N-Methylmonothiocarbamatopentamminecobalt(III): Restricted C–N Bond Rotation and the Acid-Catalyzed O- to S-Bonded Rearrangement

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High-resolution ^{1}H and ^{13}C NMR studies on the linkage isomers $[(NH_3)_5CoOC(S)NHCH_3]^{2+}$ and $[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ reveal that the O-bonded form exists as a 5:1 mixture of *Z* and *E* isomers arising from restricted rotation about the C–N bond. Similarly, restricted rotation is observed (at 20 °C) for the S-bonded isomer (*Z*/*E* ca. 18:1), but not for the isoelectronic carbamate ion $[(NH_3)_5CoOC(O)NHCH_3]^{2+}$, nor for the unsubstituted carbamato complex $[(NH_3)_5CoOC(O)NH_2]^{2+}$. An analysis of the variable-temperature NMR data for the O-bonded carbamato and urea complexes has provided quantitative data on the rotational barriers, and these ions involve much faster C–N bond rotations than the thiocarbamato complexes. The acid-catalyzed reaction of $[(NH_3)_5CoOC(S)NHCH_3]^{2+}$ is confirmed, but there is much less parallel hydrolysis (ca. 2%) than previously reported (40 ± 10%) for 0.1 M HClO$_4$. In 1 M HClO$_4$, $[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ and $[(NH_3)_5CoOH_2]^{3+}$ are formed in parallel as an 83:17 mixture. The kinetic data suggest that the protonated form is at least 20-fold more reactive than the free ion and that the linkage isomerization and hydrolysis pathways are both acid-catalyzed, the latter clearly more so than the rearrangement.

Introduction

The synthesis of the linkage isomers of O- and S-bonded $CH_3NHC(O)S^-$ to $(NH_3)_5Co(III)$ has been reported.[1] The oxygen-bonded form is the less stable and isomerizes to the sulfur-bonded form by both spontaneous and base-catalyzed routes. In neutral solution, isomerization is the sole reaction but in base, hydroxopentaaminecobalt(III) (30 ± 7%) is formed along with the S-bonded isomer.[1] The S-bonded isomer subsequently reacts in base, with production of some cobaltic sulfide. An acid-catalyzed reaction has also been reported, with significant hydrolysis to $[(NH_3)_5CoOH_2]^{3+}$ (40 ± 10%, 0.1 M HClO$_4$) apparently accompanying the reaction.[2] The kinetics revealed a linear dependence on the H$^+$ concentration, with the rate approximately twice as fast in 1 M acid, but only 10% faster under conditions where much more than 10% aqua complex is formed. Thus, it is not clear whether the O to S rearrangement or the parallel hydrolysis path (or both) are acid-catalyzed, and it is hard to understand

the H$^+$ concentration dependence for the amount of parallel hydrolysis observed. We have therefore reexamined the acid dependence of the rate and product distribution to see if they are correlated. In the course of this work, new structural detail in the NMR spectra of the complexes, not evident in the earlier 60-MHz study, became apparent, and thus we also report these data, which bear on the phenomenon of restricted rotation about the C–N bond in monothiocarbamates. Variable-temperature NMR data are also reported for the O-bonded carbamate and urea complexes $[(NH_3)_5Co–OC(O)NH_2]^{2+}$ and $[(NH_3)_5Co–OC(NH_2)_2]^{3+}$ for which the rates of C–N bond rotation have been quantified.

Experimental Section

UV–visible spectra were obtained with Cary 210 dual-beam and HP8452A diode array single-beam spectrophotometers using quartz cells. ^{1}H and ^{13}C NMR spectra were obtained with Varian XL300 and Unity Plus 400-MHz spectrometers, with a probe temperature of 20 °C using Me$_2$SO-d_6 or D$_2$O (Aldrich) as the solvent; shifts are given as parts per million downfield from TMS (Me$_2$SO, DMF-d_7) or NaDSS (D$_2$O), using internal references 1,4-dioxane (δ 69.26) for D$_2$O (^{13}C) and the central peak of the Me$_2$SO-d_6 septet (^{13}C, δ 39.37 ppm) or Me$_2$SO-d_5 quintet (^{1}H, δ 2.50 ppm). Variable-temperature NMR data were collected on a 100-MHz Varian HA100 instrument using DMF-d_7 (Aldrich) as the solvent; a methanol

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Table 1. ^1H and ^{13}C NMR Data for the Carbamato- and Thiocarbamatopentaamminecobalt(III) Complexes at 20 °C in $Me_2SO\text{-}d_6$; J = H−H Coupling Constant in Hz

| complex | salt | ^1H δ, ppm | | | ^{13}C δ, ppm | | |
		Z rotamer	E rotamer	assignment	Z rotamer	E rotamer	assignment
Co−OC(S)NHCH₃	S₂O₆·2H₂O	2.48 (d, 3H) J5	2.69 (d, 3H) J5	CH₃	28.3	31	CH₃
		2.70 (br s, 3H)	2.71 (br s, 3H)	trans-NH₃	189.1	192.6	C(S)O
			3.36 (s, 4H)	H₂O			
		4.10 (br s, 12H)	4.03 (br s, 12H)	cis-NH₃			
		7.71 (q, 1H) J5	7.56 (q, 1H) J5	NH			
	(ClO₄)₂	2.48 (d, 3H) J5	2.71 (d, 3H) J5	CH₃	27.6	30.3	CH₃
		2.57 (br s, 3H)	a	trans-NH₃	188.5	191.9	C(S)O
			3.51 (s)	H₂O			
		4.05 (br s, 12H)	4.00 (br s, 12H)	cis-NH₃			
		7.74 (q, 1H) J5	7.40 (q, 1H) J5	NH			
Co−SC(O)NHCH₃	S₂O₆·2H₂O	2.57 (d, 3H) J5	2.69 (d, 3H) J5	CH₃	26.8	a	CH₃
		3.19 (br s, 12H)	3.22 (br s, 3H)	cis-NH₃	176.2	a	C(O)S
			3.34 (s, 4H)	H₂O			
		3.48 (br s, 3H)	3.42 (br s, 3H)	trans-NH₃			
		7.98 (q, 1H) J5	7.35 (q, 1H) J5	NH			
	(ClO₄)₂	2.60 (d, 3) J5	2.88 (d, 3) J5	CH₃	26.6	28.7	CH₃
		3.18 (br s, 12H)	3.28 (br s, 12H)	cis-NH₃	176.2	179.8	C(O)S
		3.37 (br s, 3H)	3.37 (br s, 12H)	trans-NH₃			
		8.05 (q, 1H) J5	7.40 (q, 1H) J5	NH			
	ZnCl₄·H₂O	2.57 (d, 3H) J5	2.81 (d, 3H) J5	CH₃	26.3	29	CH₃
		3.30 (br s, 12H)	3.35 (br s, 3H)	cis-NH₃	176.2	179.8	C(O)S
			3.40 (s, 2H)	H₂O			
		3.61 (br s, 3H)	a	trans-NH₃			
		8.00 (q, 1H) J5	7.32 (q, 1H) J5	NH			
Co−OC(O)NH₂	NO₃·ClO₄	2.66 (br s, 3H)		trans-NH₃	166.3		C(O)O
		3.77 (br s, 12H)		cis-NH₃			
		5.25 (br s, 2H) a		NH₂			
Co−OC(O)NHCH₃	(ClO₄)₂	2.49 (s, 3H)		CH₃	27.9		CH₃
		2.60 (br s, 3H)		trans-NH₃	165.0		C(O)O
		3.75 (br s, 12H)		cis-NH₃			
		5.13 (br s, 1H) a		NH			

standard was used to calibrate temperature. Line-shape analyses and the extraction of rate and activation barrier data were performed using standard software (DNMR, UnGraph, and Kaleidagraph). The values of the line widths and chemical shifts were obtained by methods similar to those published.[3] The cation-exchange medium was SP Sephadex C-25 (Na⁺ form; Pharmacia). [CH₃NH₃]Cl was prepared by neutralization of the aqueous amine (40%) with HCl, evaporation to dryness, and recrystallization from methanol/ether. All other chemicals were AnalaR grade or equivalent.

Samples of [(NH₃)₅CoOC(S)NHCH₃]S₂O₆·2H₂O, [(NH₃)₅CoOC-(S)NHCH₃](ClO₄)₂, [(NH₃)₅CoSC(O)NHCH₃](ClO₄)₂, and [(NH₃)₅-CoOH₂](ClO₄)₃ were obtained as previously described or from batches used in concurrent work.[1] Perchlorate salts of the O-bonded complex were obtained also by direct crystallization of the concentrated eluate from Sephadex [in Ba(ClO₄)₂] or alternatively by anion exchange of the purified dithionate salt using Dowex AG50 1X-8 anion-exchange resin (200 mesh, ClO₄⁻ form); the solution was freeze-dried and the residue recrystallized from water/NaClO₄. In the separation of the O-bonded isomer from residual aqua complex, it was found convenient to physically remove the resin containing the aqua complex from the column, after first separating them by elution with 0.25 M NaClO₄ and then washing and eluting with 0.5 M Ba(ClO₄)₂ to remove the 2+ O-bonded isomer as a narrow concentrated band. The product crystallizes upon addition of NaClO₄ and ethanol and sometimes contains some of the less soluble S-bonded isomer. It is removed by selective extraction of the O-bonded form with water, crystallization with NaClO₄ and ethanol, and repetition of the extraction and recrystallization process twice, to afford fluffy needles of the pure

O-bonded isomer. The tetrachlorozincate salt was obtained by metathesis using Li₂ZnCl₄ (2 M ZnCl₂ in 5 M LiCl) and 2-propanol. Dithionate and tetrachlorozincate salts of the S-bonded complex were obtained from concentrated aqueous solutions of the perchlorate salt by addition of aqueous Li₂S₂O₆ and H₂ZnCl₄, respectively. The nitrate perchlorate salt was obtained using aqueous LiNO₃/LiClO₄ (1:1) as the precipitant. The carbamato complex [(NH₃)₅-CoOC(O)NHCH₃](ClO₄)₂ was obtained by the method described for the thiocarbamate,[1] but using methyl isocyanate in place of methyl isothiocyanate. It was recrystallized from water/NaClO₄ as the diperchlorate and from water/LiClO₄/LiNO₃ as the nitrate perchlorate monohydrate double salt. The parent [(NH₃)₅CoOC-(O)NH₂](ClO₄)₂ complex and [(NH₃)₅CoOC(NH₂)₂](ClO₄)₃ were from batches used in other work.[4,5] All of these materials analyzed satisfactorily for at least H, C, and N and, where appropriate, S and Cl (Table 1S, Supporting Information). The spectroscopic properties of the complexes are described in the text and appear in Tables 1 and 2.

Kinetic Studies. The reaction of the *N*-methylmonothiocarbamate-*O* complex in 0−1 M HClO₄ (I = 1 M, LiClO₄, 25 °C) was monitored in the range 230−360 nm using a Cary 210 or HP8452A spectrophotometer by dissolving a sample of the complex directly in acid preequilibrated at 25.00 ± 0.05 °C. All kinetic runs were performed at least in duplicate. The Co concentrations (1×10^{-4}−1×10^{-3} M) were arbitrary, but always such that the absorbance never exceeded 1.5. Below 250 nm, the absorbance decreased by a factor of up to 2, and in the lower-energy region, it increased by

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Table 2. Electronic Spectral Data for Some $[(NH_3)_5CoX]^{n+}$ Complexes in H_2O (pH 3); $\epsilon_{\lambda,nm}$, M^{-1} cm^{-1}

Co−X	ϵ_{518}	ϵ_{510}	ϵ_{295}	$\epsilon_{252}{}^a$	$\epsilon_{249}{}^b$	ϵ_{227}
Co−OC(S)NHCH₃²⁺	108.5	−	830	7440	8865	16800
Co−SC(O)NHCH₃²⁺	(108.5)^c	−	(812)^c	−	−	(16800)^c
	−	88.5	−	8970	8865	6319
	−	−	(7895)^c	(8967)^c	−	(6406)^c
	−	(84.7)^d	−	(6710)^d		(7640)^d
Co−OH₂³⁺	−	−	4.1	105	−	3040

^{a} Isosbestic point for 1 M HClO₄. ^{b} Isosbestic point for H₂O or 1 M LiClO₄. ^{c} Jackson, W. G.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1060−1064. ^{d} Balahura, R. J.; Johnson, M.; Black, T. *Inorg. Chem.* **1989**, *28*, 3933-7.

Table 3. Product Distribution Data for the Acid-Catalyzed Hydrolysis and Linkage Isomerization of $[(NH_3)_5CoOC(S)NHCH_3]^{2+}$

[HClO₄], M	S-bonded,^{a} %	aqua,^{b} %
0	100^c	0^c
0.1	79	21
	60 ± 10	40 ± 10^d
0.2	76	24
	66	34
	67	33
1.0	67	33
	57	43
	73^f (84.5^e)	27^f (15.5^e)
	83 ± 5^g	17 ± 5^g

^{a} %$[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ product observed after 5-10 $t_{1/2}$ at Co concentrations of ca. (6−10) x 10^{-3} M. ^{b} %$[(NH_3)_5CoOH_2]^{3+}$product. ^{c} Jackson, W. G.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1060-4. ^{d} Balahura, R. J.; Johnson, M.; Black, T. *Inorg. Chem.* **1989**, *28*, 3933-7. ^{e} O- plus S-isomer; incompletely reacted, for 89 min at 25 °C (ca. 1$t_{1/2}$ min). ^{f} Result corrected to 100%. ^{g} Spectrophotometric result from kinetic studies at much lower Co concentrations (1 x 10 M).

a factor of up to about 15. The data were analyzed using Specfit running on a PC, and good first-order kinetics were observed under all conditions for reaction times in excess of 3−4 half-lives. The data under conditions of either rising or falling absorbance always conformed to the simple A to B scheme, and the first-order rate constants so obtained agreed closely (±2%) for a given set of conditions, independent of the Co concentration. These facts proved important to establish, as the chromatographic product analyses, at much higher Co concentration, yielded results clearly indicative of consecutive reactions. Product proportions (Table 3) were also determined using extinction coefficient data recorded in Table 2 from absorbance−time traces at 230 and 295 nm , where the computed (or observed) relationship is $\epsilon_\infty = f\epsilon_S + (1 - f)\epsilon_{aqua}$, with f as the fraction of product that is the S-bonded complex.

Product Distribution Data. The reaction of the O-bonded monothiocarbamato complex in 0−1 M HClO₄ solution was carried out on a scale of ca. 0.25−0.3 g of complex in 100 mL of solvent. In one set of experiments, the reactions were quenched at 16 h by adding sufficient NaOAc to consume the acid, diluted to 1 L with water and sorbed on Sephadex. The column was eluted with 0.5 M NaClO₄ (pH 5) to remove the claret-colored S-bonded isomer and then with 1 M NaClO₄ (pH 3) to take off the aqua complex. The eluate volumes were recorded and the cobalt concentrations determined spectrophotometrically using $\epsilon_{295} = 7895$ (1-cm cell) and $\epsilon_{490} = 47.7$ (10-cm cell) for the two components. Cobalt recoveries generally exceeded 98%. In some experiments, a black precipitate appeared (Co₂S₃), and always the smell of H₂S was evident within one half-life of reaction in acid. This decomposition reaction producing black precipitate was not quantified. In a second set of experiments, the reaction times were restricted to about one half-life ($t_{1/2} = 89$ min, 1 M HClO₄, 25 °C), and the products were determined as above, after aging of the first band (S-bonded plus
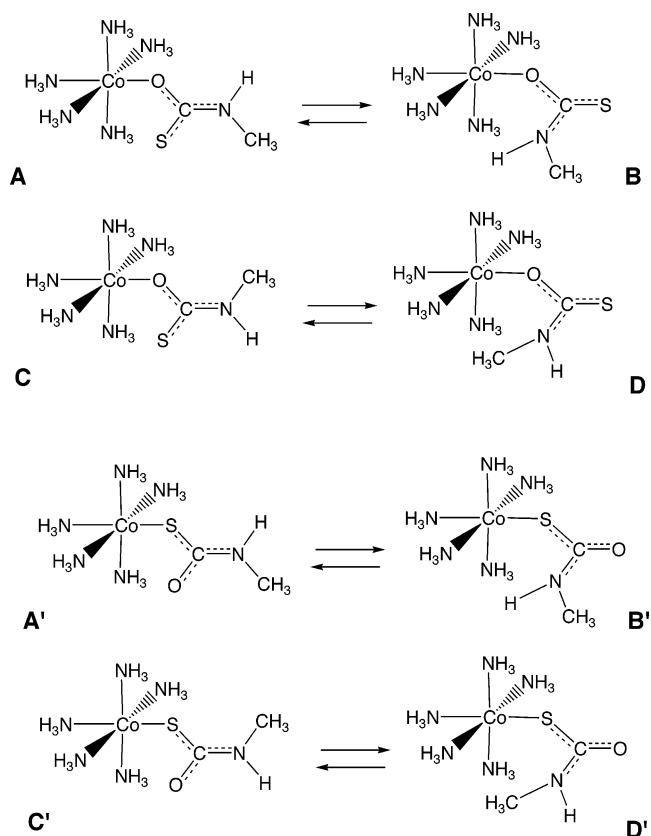

Figure 1. The eight possible conformers for $[Co(NH_3)_5OC(S)NHCH_3]^{2+}$ and $[Co(NH_3)_5SC(O)NHCH_3]^{2+}$.

unreacted O-bonded isomers) for 16 h to allow for complete isomerization[1] to the S-bonded form.

Results and Discussion

Solution Structures of the *N*-Methylmonothiocarbamate Linkage Isomers. Some of the resonances observed[1] in the 60-MHz NMR spectrum of $[(NH_3)_5CoOC(S)NHCH_3]$-S_2O_6 in Me₂SO-d_6 have been reassigned with the observation at 400 MHz of the NH-coupled methyl doublet.[2] In the course of routine recharacterization of the *N*-methylmonothiocarbamato complexes at 300 and 400 MHz, we again observed discrepancies in the reported and observed chemical shifts, in part because of the different counterions used, but also, we observed additional forms of the O- and S-bonded isomers.

In the 300- and 400-MHz spectra of a freshly prepared sample of the O-bonded complex $[(NH_3)_5CoOC(S)NHCH_3]$-S_2O_6 in Me₂SO-d_6, *two* sets of signals are observed (Figure 1S, Table 1) each with the same splitting patterns but with slightly different chemical shifts, which we assign as *Z* and *E* isomers arising from restricted rotation about the C−N bond:


E-rotamer   Z-rotamer
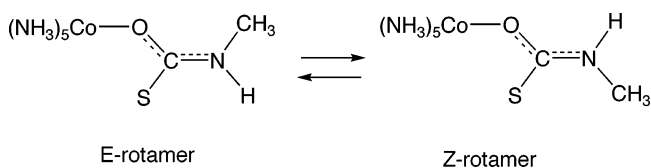
This isomerism is analogous to that seen for O-bonded *N*-methylformamide,[6] but as far as we are aware, this is the first time that it has been observed in monothiocarbamates.

The perchlorate and tetrachlorozincate salts showed the same two species, and we note the small but significant chemical shift differences for the different counterions (Table 1), no doubt a consequence of ion pairing by $S_2O_6^{2-}$ or $ZnCl_4^{2-}$, which is known[7] to cause such differences, especially for NH protons. Several independent preparations always showed the 5:1 ratio of $[(NH_3)_5CoX]^{2+}$ ions in both the proton and carbon NMR spectra (Table 1); this pattern was unchanged by repeated recrystallization. The smaller set of signals is therefore not reasonably attributed to an impurity. Indeed, the spectrum of a large single crystal of the tetrachlorozincate salt in $Me_2SO\text{-}d_6$ displayed the same two species. Further, all salts eluted as a single 2+ band on ion-exchange chromatography under a variety of conditions. The most convincing evidence, however, was the fact that both forms isomerized to the same S-bonded isomer, and the 5:1 ratio remained constant throughout the linkage isomerization. This is consistent with two rapidly interconverting O-bonded forms, an interconversion that, however, is slow on the NMR time scale at ambient temperature.

Two forms were also observed for the S-bonded isomer (Figure 1S), but with a different *Z/E* ratio (ca. 18:1, ClO_4^- salt). The same experiments described for the O-bonded form established that the minor set of signals (Table 1) were not due to an impurity.

The restricted C—N bond rotation for both the O- and S-bonded complexes is consistent with the diminished tendency of sulfur relative to oxygen to adopt a C=X double-bonded structure; the C^+—X^- form would be preferred for X = S.[8−10] Thus, although the Co is attached to oxygen, delocalization of the lone pair on N is more readily achieved as shown, whereas when the Co is attached to sulfur, the ketonic resonance form assumes increased importance:
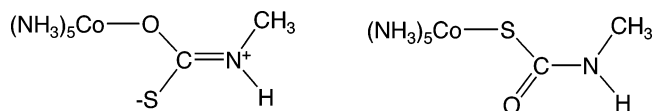
For the *N*-methylmonothiocarbamates, it is not known which form is *Z* and which is *E*. The crystal structure of the S-bonded *N*-phenylmonothiocarbamato complex reveals just the one form in the solid state and shows a planar O—C(S)—N moiety, for which the bond angles and bond lengths are consistent with electrondelocalization and partial double-bond character for C—N.[11] The phenyl substituent does not seem to be coplanar and therefore not conjugated with the C—N bond, and the structure resembles that[12] for isoelectronic $[Co(NH_3)_5NHCONH(C_6H_5)]^{2+}$ in this respect.

A reviewer suggested an alternative source for the observed isomerization, shown in Figure 1. This arises via restricted rotation about the C—O or C—S bonds, rather than C—N. In all, there are four isomers for each of the O- and S-bonded complexes. This kind of isomerism has been considered previously[13] in connection with formato and amide complexes and probed using NOE effects that are observed between the *cis*-NH_3 groups and an *endo*-CH on the ligand. However, such experiments indicate only that there can be a contribution to the complete set of conformers from such a species; they do not comment on the *rate* of restricted bond rotation, and indeed only a *single* average species has previously been observed in the NMR spectra. Further, species D and D′ (Figure 1) can be eliminated on steric grounds; the corresponding conformer for $[Co(NH_3)_5(OCH.N(CH_3)_2)]^{3+}$ was eliminated[13] on the basis of zero NOE between the N—CH_3 and *cis*-NH_3 groups. Moreover, the A′/B′ and C′/D′ equilibria are unlikely to be frozen in the ambient-temperature NMR spectra given that there is essentially *unrestricted* rotation about the C—S bond that we have argued as having little double bond character. Finally, DQCOSY (not shown) and NOESY spectra (Figure 2) were recorded for the O-bonded *N*-methylmonothiocarbamato complex in $Me_2SO\text{-}d_6$ (the NH proton is exchanged in D_2O). On the time scale of these experiments, appreciable O to S isomerization occurs, and thus we obtained the spectra for the S-bonded form as well. Under conditions where a strong NOE was observed between the NH and methyl group for each of the O- and S-bonded isomers (and for both conformers), there was a negligible correlation between either the methyl or the NH with the *cis*-NH_3 protons. This result is consistent with no appreciable contribution from the *syn*-NH (B, B′) or *syn*-Me (D, D′) conformers (Figure 1). At high amplitude, however, a very weak NOE is apparent for NH—*cis*-NH_3 interaction in the major and minor O-bonded isomers, indicating a very minor contribution from B and thus identifying the major isomer as A (and minor isomer C). Neither of the two S-bonded isomers exhibited NOEs to the *cis*-NH_3, even at high amplitude, consistent with the discussion above and eliminating any minor contribution from conformer B′.

Solution Structures of the O-Bonded Carbamate and Urea Complexes. Consistent with the rationale presented in the previous section, the all-oxygen analogue $[(NH_3)_5CoOC(O)NHCH_3]^{2+}$ shows only a single form in both the proton and carbon NMR spectra. It could be argued that the *Z/E* equilibrium lies very much to one side, as it does, for example, for $[(NH_3)_5CoOC(CH_3)NHCH_3]^{3+}$ compared to $[(NH_3)_5CoOC(H)NHCH_3]^{3+}$, but where both *Z* and *E* forms can still be observed in the complex, as in the free ligand.[6] To test this hypothesis, we attempted to observe the separate NH_2 protons in $[(NH_3)_5CoOC(O)NH_2]^{2+}$ at 400 MHz; they appear as a singlet at 60 and 100 MHz. However, a singlet

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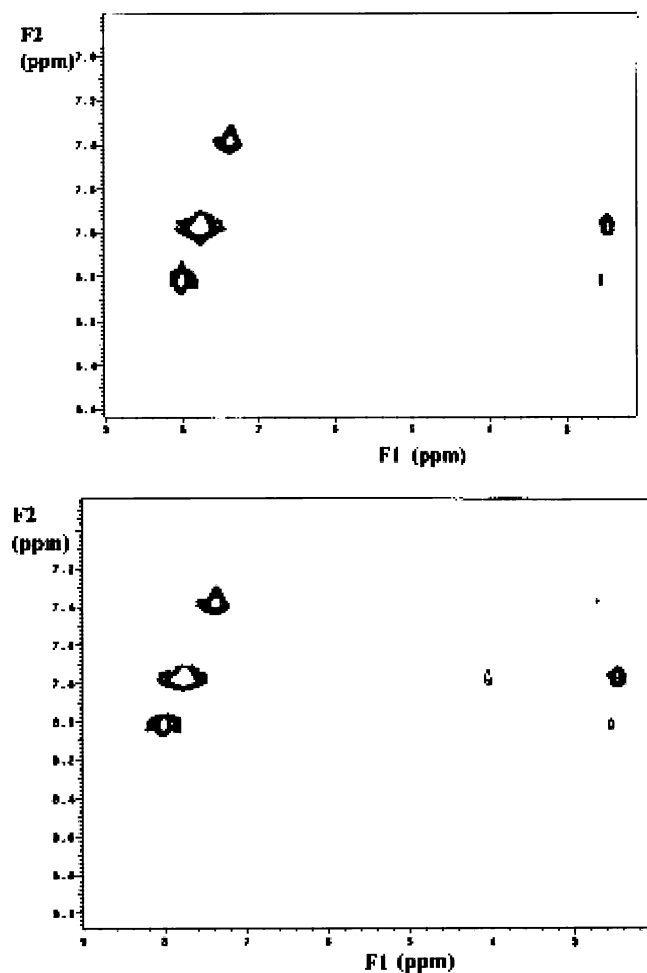(13) Balahura, R. J.; Jordan, R. B. *Inorg. Chem.* **1973**, *12*, 1438.

Figure 2. ¹H NOESY spectra for O- and S-bonded [Co(NH₃)₅-(OCSNHCH₃)](ClO₄)₂ in Me₂SO-d_6. The top spectrum shows the NOE arising from the NH to the methyl for both isomers. The bottom spectrum at higher amplitude reveals the NOE from the NH to the methyl for the minor O-bonded isomer and the NOE for the NH and *cis*-NH₃ of the major O-bonded isomer.

Figure 3. ¹H NMR line shapes for the NH₂ protons of [(NH₃)₅Co−OC-(O)NH₂]²⁺ in DMF-d_7 at 100 MHz as a function of temperature.

was again observed, and we conclude that C−N bond rotation in O-carbamates is rapid at 20 °C, more rapid than in the present O-bonded *N*-methylmonothiocarbamate.

A variable-temperature NMR study was undertaken for the [(NH₃)₅CoOC(O)NH₂]²⁺ complex in DMF-d_7 on a 100-MHz instrument (+30 to −50 °C; Table 2S), and indeed, the NH₂ doublet is observed at low temperatures (Figure 3). The coalescence point is at −20 °C (at 60 MHz, the coalescence point is at about −35 °C). As the temperature is further lowered, the peaks separate into two distinct resonances of *unequal* intensity (ca. 55:45). This suggests that both restricted O−C¹³ and C−NH₂ bond rotation are occurring, and that one of the two processes is just starting to freeze out at −40 °C. The line shape analysis for a single dynamic process provided a reasonable fit, although the data were not good enough to fit two such processes. From a standard line shape analysis, rate constants were extracted (Table 3S) and fitted to the Eyring equation by nonlinear least-squares to yield the activation parameters $\Delta H^{\#}$ = 31.5 ± 1.9 kJ mol⁻¹ and $\Delta S^{\#}$ = −83 ± 3 J mol⁻¹ K⁻¹ ($\Delta G^{\#}$ = 53 kJ mol⁻¹ at T_c = 253 K).

A data set for the O-bonded urea complex (+30 to −65 °C; Table 4S) was also collected, Figure 4. The rate data (Table 3S) yielded $\Delta H^{\#}$ = 31.0 ± 0.9 kJ mol⁻¹ and $\Delta S^{\#}$ = −66 ± 3 J mol⁻¹ K⁻¹ ($\Delta G^{\#}$ = 47 kJ mol⁻¹ at T_c = 230 K). Only one NH₂ resonance is observed at δ 6.63 ppm at room temperature, but as the temperature is lowered, this peak broadens and begins to separate into two peaks at −40 °C. Eventually, two peaks of ca. equal intensity are observed at −60 °C. On the basis of the structure below
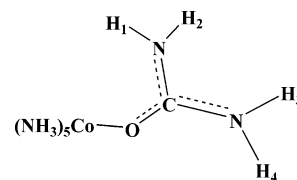
two well-separated doublets would be expected in the frozen configuration due to protons 1, 4 and 2, 3, where the pairs 1 and 2 and 3 and 4 are coupled. The doublets ($J \approx 5$ Hz) are not observed, likely because of ¹⁴N quadrupolar relaxation broadening. Restricted rotation about the O−C bond would lead to further splitting of the H1/H4 and H2/H4 singlets, but this was not observed. Only one species is possible for the O-bonded urea species, but the proton signal pattern is not necessarily symmetrical if the H1/H4 and H2/H4 signals coalesce at different temperatures, which, in principle, should be so, given that all four protons are inequivalent for the rigid (completely frozen) structure shown above. Indeed, the Lorentzian fits to the data for a single process were less than ideal at intermediate temperatures (−43, −52 °C) but surprisingly not so at the lowest temperature (−63 °C), with only minor asymmetry in the line shapes. The spectra were interpreted by assuming C−NH₂ restricted rotation alone; an additional fit to a second process was not warranted.

These O-bonded carbamate and urea complexes are clearly less restricted to rotation about the C−N bond than the *N*-methylmonothiocarbamato species.
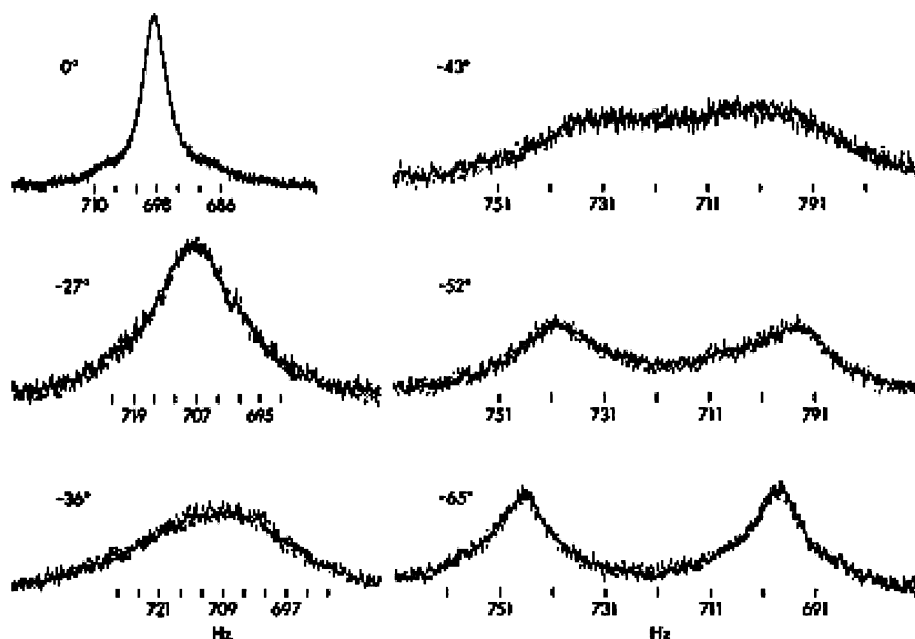
Figure 4. ^{1}H NMR line shapes for the NH$_2$ protons of [(NH$_3$)$_5$Co$-$OC(NH$_2$)$_2$]$^{3+}$ in DMF-d_7 at 100 MHz as a function of temperature.

Acid-Catalyzed O- to S-Bonded *N*-Methylmonothiocarbamate Rearrangement. We reported that the S-bonded isomer is stable in water or dilute acid.[1] Further, the zero-time spectra (220$-$310 nm) in water and 1 M HClO$_4$ are identical, demonstrating negligible protonation (at Co$-$S, or *exo*-O$-$, or $-$N). Moreover, there is a negligibly small (2%) absorbance change over 16 h in this medium, and the ^{1}H and ^{13}C NMR spectra are also unchanged. Given the complete reaction of the O-bonded form on this time frame, the complete stability of the product was important to establish. S-bonded complexes such as [(NH$_3$)$_5$CoSO$_2$CH$_3$]$^{2+}$ commonly shed their *trans*-NH$_3$ in solution,[14] and this reaction is driven in acid. Indeed, the S-bonded *N*-methylmonothiocarbamate does grow an NH$_4^+$ signal (1:1:1 triplet, centered at δ 7.1 ppm) in the ^{1}H NMR spectrum in Me$_2$SO-d_6/H$^+$, but only over a period of several days. No signals attributable to MeNH$_3^+$ (δ 2.25, q, Me; δ 6.2, br s, $-$NH$_3^+$) arising from decomposition of MeNHC(SH)O were observed.

The kinetic data (Table 5S, Supporting Information) for the acid-catalyzed reaction of the O-bonded isomer in aqueous HClO$_4$ (I = 1 M, LiClO$_4$, 25 °C) are shown in Figure 5.

Earlier data[2] are included in this plot, and they are in essential agreement in that the specific rate is close to linear in the H$^+$ concentration and the reaction is almost twice as fast in 1 M acid. The mild acid catalysis and the lack of downward concave curvature in the plot indicate that [Co(NH$_3$)$_5$(OC(SH)NHCH$_3$]$^{3+}$ is a strong acid (pK_a < 0). Because the pK_a is immeasurably small, we can conclude only that the protic form of the O-bonded isomer is considerably more reactive (a pK_a of $-$1, for example, would indicate a factor of 20).

The particular question we wished to address was whether acid accelerated the hydrolysis or linkage isomerization, or
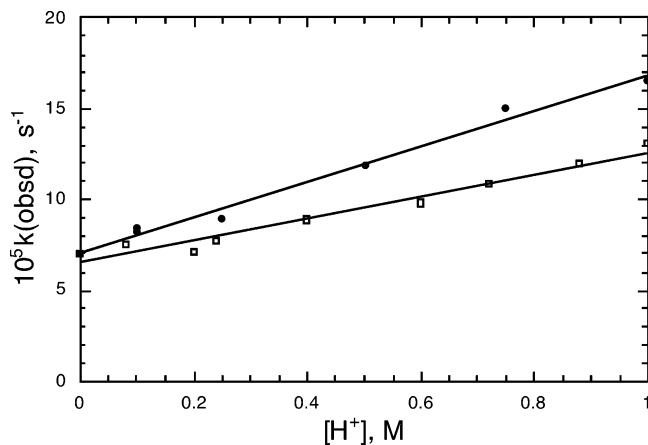
(14) Jackson, W. G.; Jurisson, S. S.; O'Leary, M. A. *Inorg. Chem.* **1993**, *32*, 445.

Figure 5. Acid dependence of the rate of hydrolysis/linkage isomerization of [(NH$_3$)$_5$Co$-$OC(S)NHCH$_3$]$^{2+}$ in HClO$_4$, I = 1 M (LiClO$_4$); the upper line represents the results of the earlier study.[2]

both. The published data[2] suggested that the hydrolysis pathway is accelerated by acid at least, as appreciable [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ was produced. We have confirmed in this work that no aqua complex is formed in neutral to mildy basic solution (<1%; k_{H_2O} < 1 × 10^{-7} s^{-1}), but it is in acid solution (Table 3). However, the reported 40 ± 10% aqua complex/60 ± 10% S-bonded isomer for 0.1 M acid seemed anomalous. At most, 5% aqua complex would be expected, even if the protonated O-bonded form yielded *all* aqua complex, because in 1 M acid, the reaction proceeds only 50% via the acid-catalyzed pathway (and thus ca. 5% in 0.1 M acid).

A sharp isosbestic point (ca. 250 nm) was observed for the spontaneous and acid-catalyzed reactions; it persisted for the entire reaction, consistent with a simple A to B reaction scheme (Figure 6). It was closely monitored for its acid dependence. It showed a very small but systematic shift, from 249 to 252 nm, on going from 0 to 1 M HClO$_4$, consistent with the production of a small amount of [(NH$_3$)$_5$CoOH$_2$]$^{3+}$

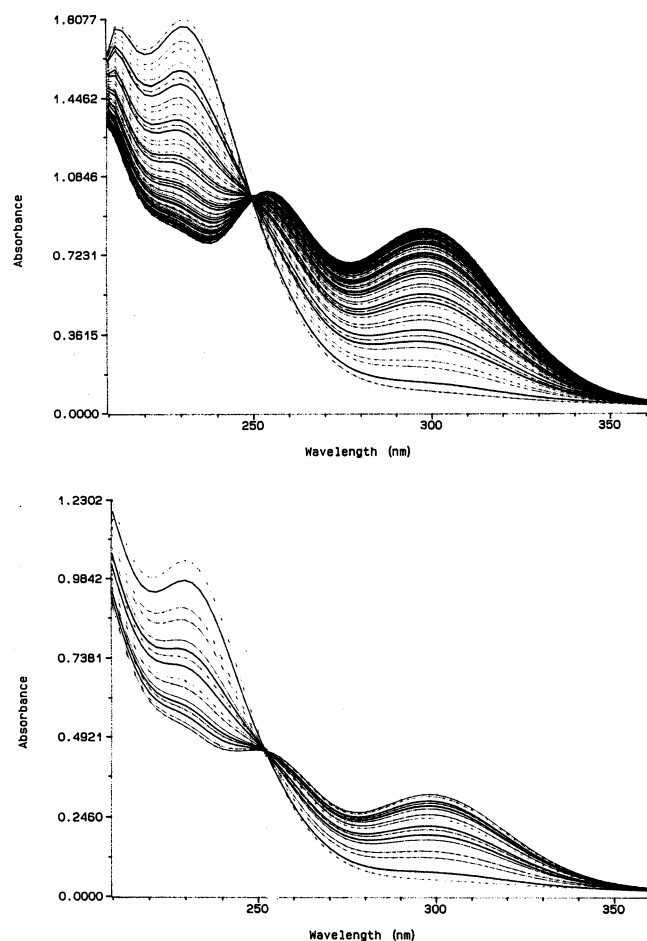**Figure 6.** UV−visible changes for the isomerization/hydrolysis of $[Co(NH_3)_5OC(S)NHCH_3]^{2+}$ in 0.2 M (top) and 1.0 M (bottom) $HClO_4$ at 25.0 °C, showing no significant shift in the isosbestic point with varying H^+ concentration. [Co] = 4×10^{-5} M (bottom) and 1.1×10^{-4} M (top). The absorbance increases with time at 300 nm.

as coproduct as the acid concentration was raised, i.e., parallel reaction. For 1 M acid, $17 \pm 5\%$ aqua complex and $83 \pm 5\%$ S-bonded *N*-methylmonothiocarbamate complex were calculated from extinction coefficient data at 252 nm (Table 2).

We carried out product analyses for the O-bonded form by reacting the starting material for 10−20 half-lives in 0, 0.1, 0.2, and 1 M $HClO_4$ and chromatographically separating the two products. Curiously, we found more aqua complex than expected (Table 3), indeed close to what was reported earlier.[2] However, the proportions were not linear in the H^+ concentration as had been anticipated, nor were they reproducible. The only clear trend was that more aqua complex was observed with increasing acid concentration.

The clue to the anomalously high proportion of aqua complex and the poor reproducibilty of the product distribution experiments was revealed when we redetermined the product distributions at much lower complex concentrations and for much shorter reaction times. Although control experiments demonstrated that both the aqua and S-bonded complexes are stable in acid, for even the longest reaction times, it became clear that liberated $CH_3NHC(SH)O$ in the acid-catalyzed pathway rapidly decomposes to H_2S, which

at higher concentrations (higher Co concentration, higher H^+ concentration), strips coordinated monothicarbamate from the complex at an appreciable rate to yield, initially, aqua complex and, ultimately, black cobaltic sulfide. Although the presence of H_2S even in trace amounts was clear from the stench, its intervention in the reaction was not initially apparent, as it did not yield the telltale black deposit (or colloidal suspension) of insoluble cobaltic sulfide as ligand was stripped from the complex.

In a reaction that is mechanistically not well understood, H_2S (or S^{2-}) is widely used to completely strip ligands from their Co(III) complexes. Although early believed to be a reductive process, it has been shown that the product is largely cobalt(III) sulfide, not cobalt(II) sulfide.[15] Furthermore, in acidic solution reduction to Co(II) and ammonia would be irreversible. Thus, although possibly redox driven, the net process is a substitution, and we have observed the early stages of such a process, loss of monothiocarabamate ligand to produce the aqua Co(III) species. Indeed, we have confirmed that addition of trace H_2S to an acidified solution of the O- (but not the S-) bonded *N*-methylmonothiocarbamate complex does indeed produce the aqua complex. Further, we had noted early on that, in attempts to convert the insoluble pink $[(NH_3)_5CoOC(S)NHCH_3]S_2O_6$ to the tetrachlorozincate salt by trituration with H_2ZnCl_4, the slurry became orange within seconds, with the formation of H_2S and the quantitative production of aqua complex.

This analysis is consistent with the kinetic studies and product analyses of the acid-catalyzed reaction carried out at the lowest Co concentration employed (ca. 10^{-4} M). The kinetic data are reproducible, and the reaction is the clean parallel formation of $[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ and $[(NH_3)_5CoOH_2]^{3+}$, with no evidence of consecutive reactions (Figure 6). Moreover, the proportions of pentaammineaqua complex formed are independent of the Co concentration provided that this concentration remains low, but more importantly, much less is formed than observed at high Co concentration. Indeed, so little is formed that the acid dependence of the product ratio could not be precisely determined: $17 \pm 5\%$ at 1 M and essentially none at 0.1 M $HClO_4$ (ca. 2% predicted, assuming that the distribution is linear in the H^+ concentration).

Site of Protonation and Effect of Acid on C−N Bond Rotation. The carbamato and monothiocarbamato complexes provide three sites for protonation: oxygen, sulfur, and nitrogen. In the study of the acid-catalyzed hydrolysis of $[Co(NH_3)_5O_2CNH_2]^{2+}$ (which yields $[Co(NH_3)_5OH_2]^{3+}$, CO_2, and NH_4^+), protonation on nitrogen was assumed, and Co−O rather than C−O cleavage ensued (the corresponding nitrosation reaction involves 80% Co−O and 20% C−O cleavage).[16] In water, the K_a value is ca. 1/8 (pK_a ca. 1), and the plot of k(obsd) vs $[H^+]$ in the H^+ concentration range of 0−1 M curves appreciably downward. This contrasts with the present O-bonded *N*-methylmonothiocarbamate system, where there is no hint of net protonation even in 1 M acid (Figure 5); this complex must be at least 100-fold less basic.

(15) Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527.
(16) Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1094.

In Me₂SO, the sharp (25 °C) NH_2 resonance of $[Co(NH_3)_5O_2CNH_2]^{2+}$ is separate from the signal because of adventitious water, but in the presence of a small amount of trifluoroacetic or triflic acid, these signals merge and appear downfield, consistent with exchange averaging through protonation on nitrogen. In stronger acid, the $Co-NH_3$ resonances also shift, consistent with net protonation. The *N*-methylcarbamate complex behaves differently; a broad average signal is seen for adventitious H_2O and the $-NH_2$ at 5−6 ppm that shifts upfield with increased $[H_2O]$. The methyl signal is a sharp singlet, i.e., there is no observable $NH-CH_3$ coupling, and separate *Z/E* isomers are not observed.

Although it is apparent that the O-bonded *N*-methylmonothiocarbamato complex is less basic than its isoelectronic all-oxygen analogue, even transient protonation on nitrogen should remove the barrier to rotation about the $C-N$ bond and equilibrate the *Z* and *E* isomers:

E-rotamer   Z/E distinction lost
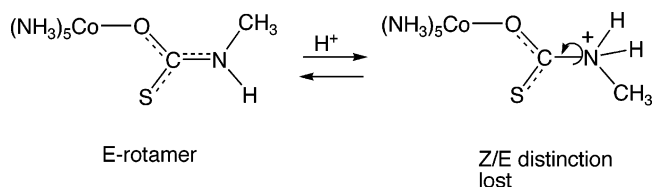
Acid had no such effect however; even the $NH-CH_3$ coupling remained, and the NH signal was not exchange averaged with the distinct water/H^+ signal (ca. 10 ppm for 0.1 M acid), for either the O- or S-bonded complex. This result not only emphasizes their greatly reduced basicity, but also suggests that the effective site for protonation in the acid-catalyzed rearrangement is not at nitrogen but rather at S or O. Protonation at S, for example, would enhance rather than diminish the $C-N$ double-bond character:
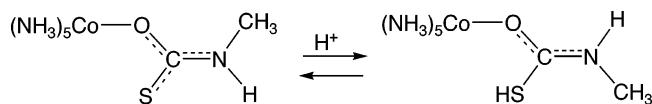
Further, although $-SH$ might be a poorer nucleophile than $-S^-$, the neutral MeNHC(SH)O ligand would be a better

leaving group than anionic $MeNHC(S)O^-$, consistent with the enhanced reactivity of the protonated form.

Summary

The $[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ ion, which exists as a *Z/E* isomer mixture in DMSO solution (ca. 18:1), is stable in 1 M $HClO_4$, but its linkage isomer $[(NH_3)_5CoOC(S)NHCH_3]^{2+}$ reacts to give a mixture of $[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ and $[(NH_3)_5CoOH_2]^{3+}$ in parallel. The $[(NH_3)_5CoOC(S)NHCH_3]^{2+}$ complex, which exists as a 5:1 *Z/E* isomeric mixture in solution (DMSO), gives entirely the S-bonded isomer, whereas its protonated form $[(NH_3)_5CoOC(SH)NHCH_3]^{3+}$, a strong acid, yields $[(NH_3)_5CoSC(O)NHCH_3]^{2+}$ ($83 \pm 5\%$) and $[(NH_3)_5CoOH_2]^{3+}$ ($17 \pm 5\%$). The kinetics suggest that the protonated form is $\geq$20-fold more reactive than the free ion; thus, both the linkage isomerization and hydrolysis pathways are acid-catalyzed, but the latter clearly more so than the rearrangement. Decomposition of both the O- and S-bonded isomers occurs at rates comparable to the hydrolysis and linkage isomerization at Co concentrations above ca. 10^{-2} M, leading to additional $[(NH_3)_5CoOH_2]^{3+}$ and ultimately black cobaltic sulfide, and this arises via H_2S production through hydrolysis of the liberated $CH_3NHCOSH$.

Barriers for $C-N$ bond rotation have been determined for $[Co(NH_3)_5OCNH_2]^{2+}$ and $[Co(NH_3)_5OC(NH_2)_2]^{3+}$; these are clearly lower than for the O- and S-bonded *N*-methylmonothiocarbamato complexes.