. μ-Peroxo-bis(pentaamminecobalt)(4+) Tetranitrate Dihydrate and Tetranitrate (Anhydrous).** The nitrate dihydrate was prepared by Gibbs' method,[2b] with some modification designed to avoid difficulties caused by precipitation of the cobalt(II) ammine complex.

Fifty grams of cobalt(II) nitrate hexahydrate was dissolved in 100 ml of water and filtered. Aqueous ammonia (15 *M*, 250 ml) was added, and, after the mixture was cooled to 20°, a current of oxygen (1000 ml/min) was passed through for 1 hr, the mixture being stirred with a magnetic stirrer. Oxygen may be replaced by air in this synthesis; in this case, longer bubbling (2–3 hr) at a lower temperature (~5°) is recommended. Sodium nitrate (20 g) dissolved in 50 ml of water was then added, and oxygen (or air) was passed in for 1 hr more, and the mixture was cooled with ice toward the end of this period. The dark brown crystals were gathered on a glass filter and washed with a small quantity of 15 *M* aqueous ammonia and then with ethanol. The dihydrate thus prepared was kept in an evacuated desiccator overnight in order to obtain the anhydrous nitrate, which has not been previously reported in the literature (yield, 44 g). It was noted that, in aqueous solution at room temperature, this peroxo complex is comparatively stable only in the presence of 2–6 *M* ammonia. The complex is particularly unstable at lower ammonia concentrations.

Anal. Calcd for $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4$: Co, 20.74; N (ammoniacal), 24.65. Found: Co, 20.77; N (ammoniacal), 24.41.

The determination of ammonia in the present research was carried out according to the method of Horan and Eppig[23] using arsenic(III) oxide to prevent the oxidizing effect of Co(III) in the distillation method.

2a. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) Sodium Tetraperchlorate. Preparation of the Crude Salt from a Monobridged

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[19] J. A. Weil and J. K. Kinnaird, *J. Phys. Chem.*, 71, 3341 (1967).

[20] W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, 88, 178 (1966).

[21] C. J. Wilkins and J. F. Young, *J. Chem. Soc.*, 2136 (1962); 5345 (1963); W. P. Griffith, *ibid.*, 3948 (1962); R. Stomberg, *Arkiv Kemi*, 23, 401 (1965).

[22] "Gmelin's Handbuch der anorganischen Chemie," Vol 58B, 8th ed, Verlag Chemie, Berlin, 1932, pp 332 ff; Suppl., Weinheim, 1964, pp 615 ff.

[23] H. A. Horan and H. J. Eppig, *J. Am. Chem. Soc.*, 71, 581 (1949).

Diamagnetic Complex. Ten grams of μ-peroxo-bis(pentaamminecobalt) (4+) tetranitrate (preparation 1) was added little by little to 100 ml of 15 *M* aqueous ammonia while the latter was constantly stirred. Potassium hydroxide (1 g) dissolved in a little water was added and the mixture was slowly warmed up to and kept at 32–35° for 90 min; it was then cooled to below 10°. Ammonium nitrate (70 g) was added, and then 200 ml of methanol was slowly added to the stirred mixture. If oily material separated out, the mixture was stirred until it became crystalline. The precipitate was washed with methanol and redissolved in 100 ml of 6 *N* aqueous ammonia; the filtered solution was stirred with 100 g of sodium perchlorate monohydrate. The precipitate of crude double perchlorate with sodium perchlorate was filtered and washed with ethanol and ethyl ether. This material (5–6 g) may be used for the preparation of other salts. However, a purer product of this double perchlorate is obtainable from the double nitrate containing ammonium nitrate, which is prepared either from the above crude double perchlorate (4a) or from the paramagnetic dibridged complex tetrachloride (preparations 10 and 4b).

2b. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) Sodium Tetraperchlorate. Preparation of the Pure Salt from the Double Nitrate. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) ammonium tetranitrate (1.5 g, preparation 4a or 4b) was dissolved in 25 ml of 5 *M* aqueous ammonia, and the filtered solution was stirred with 30 g of sodium perchlorate until the latter dissolved completely. After the mixture was cooled with ice, the precipitate was filtered and washed once with methanol containing sodium perchlorate, then with methanol and ethyl ether; yield 1.5 g.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4]Na(ClO_4)_4$: Co, 16.30; N, 17.44; Na, 3.18; ClO_4, 55.03. Found: Co, 16.46; N, 17.19; Na, 3.15; ClO_4, 55.13.

3. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) Triperchlorate Monohydrate. One gram of μ-amido-μ-peroxo-bis(tetraamminecobalt)(3+) sodium tetraperchlorate (preparation 2a or 2b) was dissolved in 30 ml of 5 *M* aqueous ammonia, and after filtration 1 g of sodium perchlorate and 40 ml of methanol were added to the stirred filtrate. After the sodium perchlorate dissolved completely, the mixture was cooled in an ice bath and the precipitate was filtered and washed with methanol; yield 0.5 g.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](ClO_4)_3\cdot H_2O$: Co, 19.05; N, 20.38; ClO_4, 48.25. Found: Co, 19.07; N, 20.00; ClO_4, 48.05.

4a. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) Ammonium Tetranitrate Hemihydrate from the Crude Double Perchlorate. The crude μ-amido-μ-peroxo-bis(tetraamminecobalt)(3+) sodium tetraperchlorate (5–6 g, preparation 2a) was dissolved in 100 ml of 6 *N* aqueous ammonia at 20°, and after filtration 40 g of ammonium nitrate and 200 ml of methanol were added to the stirred filtrate, and the mixture was cooled with ice. The precipitate was filtered, washed with methanol, and redissolved in 100 ml of 6 *M* aqueous ammonia; after filtration the complex salt was crystallized by addition of 40 g of ammonium nitrate and 100 ml of methanol and by cooling with ice. The precipitate was filtered and washed with methanol and air-dried.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](NH_4)(NO_3)_4\cdot 0.5H_2O$: Co, 20.42; N (ammoniacal, *i.e.*, contained as NH_3 and NH_2), 24.27; N (in NO_3), 9.70. Found: Co, 20.44; N (ammoniacal), 24.23; N (in NO_3), 9.60.

Another double nitrate, $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](NH_4)_3(NO_3)_6$, seems to be formed with higher concentrations of ammonium nitrate, but the conditions for its formation have not yet been well established. This is also true of preparation 4b below.

4b. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) Ammonium Tetranitrate Hemihydrate from a Dibridged Paramagnetic Compound. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(4+) tetrachloride (2.3 g, preparation 10 below) was dissolved in a mixture of 5 ml of water and 5 ml of 15 *M* aqueous ammonia at 20°. After 5 min, 1 g of ammonium nitrate was added and the mixture was stirred and filtered. Ammonium nitrate (10 g) was then added to the filtrate, and 15 ml of methanol was added to it slowly. The mixture was cooled with ice with stirring and the dark brown precipitate was filtered with suction, washed with methanol, and dissolved in a mixture of 20 ml of water and 20 ml of 15 *M* aqueous ammonia and filtered. Ammonium nitrate (20 g) was added to the filtrate and 40 ml of methanol was added to the mixture while the latter was constantly stirred. Stirring was continued until all the ammonium nitrate dissolved. The precipitate was filtered and washed with methanol and air dried; yield 1.8 g.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](NH_4)(NO_3)_4\cdot 0.5H_2O$: Co, 20.42; N (ammoniacal), 24.27; N (in NO_3), 9.70. Found: Co, 20.35; N (ammoniacal), 23.60; N (in NO_3), 9.16.

5. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(3+) Trinitrate Monohydrate. One gram of μ-amido-μ-peroxo-bis(tetraamminecobalt)(3+) ammonium tetranitrate hemihydrate (preparation 4a or 4b) was dissolved in 23 ml of 15 *M* aqueous ammonia, and after filtration 23 ml of methanol was slowly added. The mixture was cooled with ice, and the precipitate was filtered and washed with methanol.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](NO_3)_3\cdot H_2O$: Co, 23.29; N (ammoniacal), 24.91; N (in NO_3), 8.30; H, 5.58. Found: Co, 23.49; N (ammoniacal), 24.53; N (in NO_3), 8.45; H, 5.75.

II. Diamagnetic μ-Hydroperoxo Complexes. 6. μ-Amido-μ-hydroperoxo-bis(tetraamminecobalt)(4+) Tetraperchlorate Dihydrate. μ-Amido-μ-peroxobis(tetraamminecobalt)(3+) triperchlorate monohydrate (0.5 g, preparation 3) was stirred with 10 ml of ice-cold 3 *M* perchloric acid for 15 min. The red precipitate was filtered with suction, redissolved in a minimum quantity of cold 0.1 *M* perchloric acid, filtered, and immediately precipitated by adding a half-volume of ice-cold 10 *M* perchloric acid and cooling with ice. The precipitate was filtered and washed with ethanol containing a little perchloric acid, and finally once with ethanol.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2H\text{-}Co(NH_3)_4](ClO_4)_4\cdot 2H_2O$: Co, 15.99; N, 17.11; ClO_4, 53.98. Found: Co, 15.57; N, 17.09; ClO_4, 53.79.

7. μ-Amido-μ-hydroperoxo-bis(tetraamminecobalt)(4+) Tetranitrate Monohydrate. μ-Amido-μ-peroxobis(tetraamminecobalt)(3+) nitrate monohydrate (0.5 g, preparation 5) was stirred with 10 ml of ice-cold 3 *M* nitric acid for 15 min. The red precipitate was filtered with suction, redissolved in a minimum quantity of 0.1 *M* nitric acid, and immediately reprecipitated by adding a half-volume of ice-cold 10 *M* nitric acid and cooling with ice. The precipitate was filtered and washed with methanol.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2H\text{-}Co(NH_3)_4](NO_3)_4\cdot H_2O$: Co, 20.71; N (ammoniacal), 22.15; N (in NO_3), 9.85. Found: Co, 20.55; N (ammoniacal), 22.05; N (in NO_3), 9.73.

III. Paramagnetic μ-Peroxo Complexes. 8. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(4+) Disulfate Dihydrate. As stated in the Discussion, section II, this dibridged complex is formed from μ-peroxo-bis(pentaamminecobalt)(4+) nitrate. If this monobridged precusor is freshly prepared for this purpose (preparation 1 in its original scale), the brownish black precipitate of the dihydrate just separated from the mother liquor by suction may be used without washing.

Thus a fresh precipitate (~45 g) was added in several portions into 500 ml of 15 *M* aqueous ammonia with stirring. Potassium hydroxide (4.2 g) dissolved in the minimum quantity of water was added, and the mixture was heated at 35° for 90 min, then cooled to below 5°, and poured little by little with vigorous stirring into a mixture of 700 ml of concentrated nitric acid (14–15 *M*, which had been cooled to 5°), 100 g of diammonium hexanitratocerate(IV), and 1200 g of ice. The temperature of the mixture was always kept below 10°, using an ice bath if necessary. The mixture was stirred for 60 min in an ice bath. If convenient, the whole mixture after this stage may be kept in a refrigerator overnight.

The grayish green precipitate was then filtered on a glass filter and washed twice with a little 2 *M* nitric acid. The precipitate was then stirred mechanically with 2000 ml of water at 20° containing 5 ml of 15 *M* nitric acid until all the crystal blocks were dispersed and the suspension was filtered. To the filtrate was added 200 ml of 3 *M* sulfuric acid, and the mixture was stirred for 30 min. The gray crystalline precipitate of the crude μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) disulfate dihydrate was filtered on a glass filter and washed with water and ethanol. The yield of the crude sulfate was 16–17 g.

The crude sulfate can be used as such for the preparation of other salts. As examples, the preparation of the nitrate and the chloride will be described in following sections. Pure sulfate can then be obtained by adding dilute sulfuric acid to a solution of the nitrate and washing with water and ethanol. The sulfate cannot be recrystallized as such because it is almost insoluble in water.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](SO_4)_2\cdot 2H_2O$: Co, 22.22; N, 23.77; S, 12.10. Found: Co, 22.00; N, 23.53; S, 11.84.

9. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(4+) Tetranitrate. Ten grams of crude sulfate (preparation 8) was stirred with 500 ml of water, and 100 ml of concentrated nitric acid was added to this suspension little by little under constant agitation. The mixture was cooled with running water or ice and filtered. The crude nitrate was then dissolved in a minimum quantity (a little more than 1 l.) of 0.5% nitric acid and the solution was filtered. The pure nitrate can then be precipitated out by adding concentrated nitric acid of about one-fifth the volume of the solution and then cooling to 5°. Light-colored fluffy precipitate may first form, which will be changed to dark green prisms on standing. The precipitate was filtered and washed with dilute nitric acid and ethanol; yield *ca.* 9 g from 10 g of crude sulfate or 14–15 g (28–30%) from 50 g of cobalt(II) nitrate hexahydrate.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4](NO_3)_4$: Co, 21.42; N (ammoniacal), 22.91. Found: Co, 21.49; N (ammoniacal), 22.76.

10. μ-Amido-μ-peroxo-bis(tetraamminecobalt)(4+) Tetrachloride Dihydrate. To a suspension of 5 g of crude μ-amido-μ-peroxo-bis(tetraamminecobalt)(4+) sulfate dihydrate in 30 ml of water was added 20 ml of concentrated hydrochloric acid with stirring, 30 ml of ethanol was added to it, and the mixture was cooled with ice. The crude chloride thus formed was filtered by suction and dissolved in 50 ml of 0.1 *M* hydrochloric acid. After filtration 30 ml of concentrated hydrochloric acid (12 *M*) and 50 ml of ethanol were added and the mixture was cooled with ice. The precipitate was filtered and washed with ethanol; yield 3.5 g.

Anal. Calcd for $[(NH_3)_4Co\text{-}\mu\text{-}NH_2\text{-}\mu\text{-}O_2\text{-}Co(NH_3)_4]Cl_4 \cdot 2H_2O$: Co, 24.56; N, 26.26; Cl, 29.55. Found: Co, 24.42; N, 26.04; Cl, 29.73.

Semiquantitative Study of the Change of the Monobridged Complex to the Dibridged One. There were many factors which made this kind of experiment a difficult and incomplete one, but the results obtained at least give a general idea of the formation of the dibridged complex from the monobridged one and approximately the best conditions for preparation of the dibridged complex. For example, since the starting monobridged complex decomposes violently when brought in contact with aqueous ammonia at the reaction temperature from the outset, the complex (4 g of the anhydrous nitrate) was actually dissolved in cold aqueous ammonia (100 ml) and brought to the reaction temperature in the course of 5 min.

Oxidation of the dibridged complex formed was done by pouring an aliquot (2 ml) of the reaction mixture into a shaken 10% solution (5 ml) of $(NH_4)_2Ce(NO_3)_6$ in 6 *N* HNO_3 which had been chilled in a Dry Ice–acetone bath. The mixture was kept in a refrigerator for 1–2 days. The paramagnetic dibridged complex was extracted from the precipitate with ~1–3-ml portions of 0.3 *N* HNO_3, precipitated as the sulfate, and dissolved in 3 *N* perchloric acid. The amount of the complex was then estimated by the absorbance measurement at 700 mμ (ϵ 310).

The unreacted monobridged peroxo complex was oxidized by pouring a different aliquot (2 ml) into a mixture of 0.5 g of ammonium nitrate and 0.3 g of ammonium persulfate. After ~30–60 min, the mixture was acidified with dilute nitric acid and allowed to stand. The paramagnetic monobridged complex was extracted from the precipitate with 3 *N* perchloric acid and evaluated by use of absorbance measurements at 670 mμ (ϵ 822). The efficiency of the recovery of the dibridged and the monobridged complexes in the above procedures has been found to be ~96 and ~82%, respectively, but no correction factors for this efficiency were applied for the data in Figure 1.

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Hindered Ligand Systems. *cis,cis*-Triaminocyclohexane and Its Complexes with Trivalent Cobalt and Rhodium

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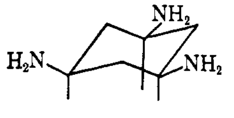
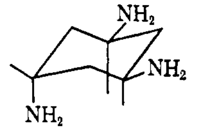
Abstract: The Birch reduction of the trioxime of α-phloroglucinol is shown to produce both *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) and the *cis,trans* isomer in nearly equal proportions. However, under the prevailing conditions, only the former reacts with Co(III) or Rh(III) to form stable bis complexes, whose ligand field spectra indicate that they must consist of nearly regular octahedra. Furthermore, the ligand field parameters are nearly identical with those of $Co(en)_3^{3+}$ and $Rh(en)_3^{3+}$. However, a noticeable difference occurs in the charge-transfer spectrum of Co(*cis,cis*-tach)$_2^{3+}$, when compared to that of $Co(en)_3^{3+}$. A qualitatively simple explanation involving orbital misdirection is tentatively offered. In addition, the decomposition of Co(*cis,cis*-tach)$_2^{3+}$ has led to the isolation of the free ligand, whose proton magnetic resonance spectrum compares favorably with known compounds of similar stereochemistry. It is also suggested that the sodium-in-alcohol reduction of the trioxime produces both isomers of the triamine.

The synthesis of 1,3,5-triaminocyclohexane (tach) was first accomplished in poor yields by Hassel and Lunde[1] through the reduction of the corresponding oxime with sodium in alcohol. Although two geometric isomers are possible (see structures below), it would appear that the X-ray data[1,2] indicated that the product consisted exclusively of the isomer with all amine groups disposed in equatorial positions, or *cis,cis*-tach. Internal rotation of this interesting ligand causes the amine groups to move into a triaxial conformation wherein, if normal bond lengths and angles are maintained, the nitrogen atoms should describe an



cis,cis



cis,trans

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(1) O. Hassel and K. Lunde, *Research* (London), 3, 484 (1950).

(2) P. Andersen and O. Hassel, *Acta Chem. Scand.*, 5, 1349 (1951).