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Oxygen Scrambling in Pentaamminenitritocobalt(III) Revisited

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Abstract

The rapid nitrosation reaction of $(NH_3)_5Co-{}^{17}OH^{2+}$ in water leads to the oxygen bound nitrite ion product $(NH_3)_5Co(ON^{17}O)^{2+}$ having one ^{17}O per cobalt but distributed equally between inner and outer sites. This result is contrary to an earlier report, and the mechanism for this reaction and those for closely related reactions are discussed.

Introduction

In recent years some remarkable new facts have emerged on metal ion nitro/nitrito rearrangements [1–6]. One of us, and others [7] have been unable to reproduce the regiospecific synthesis [1] of $(NH_3)_5Co-{}^{*}ONO^{2+}$ and $(NH_3)_5Co-ON^{*}O^{2+}$, and in this note new data are reported which necessitate the retraction of this and related significant results.

In 1956 the synthesis was reported of $(NH_3)_5Co-{}^{18}ONO^{2+}$ from $(NH_3)_5Co-{}^{18}OH_2{}^{3+}$ and excess HNO_2/NO_2^- [8]. Exactly one equivalent of labelled oxygen per cobalt was introduced, and it was inferred that the Co–O bond was retained in the synthesis. Later this isotope result was confirmed [3], and the syntheses of what were believed to be the regiospecifically labelled $(NH_3)_5Co-{}^{18}ONO^{2+}$ and $(NH_3)_5Co-ON^{18}O^{2+}$ complexes were reported. Surprisingly, acid cleavage of each species yielded $(NH_3)_5Co-{}^{18}OH_2{}^{3+}$ having the same and precisely half the original label, and it was suggested that either H^+ promoted scrambling of the nitrito-*O* oxygens*, or the oxygens had already been scrambled in the synthesis [3].

In 1982 the problem was examined using ^{17}O NMR spectroscopy, and this provided the first opportunity to observe directly the inner and outer oxygens of the nitrite-*O* species [1]. In that work regiospecific oxygen-17 labelling was claimed. Moreover, the specific rate of oxygen scrambling was determined, and perchance it was found to be very similar to the specific rate for the more familiar [10] O- to N-bonded nitrite rearrangement. Furthermore, aqua complex samples derived from $(NH_3)_5Co-{}^{17}ONO^{2+}$ or $(NH_3)_5Co-ON^{17}O^{2+}$, and acid, were shown [1] to have identical ^{17}O-enrichments.

Very recently the acid-catalyzed loss of NO_2^- from the N-bonded species was studied [5], and from an ^{17}O labelling experiment the interesting result emerged that the aqua product derived its oxygen entirely from $(NH_3)_5Co-N^{17}OO^{2+}$. In passing it was observed that $[(NH_3)_5Co-ONO](ClO_4)_2$ obtained from $[(NH_3)_5Co-OH_2](ClO_4)_3$ and $NaNO_2/HClO_4$ had the oxygen label distributed partly if not equally between the two sites, as revealed by its ^{17}O NMR spectrum. It was at first suspected that oxygen scrambling occurred subsequent to nitrito complex formation, and this was in some way catalyzed by H^+, or by a specific anion, akin to the catalysis observed [11] for the nitrosation of the aqua complex. The experiments described herein were performed to assess these prospects.

Results and Discussion

Solid $[(NH_3)_5Co-{}^{17}OH_2](ClO_4)_3$ was treated with an ice-cold $NaNO_2/HClO_4$ mixture containing minimal total acid (NO_2^-/HNO_2 = 10:1). The formation and crystallization of the nitrito species ensued very rapidly (<5 s), and yet the ^{17}O spectrum (Fig. 1a) revealed scrambled oxygens. In other experiments $(NH_3)_5Co-{}^{17}OH_2{}^{3+}$ was used as its trinitrite salt, to examine the question of specific anion analysis. Several experiments were performed, using various acids (HBr, HCl, CF_3SO_3H, CF_3CO_2H, CH_3CO_2H) to effect the nitrosation. In all cases the nitrito complex was found to have scrambled oxygens. Finally, the nitrosation of $[(NH_3)_5Co-{}^{17}OH_2](NO_2)_3$ was found to occur at a rate convenient to observe even in the absence of acid, apart from that provided by dissociation of $(NH_3)_5Co-OH_2{}^{3+}$ (pK_a 6.5). This reaction was followed directly by ^{17}O NMR (Fig. 2), and at no stage was preferential site labelling observed – the

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*Strictly, this can be evaluated only by directly examining the inner and outer oxygens of nitrite complex recovered during acid decomposition. Note that it is possible to have the label migrate from one site to the other without scrambling the oxygens of the parent nitrito species (*vide infra*) [9].

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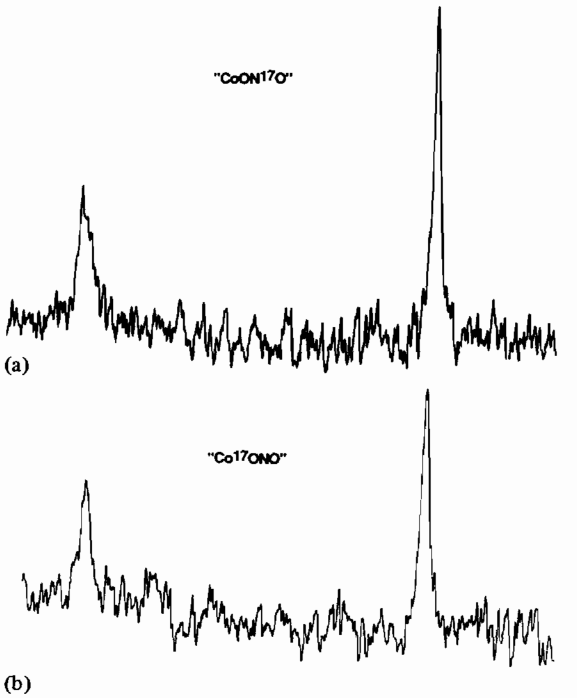


Fig. 1. (a) ^{17}O NMR spectrum (40.66 MHz) of $(NH_3)_5Co(^{17}ONO)^{2+}$ in D_2O; the complex was prepared from $(NH_3)_5Co^{17}OH_2^{3+}$ (20 at%) and unlabelled HNO_2/NO_2^-. (b) ^{17}O NMR spectrum of $(NH_3)_5Co(ON^{17}O)^{2+}$ in D_2O; the complex was prepared from unlabelled $(NH_3)_5CoOH_2^{3+}$ and ^{17}O-enriched HNO_2/NO_2^- (40 at%).

inner (430 ppm) and outer (760 ppm) signals grew in concert. Also, we should note that in none of these experiments was there any loss of the ^{17}O label to the solvent via the reverse reaction.

The spectrum shown in Fig. 1a is that for the nitrito isomer prepared from $(NH_3)_5Co{-}^{17}OH_2^{3+}$ and NO^+, ostensibly $(NH_3)_5Co{-}^{17}ONO^{2+}$. This spectrum, as well as that shown in Fig. 2, reveal that the lower field signal is smaller than the other. However this resonance is also consistently broader, although not quite sufficiently so to compensate. Intrinsic intensity differences in ^{17}O NMR signals have been noted previously [5], but it nonetheless became important to examine the possibility that the oxygens were only partly scrambled during the synthesis of $(NH_3)_5Co^{17}$-ONO^{2+}, and that once isolated, this species only slowly exchanged its oxygens. To this end we synthesized the ^{17}O labelled nitrito complex from $(NH_3)_5$-$Co{-}OH_2^{3+}$ and $HN^{17}O_2/N^{17}O_2^-$, and its spectrum is shown in Fig. 1b. The result is clear. An identical intensity pattern pertains, and the oxygens are genuinely scrambled.

Interestingly, the ^{17}O NMR spectra of the materials originally believed to be $(NH_3)_5Co{-}ON^{17}O^{2+}$ and $(NH_3)_5Co{-}^{17}ONO^{2+}$ in Me_2SO-d_6 show a single common resonance. The lower field signal ($Co{-}ON^{17}O$) is not seen because it is broadened into the baseline, but it is observed at much higher concentrations. These observations not only confirm that the oxygens are scrambled, but they also warn of the

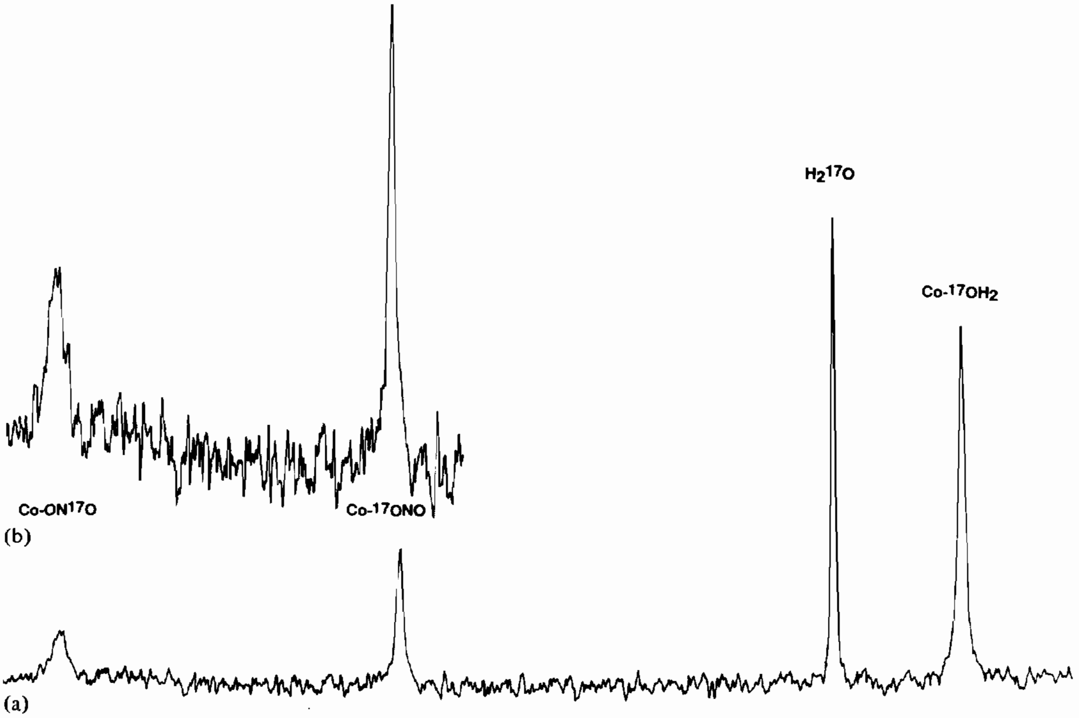


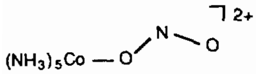
Fig. 2. ^{17}O NMR spectrum (40.66 MHz) of $[(NH_3)_5Co^{17}OH_2](NO_2)_3$ in D_2O at *ca.* 20 °C after 10 min, revealing unreacted aqua complex and the statistically-labelled nitrito complex.

dangers of inferring regiospecific labelling using only one of the pair of labelled species. Clearly it is imperative to record the spectra of both species.

It must be concluded that the usual synthesis [3–5, 8, 10] of $(NH_3)_5Co{-}ONO^{2+}$ results in the incorporation of just one labelled oxygen, but it is distributed equally between the two sites, *i.e.* the Co–O bond is not retained in the synthesis. Moreover the scrambling is neither acid nor specific anion-catalyzed (other than by HNO_2 or NO_2^-).

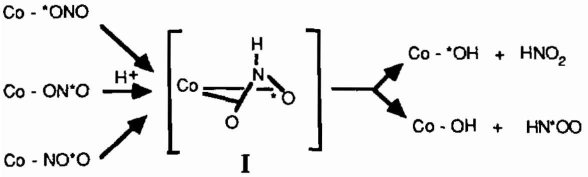
There is no precedence for the extremely rapid oxygen–oxygen rearrangement of the kind implied here. The results require a half-life shorter than the order of a minute at 20 °C (the time for a reasonable ^{17}O NMR spectrum is *ca.* 5 min for a 20% enriched sample), whereas species such as $(NH_3)_5Co{-}^{17}OCO_2^+$ or $(NH_3)_5Co{-}^{18}OC(CH_3)O^{2+}$ involve half-lives of many hours under comparable conditions [13]. In this regard, we can see no fundamental reason why $(NH_3)_5Co{-}^{17}ONO^{2+}$ or $(NH_3)_5Co{-}ON^{17}O^{2+}$, if either can be prepared, should be any different to the above species. Unfortunately the competitive O- to N-rearrangement is too fast to observe two different rates for intermolecular oxygen exchange for the $(NH_3)_5Co{-}ONO^{2+}$ ion in $H_2{}^{17}O$ under neutral conditions, as has been achieved with species such as $(NH_3)_5Co{-}OC(R)O^{2+}$ [14] and $(en)_2Co(NH_2CH_2\text{-}OCO)^{2+}$ [15], and which could have verified slow intramolecular oxygen scrambling by alternative means.

The solid-state structure [16] of $(NH_3)_5Co{-}ONO^{2+}$ reveals the transoid conformation where nitrite has inequivalent oxygens



The ^{17}O NMR data establish the persistence of inequivalent oxygens in solution, and the observation of the two resonances separated by 330 ppm (at 40.662 MHz) sets a maximum specific rate for oxygen scrambling of *ca.* 10^4 s^{-1}. However, knowledge of this rather high limit does not assist in the resolution of the present problem.

The difficulty of rapidly scrambled oxygen sites is removed if it is proposed that the oxygens become equivalent during the synthesis rather than subsequently. Such a proposal requires essential irreversibility under the conditions of the synthesis, otherwise loss of label to the solvent via HNO_2/H_2O oxygen exchange must occur. As was recently pointed out [5], species **I** accomodates the observations of the fate of the oxygen label for the reactions of both the nitro and nitrito linkage isomers. It is noted that a proton is associated with this species (probably on the nitrogen center), to accommodate the exclusive formation of the nitrito species from $(NH_3)_5Co{-}OH^{2+}$ + NO^+ (although nitro formation from $(NH_3)_5Co{-}OH^{2+}$ + NO^+ by this mechanism is not required), and also to distinguish it from similar species discussed ahead. **I** is distinct from the similar intermediate **III**, believed to be formed by capture of NO_2^- by the pentacoordinate intermediate $(NH_2)(NH_3)_5Co^{2+}$, formed during the base hydrolysis of $(NH_3)_5CoX^{n+}$ in NO_2^- media [17]. **III** is also believed to be involved in the base-catalyzed O- to N-rearrangement of the nitrito ion [3, 4, 13]. Here the decay by oxygen capture is significantly more competitive than by nitrogen (2:1). The species **I** is distinct also from **II**; the latter is the corresponding intermediate believed to be involved in the spontaneous O- to N-rearrangement [1–4, 13].



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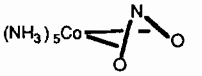

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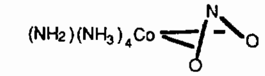

III

In summary, the oxygen sites of $(NH_3)_5Co{-}ONO^{2+}$ prepared by NO^+ addition to $(NH_3)_5Co{-}OH^{2+}$ become equivalent, if only transiently. A π-bonded HNO_2 intermediate is proposed, which of course must be the same for the forward and reverse reactions, and this intermediate may also be that involved in the acid decomposition of $(NH_3)_5Co{-}NO_2{}^{2+}$.

Until such time as a regiospecific synthesis is devised, the speed of interconversion of $(NH_3)_5Co{-}{}^*ONO^{2+}$ and $(NH_3)_5Co{-}ON^*O^{2+}$ remains unknown. It also remains unknown whether this is catalyzed by H^+ or by OH^- or both.

Experimental

^{17}O NMR spectra were recorded with the use of a Varian XL-300 spectrometer operating at 40.662 MHz, and a 5 mm probe. Quoted shifts are ppm downfield from $H_2{}^{17}O$; the solvents were D_2O or $Me_2SO\text{-}d_6$. The synthesis of $[(NH_3)_5Co^{17}ONO]\text{-}(ClO_4)_2$ has been described elsewhere [5]. The 'outer-labelled' species was prepared as follows. To a solution of $NaNO_2$ (0.20 g) in ^{17}O-water (1.00 ml; 40 at%; Amersham) chilled on ice was added concentrated $HClO_4$ (11.7 M, 25 μl) also at 0 °C; the mixture was allowed to come to isotopic equilibrium (5 min). To this stirred mixture was added finely divided $[(NH_3)_5CoOH_2](ClO_4)_3$ (0.20 g); it quickly transformed on vigorous stirring to yield the labelled orange nitrito complex essentially quantitatively. The product was recrystallized quickly from ice-water/$NaClO_4$ as described previously [5].

The salt $[(NH_3)_5Co^{17}OH_2](CF_3SO_3)_3$ [1] in saturated aqueous solution was treated with excess solid $NaNO_2$. The mixture was filtered and cooled to yield crystals of $[(NH_3)_5Co^{17}OH_2](NO_2)_3$ contaminated with a little $[(NH_3)_5Co^{17}ONO](NO_2)_2$. To the filtrate was added a quarter volume of saturated aqueous $NaClO_4$ and after a short time crystals of pure $[(NH_3)_5Co(^{17}ONO)](ClO_4)_2$ deposited.

For the NMR experiments, saturated solutions in D_2O (or Me_2SO-d_6) were employed. For the nitrosation of $[(NH_3)_5Co-^{17}OH_2](NO_2)_3$ studied *in situ*, the acid HBr, HCl, CF_3SO_3H, CF_3CO_2H, or CH_3CO_2H) was added by micropipette (30 μl) and spectra run at 5 min intervals. There was some deposition with HBr and HCl. In one set of runs no acid was added.

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