Registry No. $H_3B_3N_3H_3$, 6569-51-3; $D_3B_3N_3H_3$, 16331-01-4; $H_3B_3N_3(CH_3)_3$, 1004-35-9; $D_3B_3N_3(CH_3)_3$, 14978-51-9; $H_3B_3N_3(C_2H_5)_3$, 7360-03-4; $D_3B_3N_3(C_2H_5)_3$, 59753-01-4; DBF_2, 13709-79-0; D_2, 7782-39-0.

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Isotopic Exchange and Substitution Reactions of Sulfitopentaamminecobalt(III) and *cis*-Disulfitotetraamminecobalt(III). Direct Evidence for the Specific Trans-Labilizing Influence of the Sulfito Ligand

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The S-bonded sulfito ligand (SO_3^{2-}) has been reported to exert a marked trans-labilizing influence in a variety of cobalt(III) complexes.[2-7] Evidence for such an influence has been deduced from either (i) synthetic studies in which it was found that only the ligands trans to SO_3^{2-} are readily replaced by other ligands[4,5,8] or (ii) the observation of enhanced rates of substitution for complexes containing SO_3^{2-} ligands.[2,3,6,7] In some instances, kinetic studies have provided evidence for a limiting S_N1 mechanism for the substitution reactions of such complexes.[2,3,6,7]

While the results of the studies cited above can be accommodated most plausibly in terms of explanations involving a specific trans-labilizing influence of the sulfito ligand, such an interpretation is not in every case unequivocal. In some cases, at least, the observations are also consistent with a general labilizing influence of the sulfito ligand, the formation of the monosubstituted trans product (e.g., $[trans\text{-}Co(NH_3)_4(SO_3)(H_2O)]^+$ from $[Co(NH_3)_5(SO_3)]^+$ [3] and $[trans\text{-}Co(CN)_4(SO_3)(H_2O)]^{3-}$ from $[trans\text{-}Co(CN)_4(SO_3)(NH_3)]^{3-}$ [6]) being thermodynamically, rather than purely kinetically, favored. In order to distinguish between these two possibilities and establish unequivocally whether SO_3^{2-} exhibits a specific trans-labilizing influence in cobalt(III) complexes, two investigations were undertaken, namely, (1) determination of the extent of exchange of $[Co(NH_3)_5(SO_3)]^+$ with $^{15}NH_3$[9] and (2) examination of the substitution reactions of $[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$ with $^{15}NH_3$ and with other ligands. The results of these studies, reported in this paper, do serve to confirm unambiguously the specific trans-labilizing influence of the sulfito ligand.

Experimental Section

$[Co(NH_3)_5(SO_3)]_2SO_3\cdot 2H_2O$ (**1**) and $NH_4[cis\text{-}Co(NH_3)_4(SO_3)_2]\cdot 3H_2O$ (**2**) were prepared and isolated according to literature procedures.[4,10] Anal. Calcd for **1**: Co, 20.9; S, 17.0; O, 31.2. Found: Co, 20.6; S, 16.8; O, 30.9. Calcd for **2**: S, 17.8; N, 19.5; H, 6.2. Found: S, 17.9; N, 19.4; H, 6.2.

Table I. Exchange of $[Co(NH_3)_5(SO_3)]^+$ and $[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$ with $^{15}NH_3$

Complex	Amt, mmol	Vol of 1.2 M $^{15}NH_3$ soln,[a] ml	No. of NH_3 ligands exchanged[c]
$[Co(NH_3)_5SO_3]^+$	0.07	2.0	1.21
	0.07	2.0	1.18
	0.07	2.0	1.18
	0.07	2.0	0.96
	0.14	1.0	1.05
	0.035	4.0	0.99
	0.07	2.0[b]	0.98
		Mean	1.08 ± 0.1
$[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$	0.06	2.0	2.33
	0.06	2.0	1.97
	0.06	2.0	2.31
	0.06	2.0	1.70
	0.03	4.0	1.98
	0.03	4.0	1.92
	0.06	2.0[b]	1.70
	0.06	2.0[b]	1.63
		Mean	1.94 ± 0.2

[a] 49% $^{15}NH_3$ enrichment unless otherwise noted. [b] 12.5% $^{15}NH_3$ enrichment. [c] After approximately 10 min at 25 °C.

$[Co(NH_3)_4(^{15}NH_3)(SO_3)]_2SO_3\cdot H_2O$ and $NH_4[cis\text{-}Co(NH_3)_2(^{15}NH_3)_2(SO_3)_2]\cdot 3H_2O$ were prepared by dissolving the corresponding unlabeled salts in aqueous solutions of $^{15}NH_3$. Following equilibration for approximately 10 min, the labeled products were isolated, washed with ethanol and ether, and dried.

$^{15}NH_4NO_3$, containing 49% $^{15}NH_4^+$, was obtained from Nuclear Equipment Chemical Corp. and analyzed mass spectrometrically. An aqueous solution of $^{15}NH_3$ (1.2 M, pH 11–12) was prepared by distilling a solution of 1 g of $^{15}NH_4NO_3$ in 10 ml of 1 M NaOH and collecting the distillate in distilled water.

NaOBr was prepared by slowly adding Br_2 to an aqueous solution of NaOH (40 wt %) at 0 °C. The resulting solution was stored at 0 °C.

$NaClO_4$ was prepared by neutralizing an aqueous $HClO_4$ solution with reagent grade Na_2CO_3. The resulting solution was boiled to remove CO_2, filtered while hot, and analyzed by evaporating aliquots at 140 °C to constant weight.

Determinations of ^{15}N content were made mass spectrometrically using an AEI MS9 dual-focus mass spectrometer. NH_3 was liberated from the complex by adding 1 M NaOH, distilling the resulting mixture, and collecting the distillate in 0.25 M H_2SO_4. Argon was bubbled through the solution during distillation to ensure complete liberation of NH_3. The distillate solution was placed in one arm of a Y-tube. A solution of NaOBr was placed in the other arm and the solutions were frozen by immersion in liquid nitrogen. The system was evacuated to below 5 μ for 15 min. To convert the NH_3 to N_2, the solutions were allowed to melt and were mixed. When N_2 liberation ceased, the solution was frozen and all of the N_2 was introduced into the mass spectrometer. The peak heights corresponding to $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ were measured and the percent of ^{15}N was computed. In each case the known amount of nitrogen initially present agreed with the amount recorded by the mass spectrometer.

The kinetics of the substitution reactions were determined at 25.0 °C in solutions in which the ionic strength was held constant at 1.05 M with $NaClO_4$. The reactions were followed spectrophotometrically using a stopped-flow spectrometer in those cases where the rate was too fast for conventional measurement.

Results and Discussion

The results of experiments on the exchange of $[Co(NH_3)_5SO_3]^+$ and $[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$ with $^{15}NH_3$ are summarized in Table I.

The observation that only *one* (1.08 ± 0.10) NH_3 ligand in $[Co(NH_3)_5SO_3]^+$ exchanges with $^{15}NH_3$ demonstrates unequivocally the specific trans-labilizing influence of the SO_3^{2-} ligand. The product of this exchange reaction must be the specifically trans-labeled complex $[trans\text{-}Co(NH_3)_4(^{15}NH_3)(SO_3)]^+$ and the reaction, accordingly, has provided a unique route for the preparation of this and other specifically trans-$^{15}NH_3$-labeled pentaamminecobalt(III) complexes.[11]

To further characterize the labilizing influence of sulfito ligands similar $^{15}NH_3$ exchange experiments were performed on the complex $[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$. The results, also summarized in Table I, reveal that in this case *two* (1.94 ± 0.2) NH_3 ligands exchange with $^{15}NH_3$, the product presumably being $[(trans\text{-}(NH_3)_2)(cis\text{-}(^{15}NH_3)_2)(cis\text{-}(SO_3)_2)Co]^-$. This result confirms the specific trans-labilizing effect of the sulfito ligand and further demonstrates the essential independence of this effect for each sulfito ligand when two such ligands are present in the same complex.

Control $^{15}NH_3$-exchange experiments were performed on $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(S_2O_3)]^+$. Each complex was allowed to react with excess aqueous $^{15}NH_3$ (49% enrichment) for several hours. Samples of the thiosulfato complex contained 0.6% ^{15}N after 0.5 h of reaction, 0.9% ^{15}N after 2.5 h, 1.1% after 5 h, 1.5% after 15 h, and 1.8% after 26 h. One sample of the nitrite complex reaction contained 0.9% ^{15}N after 26 h of reaction. After 26 h, decomposition of the complex was observed in both cases.

The results indicate that fewer than 0.2 of the 5 NH_3 ligands were exchanging with $^{15}NH_3$ after 26 h of reaction and demonstrate that, in contrast to the sulfito ligand, the nitrite and thiosulfato ligands do not exert strong trans-labilizing influences on Co(III) complexes.

As expected, the presence of two SO_3^{2-} ligands in $[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$ also gave rise to facile substitution of two NH_3 ligands by other ligands, for example CN^-, SO_3^{2-}, and NCS^-. In each case two distinct consecutive substitution reactions could be identified spectrophotometrically,[12] as the concentration of the substituting anion was increased, for example

$$[Co(NH_3)_4(SO_3)_2]^- + CN^- \rightleftarrows [Co(NH_3)_3(SO_3)_2(CN)]^{2-} + NH_3 \quad (1)$$

$$[Co(NH_3)_3(SO_3)_2(CN)]^{2-} + CN^- \rightleftarrows [Co(NH_3)_2(SO_3)_2(CN)_2]^{3-} + NH_3 \quad (2)$$

Preliminary kinetic measurements at 25 °C yielded a limiting first-order rate law, i.e., $k[Co(NH_3)_4(SO_3)_2^-]$, for reaction 1, as well as for the corresponding reactions with SCN^- and SO_3^{2-}. In each case the rate of reaction was independent of the concentration of the substituting anion (for example, over the concentration range 0.01–0.05 M, in the case of CN^-), and in each case the value of k was found to be 0.15 ± 0.02 s^{-1}. This kinetic behavior is consistent with, but does not unequivocally demonstrate, a dissociative mechanism similar to that proposed for related substitution reactions of $[Co(NH_3)_5(SO_3)]^+$ and $[trans\text{-}Co(CN)_4(SO_3)(H_2O)]^{3-}$. The value $k = 0.15$ s^{-1} compares with a value of 0.012 s^{-1} for the corresponding limiting first-order rate constants for the substitution reactions of $[Co(NH_3)_5(SO_3)]^+$ with various ligands, i.e.

$$[Co(NH_3)_5(SO_3)]^+ + X^- \rightarrow [trans\text{-}Co(NH_3)_4(SO_3)X] + NH_3 \quad (3)$$

where $X^- = OH^-, CN^-, NO_2^-$, or SCN^-. The effect of introducing a second SO_3^{2-} ligand into the complex (i.e., in a cis position to the NH_3 ligand undergoing replacement) is, thus, to enhance the lability of the complex, but only by a factor of about 12 which seems surprisingly small, especially in view of the change in charge on going from $[Co(NH_3)_5(SO_3)]^+$ to $[cis\text{-}Co(NH_3)_4(SO_3)_2]^-$.

Introduction of a third sulfito ligand was accompanied by only a very slight further enhancement of lability, as reflected in a value of 0.22 ± 0.03 s^{-1} for the limiting first-order rate constant (invariant over the concentration ranges 0.01–0.02 M NH_3 and 0.25–0.35 M SO_3^{2-}) for the reaction

$$[Co(NH_3)_3(SO_3)_3]^{3-} + SO_3^{2-} \rightarrow [Co(NH_3)_2(SO_3)_4]^{5-} + NH_3 \quad (4)$$

These comparisons serve to emphasize the strikingly specific trans-labilizing influence of each SO_3^{2-} ligand (and apparent absence of accompanying cis influences) even when several such ligands are present in the same cobalt(III) complex. The origin of this remarkable influence remains to be fully elucidated.

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Registry No. **1**, 59753-02-5; **2**, 53165-58-5; $[Co(NH_3)_4(^{15}NH_3)(SO_3)]_2SO_3$, 59753-04-7; $NH_4[cis\text{-}Co(NH_3)_2(^{15}NH_3)_2(SO_3)_2]$, 59753-05-8.

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Structure of 1,6-Dioxa-4,9-diaza-5λ^5-phosphaspiro[4.4]nonane, $(OCH_2CH_2NH)_2PH$, by X-Ray Diffraction and Computer Simulation

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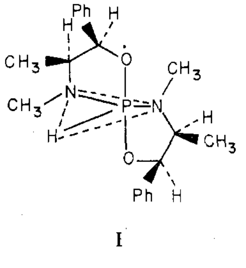
In the context of the Gillespie–Nyholm electron pair repulsion theory (VSEPR),[1] it is of some importance to establish if a small atom like hydrogen, equatorially bonded to phosphorus in a trigonal-bipyramidal framework, is capable of exerting a greater repulsion effect than larger more electronegative atoms positioned at similar equatorial sites. The only substance so far investigated for which an equatorial P–H bond is indicated is HPF_4 whose P–H bond distance was assumed in a structural analysis of its microwave rotational spectrum.[2] The F_{ap}–P–H_{eq} angle was reported[2] as 90 ± 4°. By way of contrast, x-ray analysis[3] of the interesting tricyclophosphorane $[HP(OCH_2CH_2)_3N]BF_4$ revealed an apical P–H bond in a trigonal-bipyramidal frame containing an internal P←N dative bond.

An x-ray diffraction study[4] of the highly substituted spirophosphorane I showed the apical oxygen atoms tilted



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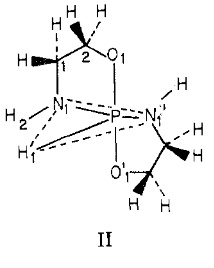

II