length of more than 1.8 Å. It is known the N_2H_2 complex gives two types of reduction products, NH_3 and N_2H_4.[2] Therefore, **5** is concerned with the formation of the N_2H_4 complex and **6** will give NH_3.

In the case of the $NHNH_2$ complex, Figure 2 shows that the third protonation to N_A has the $NHNH_2$ fragment released. The net charge of the fragment with $r_{Cr-N} = 2.57$ Å is calculated to be 1.053+ ($NHNH_2^+$), which shows two electrons to be transferred from the metal moiety, $Cr(PH_3)_4$. The $NHNH_2^+$ released will decompose to give NHNH and H^+. It should be noted here that the experimental results showed that two molecules of NHNH react to form N_2 and N_2H_4.[10] The reaction is theoretically discussed by Yamabe et al.[11] on the basis of MINDO/3 calculations. Therefore, equimolar N_2H_4 and N_2 are expected to be evolved when the reduction goes through this mechanism. $WCl_3H(PMePh_2)_2(NNH_2)$ in methanol solution gives almost equimolar N_2H_4 and N_2 as the reduction products.[3] For this reaction, the $NHNH_2$ complex is considered to be along the route to N_2H_4. The mechanism mentioned above will account for the proportion of the products from the W complex. However, it is necessary to note that the effect of the trans ligand is neglected in the calculations.

It is necessary to break the N–N bond for the production of NH_3 in the mechanism of the N_2H_3 complex. The N–N bonds optimized in the N_2H_2 and N_2H_3 complexes are 1.273 and 1.434 Å, respectively. Though the N–N bond is weakened by the third protonation, the bond does not break to form NH_3 at this stage. On the other hand, Figure 2 also shows that the N_2H_3 fragment of **6** is released from the complex. The net charge of the fragment with $r_{Cr-N} = 2.5$ Å is 1.073+ ($N_2H_3^+$), which confirms that it accepts two electrons from the metal fragment. However, the formation of NH_3 is not expected even though $N_2H_3^+$ is released from the N_2H_3 complex. On the other hand, it is known that the substitution of phosphine ligands with halogen atoms in the reduction of the ligand nitrogen molecule occurs. Therefore, further calculations including this effect are needed in order to account for the process of NH_3 and N_2H_4 formation as the reduction products.

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Registry No. **5**, 81522-87-4; **6**, 81522-86-3.

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(10) Willis, C.; Back, R. A. *Can. J. Chem.* **1973**, *51*, 3605.

(11) Yamabe, T., Fukui, K. *Kagaku, Zokan (Kyoto)* **1978**, *No. 18.*

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Mechanistic Information from Oxygen-17 NMR Measurements. Evidence for the Existence of Oxygen-Bonded (Sulfito)pentaamminecobalt(III) in Weakly Acidic Aqueous Solution

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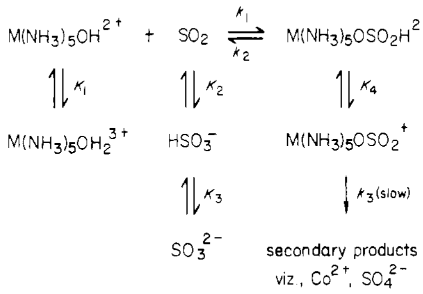
It has been suggested in the literature that $Co(NH_3)_5OH^{2+}$ reacts with SO_2 in aqueous solution to produce an O-bonded sulfito complex $Co(NH_3)_5OSO_2^+$, which on acidification releases SO_2 and forms the corresponding aquo complex. The kinetics of both processes suggested that no Co–O bond breakage is involved. ^{17}O-exchange experiments have now been performed with ^{17}O NMR and indicate that the earlier suggestions are correct.

Introduction

In contrast to numerous studies reported on the formation and stability of S-bonded sulfito complexes (see the literature cited in ref 1), very little has until recently been reported on the formation and reactivity of O-bonded sulfito complexes. A number of authors[2-7] have speculated on the possible formation of such species but, due to the lack of direct evidence in many cases, failed to illustrate their chemical significance.

Kinetic evidence for the formation of O-bonded sulfito complexes of the type $M(NH_3)_5OSO_2^+$ (M = Co(III), Rh(III), and Cr(III)) was reported recently.[1,8] In these studies the kinetics and mechanism of SO_2 uptake by the $M(NH_3)_5OH^{2+}$ species in weakly acidic medium and of the acid-catalyzed aquation (loss of SO_2) of $M(NH_3)_5OSO_2^+$ were investigated. Such reactions are very rapid and similar in nature to the corresponding CO_2 uptake/acid-catalyzed decarboxylation processes.[9-11] The suggested mechanism is outlined in Scheme I, in which the participating hydrogen ions

Scheme I



M ≡ Co(III), Rh(III), Cr(III)

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(1) van Eldik, R; Harris, G. M. *Inorg. Chem.* **1980**, *19*, 880.

(2) Tsiang, H. G.; Wilmarth, W. K. *Inorg. Chem.* **1968**, *7*, 2535.

(3) Murray, R. S.; Stranks, D. R.; Yandell, J. K. *J. Chem. Soc. D* **1969**, 604.

(4) Caryle, D. W.; King, E. L. *Inorg. Chem.* **1970**, *9*, 2333.

(5) Thacker, M. H.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1975**, 704.

(6) Bazsa, G.; Diebler, H. *React. Kinet. Catal. Lett.* **1975**, *2*, 217.

(7) Ramasami, T.; Wharton, R. K.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 359.

(8) van Eldik, R. *Inorg. Chim. Acta* **1980**, *42*, 49.

(9) Chaffee, E.; Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4169.

(10) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965.

(11) van Eldik, R.; Palmer, D. A.; Kelm, H.; Harris, G. M. *Inorg. Chem.* **1980**, 19, 3679.

0020-1669/82/1321-2818$01.25/0

are omitted for simplicity reasons and all *K*'s are defined as acid dissociation constants. Typical values for M = Co(III) are[1] $pK_1 = 6.30 \pm 0.05$, $pK_2 = 1.74 \pm 0.05$, $pK_3 = 6.3 \pm 0.1$, $k_1 = (2.6 \pm 0.6) \times 10^8$ M^{-1} s^{-1}, and $k_2/K_4 = (2.2 \pm 0.4) \times 10^6$ M^{-1} s^{-1} at 10 °C, and k_3 (intramolecular redox reaction) $= (2.5 \pm 0.4) \times 10^{-3}$ s^{-1} at 15 °C. Similar values for k_1 were reported[8] for M = Rh(III) and Cr(III), which are approximately 10^6 times larger than the corresponding rate constants for CO_2 uptake.[9,10] The rates of these processes (uptake and loss of SO_2) suggest that the reactions occur via the formation and breakage of O–S bonds, respectively, during which the M–O bonds remain intact. No direct evidence for this suggestion could be presented[1,2] since the O-bonded sulfito species could not be isolated in any of the studied systems due to subsequent secondary reactions. These include an intramolecular redox reaction for the Co(III) system during which Co^{2+} and SO_4^{2-} are produced and possible isomerization (O to S bonded) and/or subsequent substitution reactions (e.g., formation of *trans*-$M(NH_3)_4(SO_3)_2^-$) for the Rh(III) and Cr(III) systems.

Isotope-labeling techniques offer an alternative approach to obtain further information on the intimate mechanism of such reactions. An ^{18}O-labeled carbonato complex was used to illustrate[12,13] that the Co–O bond remains intact during the acid-catalyzed decarboxylation of $Co(NH_3)_5OCO_2^+$, thus providing direct evidence for O–C bond breakage. We have now performed similar experiments on the O-bonded $Co(NH_3)_5OSO_2^+$ species using ^{17}O labeling and NMR as analytical techniques.

Experimental Section

$[Co(NH_3)_5OH_2](ClO_4)_3$ was prepared as described elsewhere.[1,14] Chemical analyses[15] are in agreement with the theoretical values and the UV–visible spectra (recorded on a Perkin-Elmer 555 spectrophotometer) are similar to those reported in the literature.[16,17] The ^{17}O-enriched aquo complex was prepared by heating a saturated solution of the complex in 20% $H_2{}^{17}O$ (Ventron) for 3 days at 40 °C and pH ~4. As shown by the ^{17}O NMR spectra, the water exchange process is complete within this period,[18] after which the labeled complex was isolated by freeze-drying. Alternatively, the labeled complex can be precipitated by adding $HClO_4$ (concentrated) dropwise to the solution. The complex was washed with alcohol and ether and dried at 50 °C. UV–visible spectra of the labeled complex were identical with those of the unlabeled species.

^{17}O NMR FT spectra were recorded at 13.56 MHz on a Varian XL-100 spectrometer. The labeled complex was dissolved in 99.99% $H_2{}^{16}O$ (Ventron) to minimize the influence of the natural ^{17}O contents of pure water.

Results and Discussion

The validity of the suggested mechanism in Scheme I for M = Co(III) depends on our ability to present direct evidence for the existence of the $Co(NH_3)_5OSO_2^+$ species. If $Na_2S_2O_5$ is added to a solution containing $Co(NH_3)_5OH_2^{3+}$ (pH ~4–5) (λ_{max} = 490, 343 nm; ϵ_{max} 49, 47 M^{-1} cm^{-1}), an almost instantaneous color change occurs due to the formation of the sulfito complex (λ_{max} = 518, 330 nm; ϵ_{max} ~88, 2100 M^{-1} cm^{-1}). This step is immediately followed by the mentioned redox reaction (k_3), which has a half-life on the order of 10–20 s at room temperature. Acidification of the sulfito complex, therefore, results only in the partial recovery of $Co(NH_3)_5OH_2^{3+}$ since in the meantime some of the complex has decomposed to Co^{2+} and SO_4^{2-}. This secondary effect can be minimized by performing the acidification almost immediately after the completion of the fast formation reaction (see kinetic data in ref 1). If this reaction sequence is repeated with the ^{17}O-labeled complex, NMR spectra should show whether any significant M–O bond breakage occurred during the formation and acidification reactions of the sulfito complex. Such NMR measurements require a fairly concentrated solution of the cobalt complex in order to achieve reasonably short data accumulation times. Under such conditions (recording times of ca. 1 h), the slow water exchange of $Co(NH_3)_5OH_2^{3+}$ with the bulk solvent can be neglected. In addition, acidification with perchloric acid following the sulfito complex formation process places a further restriction on the solubility of the aquo complex. Therefore, a series of preliminary experiments were performed to determine the ideal conditions for the actual measurements. Similarly, NMR spectra were recorded under various conditions to optimize the measurements for bound water.

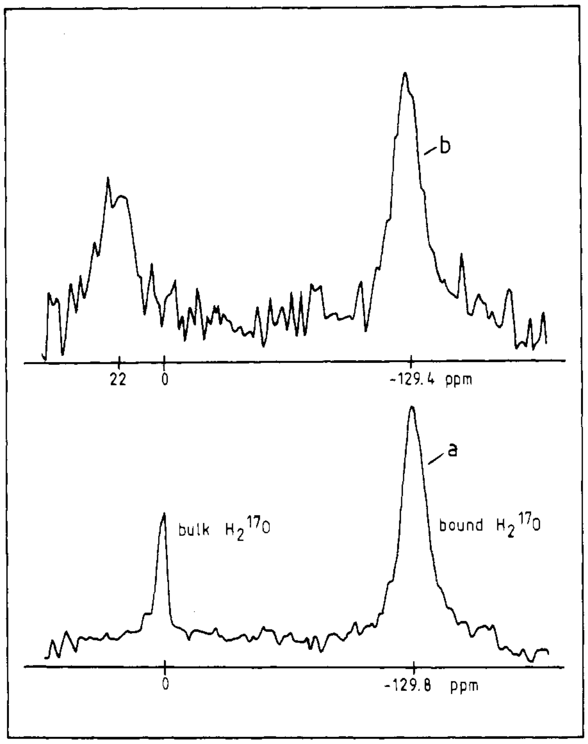

Figure 1. ^{17}O NMR spectrum of $Co(NH_3)_5{}^{17}OH_2^{3+}$ dissolved in $H_2{}^{16}O$ (a) before and (b) after formation and acidification of sulfito complex—see discussion.

A typical experiment, for which the results are presented in Figure 1, was performed in the following way: 100 mg of $[Co(NH_3)_5{}^{17}OH_2](ClO_4)_3$ was dissolved in 3.0 mL of $H_2{}^{16}O$ (i.e., 0.072 M) and the NMR spectrum recorded by accumulating 90000 pulses over a period of 1 h at 32 °C. A 50-mg sample of $Na_2S_2O_5$ (≡0.17 M HSO_3^-) was then added to the solution and dissolved, after which 5 s were allowed for proper mixing and the formation of the sulfito complex before the solution was acidified to pH ~1 by a dropwise addition of $HClO_4$ (concentrated). The two very distinct color changes associated with the formation and acidification of the sulfito complex were clearly observed during these operations. A control experiment demonstrated that the formation of the sulfito complex occurs instantaneously and goes to completion under these conditions ($k_{obsd} \approx 3 \times 10^5$ s^{-1} pH 4.5 and 32 °C according to the kinetic data reported in ref 1). The NMR spectrum was recorded immediately after, under the same conditions. The UV–visible spectrum of the final solution indicated that approximately 0.058 M of the aquo complex had been regenerated during the acidification process. This

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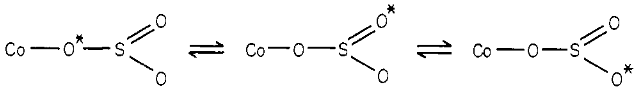
(12) Hunt, J. B.; Rutenberg, A. C.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 268.
(13) Bunton, C. A.; Llewellyn, D. R. *J. Chem. Soc.* **1953**, 1692.
(14) Basolo, F.; Murmann, R. K. *Inorg. Synth.* **1953**, *4*, 172.
(15) Hoechst, AG, Analytical Laboratory, Frankfurt/Main, FRG.
(16) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1975**, *14*, 10.
(17) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1968**, *90*, 6360.
(18) Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642.

means that approximately 0.014 M Co^{2+} was produced during the 5-s time interval, which is in good agreement with the amount expected from the kinetic data for the redox decomposition of the sulfito complex[1] at 32 °C, viz., $k_{obsd} = 3.8 \times 10^{-2}$ s^{-1}.

The NMR spectrum recorded in Figure 1a is—besides having a higher resolution—in very good agreement with that reported by Taube and co-workers.[19] A resonance for the metal-bound water is observed upfield (−130 ppm) from the resonance for the bulk water (0 ppm) and is markedly broader than the latter. The spectrum after formation and acidification of the sulfito complex (Figure 1b) shows a similar upfield shifted resonance for the bound water. However, the bulk water ^{17}O resonance is shifted downfield by 22 ppm and is broadened markedly. Both effects can be ascribed to the presence of paramagnetic Co^{2+} in such reaction mixtures. In addition, an independent experiment was performed to illustrate that the ^{17}O water resonance in a series of aqueous $Co(NO_3)_2$ solutions shifts downfield and broadens in the same way as it was observed for the reaction mixtures under consideration. It was found that 0.016 M Co^{2+} caused a downfield shift of approximately 20 ppm, which is in close agreement with the shift observed in Figure 1b and the predicted Co^{2+} content of the solutions as deduced from their UV–visible spectra.

The spectra of Figure 1 clearly indicate that, besides line broadening and the shifting mentioned above, no major intensity changes occur for both the bound and bulk water resonances. This proves that the $Co{-}^{17}OH_2$ bond remains intact during both the formation and the acid-catalyzed aquation reactions of the sulfito complex such that these processes must involve secondary ligand bond formation and breakage, respectively. These results, therefore, underline the suggested formation and existence of the O-bonded sulfito species as outlined in Scheme I.

Additional conclusions can be drawn from the ^{17}O NMR spectra: It is conceivable that the O-bonded sulfito ligand undergoes a linkage rotation process during which different oxygen atoms are bound to the metal center, viz., O-scrambling.



If such a process is fast compared to the lifetime of the sulfito complex, one would first of all expect the bound-oxygen peak to reduce to one-third of its intensity during the performed reactions (due to statistical reasons) and second, that a signal for labeled SO_2/HSO_3^- should appear in the spectrum. The results in Figure 1 illustrate that no such linkage rotation occurs. Furthermore, an intensive search for a signal of ^{17}O-labeled SO_2/HSO_3^- did not reveal any minor peaks in the characteristic regions (SO_2 513 ppm; SO_3^{2-} 235 ppm).[20] However, a very small peak was observed at ~153 ppm which is ascribed to the presence of labeled HSO_4^- in solution.[20] This is within expectation since sulfate is produced along with Co^{2+} in a ratio[1] of 1:2 during the redox reaction and will be present as bisulfate in acidic solution (pH ~1). Alternatively, if the O-bonded sulfito ligand was capable of undergoing such a rapid linkage rotation process along with a rapid oxygen-exchange reaction with the bulk solvent, the bound-water resonance is expected to disappear almost completely during the performed reactions. This is once again not the case, and we must conclude that the O-bonded sulfito species is indeed stable toward oxygen exchange. The metal–oxygen bond is only broken during the electron-transfer reaction, and the released ^{17}O then shows up as labeled HSO_4^-/SO_4^{2-}, depending on the pH of the solution.

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(19) Jackson, J. A.; Lemons, J. F.; Taube, H. *J. Chem. Phys.* **1960**, *32*, 553.

(20) Kintzinger, J.-P. "NMR Basic Principles and Progress"; Diehl P., Fluck, E., Kosfield, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17, p 32.