

numbers would not be consistent with the  $R_{2p}$  data.

The simplest explanation for the two exchanging solvent molecules would be to assign them to the axial solvent molecules in the tetragonally distorted complex  $\text{Cr}(\text{CH}_3\text{OH})_6^{2+}$ . The remaining four equatorial ligands might be exchanging much more rapidly, but that seems inconsistent with the shorter bond lengths. The equatorial ligands might be exchanging too slowly to be observed and/or  $R_{2m}$  and  $\Delta\omega_m$  of the equatorial positions could be much smaller than those for the axial positions so that the equatorial ligands are essentially transparent to the nuclear relaxation measurements. However the results do require that the axial-equatorial interconversion is slow on our NMR time scale. Otherwise, all the coordinated solvent molecules would equilibrate to give effectively six exchanging solvent ligands as opposed to the two observed.

### Conclusions

With the known number of exchanging ligands, it is possible to calculate the kinetic parameters for exchange of one  $\text{CH}_3\text{OD}$ . The values are  $k = 1.2 \times 10^8 \text{ s}^{-1}$  (25 °C),  $\Delta H^\ddagger = 7.6 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = 4 \text{ cal mol deg}^{-1}$ .

The great lability of chromium(II) has the effect of preventing analogous solvent exchange studies in water over the available liquid range. Studies on iron(II), cobalt(II), and nickel(II) indicate that the activation enthalpy is about 2 kcal mol<sup>-1</sup> less in water than in methanol.<sup>14</sup> Therefore one can estimate an activation enthalpy of ~6 kcal mol<sup>-1</sup> for chromium(II) in water, but this extrapolation must be viewed with caution because of the tetragonal distortion of the solvated chromium(II) species.

### Experimental Section

**Materials.** The solutions of chromium(II) trifluoromethanesulfonate in  $\text{CH}_3\text{OD}$  were prepared on a standard vacuum line by distilling  $\text{CH}_3\text{OD}$  and  $\text{F}_3\text{CSO}_3\text{H}$  onto a weighed amount of chromous acetate (prepared by standard methods). The solvent containing acetic acid was

removed by vacuum distillation and the process was repeated twice. The final blue solution was sealed under vacuum in a 10 mm flat-bottomed tube. The final amount of  $\text{CH}_3\text{OD}$  in the sample was determined by weight. The four samples used were in the range of  $0.96 \times 10^{-3}$  to  $4 \times 10^{-3} \text{ m}$  in chromium(II).

**NMR Measurements.** The  $R_1$  and  $R_2$  values were determined by 180- $\tau$ -90 and Carr-Purcell-Meiboom-Gill methods, respectively, on a Bruker SXP 4-100 pulsed spectrometer at 89.5 MHz. The instrumentation has been fully described elsewhere.<sup>7,15</sup> Relaxation rates are the average of at least five determinations for a particular sample and temperature. Chemical shifts were measured on a Bruker WP-80 spectrometer using cyclohexane as an internal standard.

**Data Analysis.** The relaxation rates were analyzed by eq 8,<sup>6</sup> where  $R_{2\text{obsd}}$  and  $R_{2\text{solv}}$  are the relaxation rates in the presence and absence of

$$R_{2p} = (R_{2\text{obsd}} - R_{2\text{solv}}) \frac{(\text{solv})}{n(\text{Cr}^{2+})} = r_m \frac{R_{2m}(R_{2m} + r_m) + \Delta\omega_m^2}{(R_{2m} + r_m)^2 + \Delta\omega_m^2} + R_{2o} \quad (8)$$

chromium(II) respectively, (solv) and  $(\text{Cr}^{2+})$  are the molality of the solvent and chromium(II),  $n$  is the number of exchanging solvent molecules,  $R_{2o}$  is the outer-sphere relaxation rate and the other terms have the usual meaning. A similar expression gives  $R_{1p}$  in terms of  $R_{1\text{obsd}}$  and  $R_{1\text{solv}}$  by substituting  $R_{1m}$  for  $R_{2m}$  and setting  $\Delta\omega_m = 0$ .

The temperature dependence of the terms in eq 1 are given by the following equations:<sup>11</sup>

$$R_{1m} = C_{1m}/T \exp(E_{1m}/RT) \quad (9)$$

$$r_m = 2.083 \times 10^{10} T \exp(\Delta H^\ddagger - T\Delta S^\ddagger/RT) \quad (10)$$

$$\Delta\omega_m = C_\omega/T \quad (11)$$

The chemical shifts could be measured only in the fast-exchange region because the lines became too broad at lower temperatures. Therefore

$$\Delta\omega_{\text{obsd}} = -\frac{n(\text{Cr}^{2+})}{(\text{solv})} \Delta\omega_m = \frac{n(\text{Cr}^{2+})C_\omega}{(\text{solv})T} \quad (12)$$

**Registry No.**  $\text{Cr}(\text{O}_3\text{SCF}_3)_2$ , 99329-21-2;  $\text{CH}_3\text{OD}$ , 1455-13-6.

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## Facile Conversion of a Coordinated Nitro Group into an Aqua Group: Acid-Induced Nitro-to-Nitrito Rearrangement

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The nitro complex  $(\text{NH}_3)_5\text{CoNO}_2^{2+}$  reacts rapidly and completely with neat anhydrous trifluoromethanesulfonic acid to generate the aqua species  $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ . Oxygen-17 NMR results show that the oxygen in the bound water is derived from the original nitro group. A mechanism involving acid-catalyzed nitrogen-to-oxygen nitrite rearrangement is considered. The relationship between the mechanisms for oxygen scrambling and acid-catalyzed loss of  $\text{NO}^+$  from the nitrito linkage isomer is discussed, together with the mechanism for the present reaction.

### Introduction

The classic example of linkage isomerism in inorganic chemistry is the N-bound nitro and O-bound nitrito pair  $(\text{NH}_3)_5\text{Co}-\text{NO}_2^{2+}$  and  $(\text{NH}_3)_5\text{Co}-\text{ONO}^{2+}$ , synthesized nearly a century ago.<sup>1</sup> Nonetheless, despite their extensive history, significant facts on their rearrangement chemistry continue to emerge,<sup>2-6</sup> and herein

we report another.

We sought a means of rapidly generating *trans*- $\text{Co}(\text{en})_2$ -(amine)( $\text{O}_3\text{SCF}_3$ )<sup>2+</sup> from *trans*- $\text{Co}(\text{en})_2$ (amine) $\text{X}^{n+}$  under ambient conditions. However, in the usual procedure<sup>7,8</sup> of heating

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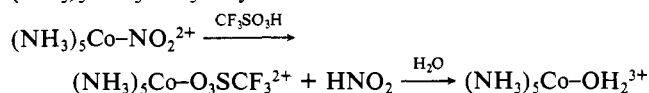
(amine)<sub>5</sub>CoCl<sup>2+</sup> (e.g., *trans*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)Cl]Cl<sub>2</sub>) in neat CF<sub>3</sub>SO<sub>3</sub>H, *cis*-[Co(en)<sub>2</sub>(NH<sub>3</sub>)(O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub>] results because of rapid isomerization of the first-formed *trans*-Co(en)<sub>2</sub>(NH<sub>3</sub>)(O<sub>3</sub>SCF<sub>3</sub>)<sup>2+</sup> ion via CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> exchange.<sup>9</sup> Furthermore, only *trans*-Co(en)<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>)Cl<sup>+</sup> is derived from either Δ-*cis*- or *trans*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> in CF<sub>3</sub>SO<sub>3</sub>H, albeit the loss of the first Cl<sup>-</sup> is rapid; the thermodynamically preferred form arises from subsequent *cis*-/*trans*-Co(en)<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>)Cl<sup>+</sup> equilibration.<sup>10</sup> Since acid-catalyzed loss of Cl<sup>-</sup> is observed in neat CF<sub>3</sub>SO<sub>3</sub>H but not in aqueous acid, we reasoned that a ligand such as N<sub>3</sub><sup>-</sup> or NO<sub>2</sub><sup>-</sup> should be a much better leaving group than Cl<sup>-</sup> in CF<sub>3</sub>SO<sub>3</sub>H, because the hydrolyses of their metal complexes in water are strongly acid-catalyzed,<sup>11</sup> and this could provide a solution to the problem of stereoselectively synthesizing the *trans* isomer mentioned above. For NO<sub>2</sub><sup>-</sup> as a leaving group, this proved to be the case as now described, but not for the anticipated reason.

### Results and Discussion

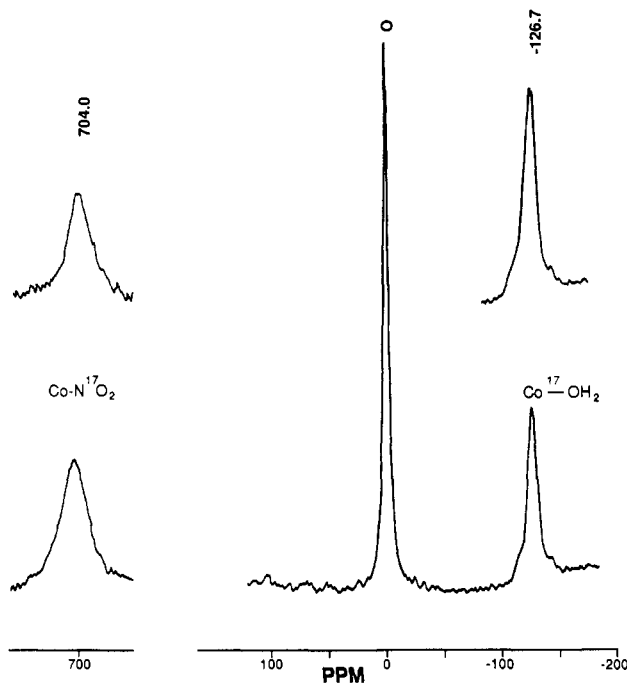
The treatment of *trans*-Co(en)<sub>2</sub>(py)NO<sub>2</sub><sup>2+</sup> (py = pyridine) with CF<sub>3</sub>SO<sub>3</sub>H, followed by reaction of the presumed *trans*-Co(en)<sub>2</sub>(py)(O<sub>3</sub>SCF<sub>3</sub>)<sup>2+</sup> intermediate with aqueous HCl, affords *trans*-[Co(en)<sub>2</sub>(py)Cl]Cl<sub>2</sub>,<sup>12</sup> previously an elusive complex.<sup>13</sup> The nitro group is lost in seconds at 0 °C, without rearrangement at the cobalt center. The presumed *trans*-Co(en)<sub>2</sub>(py)(O<sub>3</sub>SCF<sub>3</sub>)<sup>2+</sup> intermediate was not characterized until a need for a synthesis of *trans*-Co(en)<sub>2</sub>(py)(OSMe<sub>2</sub>)<sup>3+</sup> arose. The obvious route for this latter complex, reaction of this supposed triflate species in Me<sub>2</sub>SO, surprisingly and consistently yielded instead *trans*-Co(en)<sub>2</sub>(py)-OH<sub>2</sub><sup>3+</sup>. Both *trans*-Co(en)<sub>2</sub>(py)(OSMe<sub>2</sub>)<sup>3+</sup> and *trans*-Co(en)<sub>2</sub>(py)(O<sub>3</sub>SCF<sub>3</sub>)<sup>2+</sup> have since been synthesized by alternative routes,<sup>12</sup> and they are *not* hydrolyzed to the observed aqua complex by adventitious water under the preparative conditions. Thus, it seems the aqua ion is derived directly from the nitro complex, implicating NO<sub>2</sub><sup>-</sup> as the source of oxygen in the *trans*-Co(en)<sub>2</sub>(py)OH<sub>2</sub><sup>3+</sup> product.

We turned our attention to the behavior of the (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup> complex in CF<sub>3</sub>SO<sub>3</sub>H because of its direct relevance to the long-known, corresponding reaction of the pentaammine nitrito complex.<sup>2,14</sup> As expected, (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup> yielded (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> rather than (NH<sub>3</sub>)<sub>5</sub>Co(O<sub>3</sub>SCF<sub>3</sub>)<sup>2+</sup>. A spectrophotometric study established that the primary reaction was complete in 2–3 min at ambient temperature. Furthermore, the nitro complex and the aqua product were the only species observed during the reaction, as evidenced by the sharp isosbestic points and the quantitative comparison of the initial and final spectra with authentic specimens of (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> in CF<sub>3</sub>SO<sub>3</sub>H. The (NH<sub>3</sub>)<sub>5</sub>CoO<sub>3</sub>SCF<sub>3</sub><sup>2+</sup> ion is eventually formed via acid-catalyzed substitution of the H<sub>2</sub>O group in (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup>, but very much more slowly.

The extraordinary facility of the nitro-to-aqua complex conversion is clear. It remained to eliminate the trivial possibility that the reaction was a simple metal ion substitution process and that (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> derived from subsequent hydrolysis of (NH<sub>3</sub>)<sub>5</sub>CoO<sub>3</sub>SCF<sub>3</sub><sup>2+</sup> by adventitious water:



The upper part of Figure 1 shows the <sup>17</sup>O NMR spectra for samples of (NH<sub>3</sub>)<sub>5</sub>CoN<sup>17</sup>O<sub>2</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>Co<sup>17</sup>OH<sub>2</sub><sup>3+</sup> derived from the same H<sub>2</sub><sup>17</sup>O (~25 atom %) and recorded in D<sub>2</sub>O at identical cobalt concentrations with the same instrument parameters. It is important to note that (i) the nitro complex has each of its oxygen atoms at exactly half the <sup>17</sup>O enrichment of the aqua complex, because of its method of synthesis (see Experimental



**Figure 1.** <sup>17</sup>O NMR spectra (D<sub>2</sub>O): (lower) labeled (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> derived from it by using neat CF<sub>3</sub>SO<sub>3</sub>H; (upper) (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup>, each obtained from the same sample of H<sub>2</sub><sup>17</sup>O.

Section), and (ii) the relative intensities do not quite reflect relative <sup>17</sup>O abundances (the aqua signal is ca. 1.2 times that of the nitro signal). The lower part of Figure 1 shows the spectra of the <sup>17</sup>O-nitro complex and the aqua complex derived from it, in an equimolar mixture. When one corrects for the intrinsic intensity difference, it is clear that the (NH<sub>3</sub>)<sub>5</sub>Co<sup>17</sup>OH<sub>2</sub><sup>3+</sup> species retains ca. 50% of the label/mol of labeled (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup>. This result demonstrates beyond doubt that *all* of the oxygen of the aqua product is derived from the bound NO<sub>2</sub><sup>-</sup>.

Harris et al. have reported that (NH<sub>3</sub>)<sub>5</sub>CoNO<sub>2</sub><sup>2+</sup> in 98% H<sub>2</sub>SO<sub>4</sub> containing H<sub>2</sub><sup>18</sup>O yields (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> with no detectable <sup>18</sup>O label.<sup>15</sup> Subsequently, (NH<sub>3</sub>)<sub>5</sub>CoOSO<sub>3</sub><sup>+</sup> is formed by displacement of the bound H<sub>2</sub><sup>18</sup>O group by HSO<sub>4</sub><sup>-</sup>, a reaction involving Co–O cleavage. The primary reaction in H<sub>2</sub>SO<sub>4</sub> is considerably slower than in CF<sub>3</sub>SO<sub>3</sub>H, and there is appreciable overlap in the two stages. However the two studies are in agreement in that the NO<sub>2</sub><sup>-</sup> group is the source of oxygen for the (NH<sub>3</sub>)<sub>5</sub>CoOH<sub>2</sub><sup>3+</sup> product.

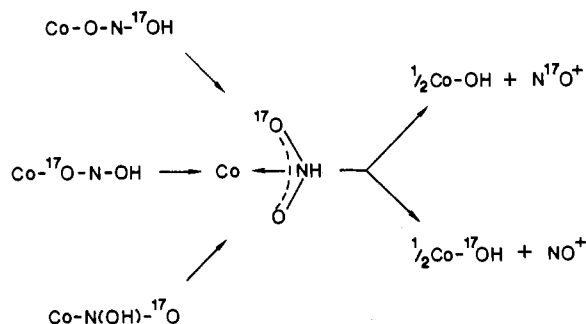
It can be argued that finding the expected percent label in the product derived from labeled reactant, as we have done here, offers more compelling evidence for the mechanism than finding no label<sup>15</sup> when enriched solvent is used, especially when workup requires separation procedures in water of normal isotopic composition, which can lead to the loss of the tracer.

The question should now be asked whether the acid-catalyzed hydrolysis of the nitro complex is related mechanistically to the corresponding reaction of the nitrito linkage isomer.<sup>2,5,14</sup> We have reported<sup>2</sup> that both (NH<sub>3</sub>)<sub>5</sub>CoN<sup>17</sup>O<sub>2</sub><sup>2+</sup> and (NH<sub>3</sub>)<sub>5</sub>Co<sup>17</sup>ONO<sub>2</sub><sup>2+</sup> very rapidly yield <sup>17</sup>O-labeled aqua complexes of identical enrichments in acid solution. It seems that the oxygen atoms have become equivalent en route to the aqua species. However, we have not as yet performed the experiment where the nitrito complex is recovered after partial acid decomposition to test for the possibility of acid-catalyzed scrambling in the unreacted nitrito complex.

An intermediate of the kind shown as follows accommodates our observations, and the present work now suggests the inclusion of a path from the nitro complex to the same intermediate:

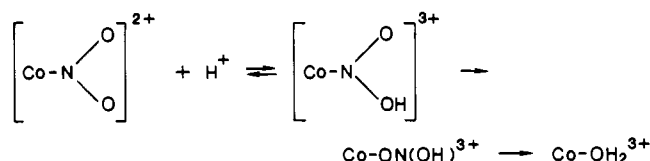
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This scheme does *not* imply that, in the reverse reaction,  $\text{NO}^+$  addition to the  $(\text{NH}_3)_5\text{CoOH}^{2+}$  complex would lead to some nitro complex, but it does require the nitrito complex formed by this route to have its oxygen atoms scrambled. Interestingly, we have had recent difficulty in repeating the synthesis of the stereospecifically labeled nitrito complexes,<sup>2</sup> and until such time that the matter is resolved unequivocally, the above mechanism is regarded as viable.

Note that the present results do not *require* such a mechanism. There are alternatives, one of which is an acid-catalyzed O-to-N-bonded nitrite rearrangement, followed by conversion of the nitrito complex to the aqua species in acid:



The observation of only nitro and aqua complexes during the rearrangement is not inconsistent with such a proposal, since the nitrito complex reacts with  $\text{CF}_3\text{SO}_3\text{H}$  far more rapidly than does the nitro complex, and hence it does not accumulate.

Finally, it is noted that the facile conversion of a bound nitro group to a coordinated aqua group using triflic acid could attract synthetic utility. Indeed, it might be possible to generate aqua complexes stereospecifically. For example, a *trans*- $\text{Co}(\text{en})_2\text{AX}$  complex could yield *trans*- $\text{Co}(\text{en})_2\text{A}(\text{OH}_2)$  exclusively in triflic acid when  $\text{X} = \text{NO}_2^-$ , but a mixture of *cis*- and *trans*-substitution product for  $\text{X} = \text{Cl}^-$  or  $\text{Br}^-$ . The analogy here is to the stereospecific and intramolecular rearrangement of *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{ONO}^+$  to *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{NO}_2^+$  in water,<sup>3,12</sup> whereas the hydrolysis of *trans*- $\text{Co}(\text{en})_2(\text{NCS})\text{X}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{OSMe}_2$ ) leads to substantial geometric change about the metal ion,<sup>16</sup> resulting in 55% *trans*- and 45% *cis*- $\text{Co}(\text{en})_2(\text{NCS})\text{OH}_2^{2+}$ .

We have already exploited this facile reaction in a general synthesis<sup>17</sup> of *trans*- $\text{Co}(\text{en})_2(\text{amine})\text{Cl}^{2+}$  complexes from the aqua complexes, which in turn are prepared from the reaction of the readily available *trans*-nitro(amine) species in triflic acid. [The use of the *trans*-labilizing  $\text{NO}_2^-$  group is analogous to the use of the *trans*-labilizing  $\text{SO}_3^{2-}$  group in synthetic  $\text{Co}(\text{III})$  chemistry, with the  $\text{SO}_3^{2-}$  group being ultimately removed with strong

acid].<sup>18-20</sup> Since the  $\text{Co}(\text{en})_2(\text{amine})\text{X}$  complexes substitute with geometric retention anyway,<sup>16</sup> it cannot be concluded that the nitro-to-aqua complex conversion in triflic acid is inherently stereoretentive about the metal ion, but experiments with  $\text{Co}(\text{en})_2\text{AX}$  complexes, where X is such that the loss of X normally leads to rearrangement, could resolve the question. Nonetheless, these experiments will be difficult because steric change in such complexes is observed only when the A group has a lone pair of electrons, which can form a ligand-to-metal  $\pi$ -bond,<sup>11,16</sup> and it is precisely these ligands that are rapidly stripped from the metal ion with triflic acid. Thus one will need to find  $\text{Co}(\text{en})_2\text{A}(\text{NO}_2)$  species where the loss of the nitro group is much faster than the acid-catalyzed loss of the A group.

### Experimental Section

Oxygen-17 NMR spectra were recorded with use of a Varian XL-200 spectrometer and  $\text{D}_2\text{O}$  solvent. Peak areas were determined by cutting and weighing the chart paper. Trifluoromethanesulfonic acid (MMM Co.) was purified by vacuum distillation. The  $^{17}\text{O}$ -labeled aqua complex was prepared from  $(\text{NH}_3)_5\text{CoO}_3\text{SCF}_3$  ( $\text{CF}_3\text{SO}_3$ )<sub>2</sub> and  $\text{H}_2^{17}\text{O}$  (ca. 25 atom %). It was recrystallized quickly from cold water by using  $\text{NaClO}_4$  (pH 2,  $\text{HClO}_4$ ) immediately prior to use. Visible absorption spectra were recorded on a Cary 210 spectrophotometer.

The  $^{17}\text{O}$ -labeled nitrito complex was prepared as follows. To  $\text{NaNO}_2$  (2.80 g; 0.041 mol) in  $\text{H}_2\text{O}$  (10 mL) cooled to 0 °C was added  $\text{HClO}_4$  (1.17 M; 6.0 mL; 0.0070 mol). This mixture, recooled to 0 °C, was added in one lot to solid  $(\text{NH}_3)_5\text{Co}^{17}\text{OH}_2(\text{ClO}_4)_3$  chilled in an ice-salt bath. With rapid stirring, the aqua complex dissolved only to be replaced within seconds by crystalline nitrito complex. After 1.0 min, the complex was filtered out, washed with ethanol and ether, and dried at the pump. It was recrystallized quickly from water by using concentrated aqueous  $\text{NaClO}_4$  as precipitant. Surprisingly, the  $^{17}\text{O}$  NMR spectrum indicated that the inner and outer oxygen sites were equivalently labeled, this despite the rapid synthesis and crystallization at pH ca. 6 at 0 °C.

The  $^{17}\text{O}$ -labeled nitro complex was synthesized by boiling a concentrated solution of the nitrito complex in water for 5 min. It was crystallized by using  $\text{LiCl}$  and recrystallized from  $\text{H}_2\text{O}/\text{HCl}$ .

A sample of the above  $^{17}\text{O}$ -labeled  $(\text{NH}_3)_5\text{CoNO}_2\text{Cl}_2$  (0.5 g) was added in small portions over ca. 30 s to well-stirred  $\text{CF}_3\text{SO}_3\text{H}$  (7 mL) at ca. 20 °C. The initially yellow solution quickly became deep orange-pink, and after 5 min the solution was poured carefully into chilled and well-stirred dry ether (600 mL) to precipitate a pink-orange solid. This was recrystallized from water by using  $\text{NaClO}_4/\text{HClO}_4$ , and the product was identified as  $^{17}\text{O}$ -labeled  $(\text{NH}_3)_5\text{CoOH}_2(\text{ClO}_4)_3$  (ca. 13% enriched) from its visible spectrum ( $\epsilon_{490}(\text{max})$  47.7; 3 M  $\text{HCl}$ ) and  $^{17}\text{O}$  NMR spectrum in  $\text{D}_2\text{O}$ .

**Acknowledgment.** Financial support from the Australian Research Grants Scheme is gratefully acknowledged. We are also indebted to Leslie Harland of ANU, who recorded the  $^{17}\text{O}$  NMR spectra, and to the Research School of Chemistry of ANU for a Visiting Fellowship. We thank Dr. E. A. Magnusson for helpful comments.

**Registry No.**  $(\text{NH}_3)_5\text{CoO}_3\text{SCF}_3(\text{CF}_3\text{SO}_3)_2$ , 75522-50-8;  $[\text{Co}(\text{NH}_3)_5(^{17}\text{ON}^{17}\text{O})]^{2+}$ , 110486-26-5;  $(\text{NH}_3)_5\text{Co}^{17}\text{OH}_2(\text{ClO}_4)_3$ , 110509-40-5;  $(\text{NH}_3)_5\text{CoN}^{17}\text{O}_2\text{Cl}_2$ , 110486-27-6;  $(\text{NH}_3)_5\text{CoNO}_2^{2+}$ , 14482-68-9;  $\text{CF}_3\text{SO}_3\text{H}$ , 1493-13-6;  $\text{NO}_2^-$ , 14797-65-0.

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