mixture was diluted with ice water (1.5 L), sorbed on SP-Sephadex C-2k cation-exchange resin, and eluted with 1 M NaCl (pH ca. 3). The two cations that separated were identified by their visible absorption spectra as $[(NH_3)_5CoO_2CNH_2]^{2+}$ (ϵ_{508}^{max} 77.5; 2.2%) and $[(NH_3)_5CoOH_2]^{3+}$ (ϵ_{492}^{max} 47.7; 97.8%). Triplicate experiments gave 2.5, 2.1, and 1.9% $[(NH_3)_5CoO_2CNH_2]^{2+}$ (Co recoveries = 100 ± 1.5%).

Reactions of $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$. $[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (0.290 g, 6.4×10^{-4} mol) was reacted with aqueous 1.17 M $HClO_4$ (25.0 mL, 10^{-2} M H^+) for 20 min (25 °C) before quenching with ice and diluting the solution 20-fold with ice water. The mixture was sorbed on SP-Sephadex C-25 resin and chilled in a jacketed column to 2 °C. Elution commenced with 0.23 M Na^+ (pH 6.9, 0.2 M Cl^-, 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}) eluant, and later elution proceeded with eluant twice this concentration. The product distribution (Table II) was determined by measuring visible absorption spectra for the separated complexes and using the following molar absorptivities: $[(NH_3)_5CoOH_2]^{3+}$, ϵ_{492}^{max} 50.3; $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$, ϵ_{495}^{max} 80.8; $[Co(NH_3)_6]^{3+}$, ϵ_{476}^{max} 57.6; $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$, ϵ_{509}^{max} 68.

$[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (0.187 g, 4.15×10^{-4} mol) was reacted with 0.117 M $HClO_4$ (50 mL, I = 1.17 M ($NaClO_4$)) for 60 min (25 °C) before quenching with ice and assaying as above. This experiment was repeated on the 2.0-g scale; no 2+ ion (>0.05%) was detected.

$[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (0.993 g, 2.055×10^{-3} mol) was reacted on dimethyl sulfoxide containing methanesulfonic acid (>5 equiv) for 60 min (25 °C) before cooling, diluting with water, and chromatographing as described above. A pink 2+ ion (λ_{max} = 512, 358 nm) was detected and observed to transform to $[(NH_3)_5CoOH_2]^{3+}$ (see Table II). This 2+ ion was absent when CF_3SO_3H was substituted for CH_3SO_3H. To test for $[(NH_3)_5CoNCO]^{2+}$, $[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (1.175 g, 2.62×10^{-3} mol) was reacted for $10t_{1/2}$ in dimethyl sulfoxide containing $\sim 3 \times 10^{-2}$ mol of CF_3SO_3H. Chromatographic analysis showed only $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ eluting ahead of $[Co(NH_3)_6]^{3+}$. No 2+ ion (>0.5%) was detected.

Reactions of $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$. $[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3 \cdot 3H_2O$ (1.034 g, 2.069×10^{-3} mol) was reacted with aqueous 0.1 M NaMES buffer (pH 6.3, 50 mL, I = 1.0 M ($NaClO_4$)) for $5t_{1/2}$ (16 h, 25 °C). The product solution was diluted (10x) with water and sorbed on SP-Sephadex C-25 resin, and elution with 0.46 M Na^+ (0.4 M Cl^-, 0.02 M $H_2PO_4^-$, 0.02 M HPO_4^{2-}, pH 6.9) eluant separated two products that were identified by visible spectra as 2.0 ± 0.2% $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ (ϵ_{495}^{max} 80.8) and 98.0% $[(NH_3)_5CoOH_2]^{3+}$ (ϵ_{492}^{max} 50.3); average Co recovery = 101.1%.

When $[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3 \cdot 3H_2O$ (0.486 g, 9.7×10^{-4} mol) was reacted with 0.1 M NaOH (25 mL, I = 1.0 M ($NaClO_4$)) for 60 s before quenching to pH 5 and assaying as above, only the $[(NH_3)_5CoOH_2]^{3+}$ ion was chromatographically detected (≥99% [Co]).

Acknowledgment. This work was supported by a grant from the Australian Research Grants Scheme.

Registry No. $[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3$, 128444-74-6; $[(NH_3)_5CoNHCOOC_2H_5](ClO_4)_2$, 128444-76-8; $[(NH_3)_5CoNHCO_2]^+$, 128444-77-9; $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, 75522-50-8; $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(NH_3)_5CoNCO](ClO_4)_2$, 27427-52-7; $[(NH_3)_5CoO_2C(NH_2)]^{2+}$, 19173-65-0; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $NH_2C(O)OCH_2CH_3$, 51-79-6.

Supplementary Material Available: Table III, containing rate constants (1 page). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Northcott Drive, Campbell, ACT, Australia 2600

Linkage Isomeric Pentaamminecobalt(III) Complexes of Methanesulfinamide

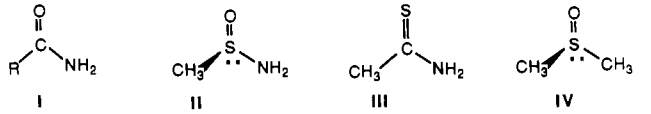
David P. Fairlie, W. Gregory Jackson,* and Katherine H. Thompson

Received October 16, 1989

The selective syntheses and reactivities of the linkage isomeric pentaamminecobalt(III) complexes containing N- and O-bound methanesulfinamide ($MeSONH_2$) are described. The N-bonded isomer is isolated as the deprotonated form $[(NH_3)_5Co-NHSOCH_3]^{2+}$, which is stable above pH ca. 4. It protonates in more acidic media, forming the reactive intermediate $[(NH_3)_5Co-NH_2SOCH_3]^{3+}$. The acidity constant was determined both kinetically (pK'_a = 2.91 ± 0.03, 1.0 M KCl; pK'_a = 2.44 ± 0.06, 1.0 M $NaClO_4$, 25 °C) and spectrophotometrically (pK'_a = 2.83 ± 0.04, 1.0 M KCl, 25 °C). The site of protonation was established by ^1H NMR spectra in Me_2SO-d_6; the NH_2 protons are diastereotopic and appear as two separate signals because of the presence of the chiral sulfur center, and neither is in rapid exchange with free H^+. This protonated N-bonded isomer rearranges rapidly in solution, yielding $[(NH_3)_5Co-OS(NH_2)CH_3]^{3+}$ (95%) and $[(NH_3)_5Co-OH_2]^{3+}$ (5%); k(obsd) = (1.30 ± 0.03) × 10^{-2} s^{-1}, I = 1.0 M (KCl), 25 °C. The rearrangement rate is comparable in Me_2SO; k(obsd) = (1.47 ± 0.02) × 10^{-2} s^{-1}, 25 °C. The O-bonded isomer is less reactive, undergoing complete but slow solvolysis (25 °C, k_s = 1.0×10^{-5} s^{-1}, 0.1–2.0 M $HClO_4$, I = 1 or 2 M) to $[(NH_3)_5Co(solvent)]^{3+}$ (and free NH_2SOCH_3). The disappearance of the O-bonded sulfinamide complex is appreciably acid catalyzed but only in the presence of Cl^-, and here the reaction is mainly ligand hydrolysis, producing NH_4^+ and the O-bonded sulfinate complex $[(NH_3)_5CoOS(CH_3)O]^{2+}$, which has been synthesized independently. The sulfinamide NH_2 group on the O-bonded isomer is rapidly nitrosated (NO^+) under milder acidic conditions to give the O-bonded sulfinate complex. In aqueous solution above pH ca. 3 an O- to N-linkage isomerization competes with hydrolysis; this competition is more effective via the spontaneous (pH 6.2; 24% isomerization, 76% aquation) compared with the base-catalyzed route (0.1 M OH^-, 8.5% isomerization). From these data k_{ON} could be obtained, and k_{ON} coupled with k_{NO} enabled the calculation of the isomeric equilibrium constant K'_{NO} ($=k_{NO}/k_{ON}$ = 4450). This result indicates the greater stability of the O-bonded form over the (protonated) N-bound form in aqueous acid, consistent with results for analogous $[(NH_3)_5Co(NH_2COR)]^{3+}$ systems (e.g., R = OH, H, aryl, alkyl, NR′R″, OR′); however, in neutral to basic solution, the calculated relative stability constant shows that the N-bound form is more stable, and this is because it is selectively deprotonated.

Introduction

Carboxylic acid amides (I, R = H, alkyl, aryl)[1-3] and related molecules (I, R = NH_2,[4] NMe_2,[5] OH,[6] OEt[7]) interact with transition-metal ions through either the carbonyl oxygen or nitrogen atoms, and the synthesis and interconversion of the linkage



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0020-1669/90/1329-3145$02.50/0

Table I. ^{1}H NMR Chemical Shift Data for Methanesulfinamide, Its Pentaamminecobalt(III) Complexes, and Related Methanesulfinate Complexes

substance[b]	δ, ppm[a] cis-NH_3	trans-NH_3	CH_3	CoNH	NH_2
H_3CSONH_2			2.50		5.72
$[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$	3.88	2.63	2.85		6.43
$[(NH_3)_5CoNHSOCH_3]^{2+}$	3.17	3.73	2.57	1.67	
$[(NH_3)_5CoNH_2SOCH_3]^{3+}$[c]	3.80	3.50	3.05		6.40, 6.97
$[(NH_3)_5CoOSOCH_3]^{2+}$	3.75	2.63	2.30		
$[(NH_3)_5CoS(CH_3)O_2]^{2+}$	2.98	3.75	3.06		

[a] Downfield from TMS in Me_2SO-d_6. [b] Perchlorate salts. [c] Generated in situ by using CH_3SO_3H (CH_3, δ = 2.62 ppm).

isomeric pairs have been the subject of several recent studies.[1,3,4,7] Methanesulfinamide $MeSONH_2$ (II), the sulfur analogue of acetamide, $MeCONH_2$ (but distinct from thioacetamide, $MeCSNH_2$ (III)), is an ambidentate ligand, but in addition to the oxygen and nitrogen centers, the central sulfur can also function as a donor atom for a metal ion. Linkage isomeric complexes of the structural analogue dimethyl sulfoxide (IV) bonded through O or S have been identified for a number of transition metals (notably Ru^{II}, Ru^{III}, Rh^{II}, and Pt^{II}),[8-10] although only the O-bound form is known for $[(NH_3)_5Co(Me_2SO)]^{3+}$.[11]

The central sulfur atom of II has a tetrahedral environment, in contrast to the flat arrangement in I, and this geometry coupled with the larger size of sulfur is likely to exert an influence on both the preferred coordination modes and the mechanisms for any rearrangement processes. Indeed, we hoped to obtain all three possible linkage isomers and examine the rearrangement of each.

S-coordination of sulfite SO_3^{2-},[12] sulfinate RSO_2^-,[13,14] sulfenate RSO^-,[13] monothiocarbamate $RNHCOS^-$,[15] and thiosulfate $S_2O_3^{2-}$[16] ligands to Co(III) is known, and many of the properties common to such complexes, such as their yellow-brown color, intense UV absorption around 290 nm diagnostic of Co–S bonding, lability of the NH_3 group trans to coordinated sulfur, and characteristic low-field ^{1}H NMR signal for the trans-NH_3 ligand, could be anticipated for (methanesulfinamide-*S*)pentaamminecobalt(III). O-bonding of these anionic sulfur–oxygen ambidentate ligands is more difficult to achieve, although known for all the ligands listed above. The S-bonded form is the more thermodynamically stable in every case, and so kinetic (or photochemical) routes to the less stable linkage isomers were required for their syntheses. Of the few uncharged sulfur–oxygen ligands examined (Me_2SO,[11] $NH_2CH_2CH_2SOMe$,[17] and $NH_2CH_2CH_2SOCl$[18]) on cobalt(III), the O-bonded forms are more stable, and a similar situation might be anticipated for methanesulfinamide. Sulfinamides are more acidic than their related carboxamides, and so formation of a deprotonated N-coordinated methanesulfinamide complex of pentaamminecobalt(III), akin to $[(NH_3)_5CoNHCOCH_3]^{2+}$, was also expected.

In summary, all three bonding modes were viable prospects, and we now report on the competition between these when suitable $[(NH_3)_5Co^{III}X]$ precursors are reacted with II.

Results and Discussion

Syntheses and Characterization. The labile complex $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ reacts with methanesulfinamide in the weakly coordinating solvent acetone to yield principally the oxygen-bonded sulfinamide complex $[(NH_3)_5CoOS(CH_3)NH_2](CF_3SO_3)_3$. Accompanying its production were the pink $[(NH_3)_5CoOSOCH_3]^{2+}$ (ca. 9%) and a trace (ca. 1%) of the yellow-brown $[(NH_3)_5CoS(CH_3)O_2]^{2+}$. The latter two ions were produced despite the fact that the free methanesulfinamide ligand contained no detectable (<1% ^{1}H NMR) methanesulfinate (as CH_3SO_2H). The trace impurities were readily removed by recrystallization.

The exclusive formation of the O-bonded isomer parallels the amide[3] and urea[4] chemistry where oxygen is preferred kinetically to nitrogen. For the sulfinamide ligand the oxygen is also preferred to the sulfur center, which is an additional potential nucleophile. For sulfite[12] and thiosulfate[16] ions, sulfur appears to be the preferred nucleophile—although the oxygen can also compete in substitution at Co(III),[16] the S-bonded forms are the thermodynamically more stable isomers. These observations emphasize the low selectivity of cobalt(III) amine complexes for nucleophiles in general; there is no appreciable bond-making component in the activation process for the substitution reaction.

The N-bonded isomer was obtained in its deprotonated form by the general procedure[1,19] developed for the syntheses of pentaamminecobalt(III) complexes of N-bound amides, ureas, carbamates, sulfonamides, and sulfamate. The mechanism for this reaction

$$[(NH_3)_5CoOS(CH_3)_2]^{3+} \xrightarrow[\text{base/Me}_2\text{SO}]{NH_2SOCH_3} [(NH_3)_5CoNHSOCH_3]^{2+} + \text{baseH}^+$$

is discussed in detail elsewhere[19] in connection with related syntheses. It likely involves prior formation of $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ (kinetic control), which then rearranges slowly but irreversibly to $[(NH_3)_5CoNHSOCH_3]^{2+}$. The overall reaction is faster than those involving amides and ureas, and this observation may be related to the greater acidity of CH_3SONH_2 relative to $RCONH_2$. The reaction is base catalyzed (as in aqueous solution), and proceeds via either $[(NH_3)_5CoOS(CH_3)NH]^{2+}$ or $[(NH_3)_4(NH_2)CoOS(CH_3)NH_2]^{2+}$.

The synthesis is not clean. Traces of two unidentified ions, as well as $[Co(NH_3)_6]^{3+}$, $[(NH_3)_5CoS(CH_3)O_2]^{2+}$, $[(NH_3)_5CoOSOCH_3]^{2+}$, and an unidentified yellow-brown more slowly eluting 2+ ion, were also observed. A suspicion that this latter ion may be $[(NH_3)_5CoS(O)(=NH)CH_3]^{2+}$ was given credence by the observation of a charge-transfer band at 280 nm (typical of a Co–S linkage) but is yet to be proven because it has been observed in amounts insufficient to allow successful isolation.

The two isolated forms of (methanesulfinamide)pentaamminecobalt(III) are easily distinguished on the basis of their charge and elution order on cation-exchange resins as well as by their ^{1}H NMR spectral characteristics (Table I). The absolute

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positions of, and separation between, cis-NH_3 (12 H) and trans-NH_3 (3 H) proton resonances for $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ are typical of other pentaamminecobalt(III) complexes containing O-bonded $RCONH_2$ molecules.[1-7] A single resonance (6.43 ppm, 2 H) was observed for the sulfinamide exo-NH_2 protons, and the location is similar to that for corresponding protons in $[(NH_3)_5CoOC(NH_2)_2]^{3+}$. Like the NH resonances of free urea and its O-bonded complex,[4,5] a broad NH_2 singlet for CH_3SONH_2 and $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ indicates a relatively low energy barrier to rotation about the S–N bond, since the two NH protons were not magnetically distinguishable at ambient temperatures. It also indicates a low barrier to nitrogen inversion because even in the absence of S–N π-bonding, the NH_2 protons are otherwise diastereotopic because of the chiral S center.

The ^1H NMR spectrum of $[(NH_3)_5CoNHSOCH_3]^{2+}$ exhibited a high-field resonance (δ 1.67 ppm, 1 H) characteristic of the $CoNH^{\neg}$ grouping.[4,5] Also the chemical shifts for the cis- and trans-NH_3 protons (12:3 H:H) are closer together than for the O-bonded isomer, as observed for the corresponding urea and amide complexes.[3-5] Furthermore, the usual trend for such resonances in pentaamminecobalt(III) complexes of N-bound ligands is reversed here with the trans-NH_3 resonance at lower field than the cis-NH_3 signal.

The protonated N-bonded isomer shows a characteristic ^1H NMR spectrum with the positions of, and separation between, cis- and trans-NH_3 signals conforming to the pattern observed for analogous neutral amide-*N* and urea-*N* complexes.[3-5] Moreover, all three of these methanesulfinamide complexes can be distinguished by their characteristic methyl proton resonance, not only from one another but also from free methanesulfinamide and O- and S-bonded sulfinate complexes (Table I), which were potential impurities. [Note that the trans-NH_3 proton resonance for $[(NH_3)_5CoS(CH_3)O_2]^{2+}$ is also unusual in being to lower field of the cis-NH_3 signal.]

The electronic absorption spectra (see Experimental Section) are diagnostic of the mode of coordination of methanesulfinamide to $(NH_3)_5Co^{III}$, following the patterns established for other N- and O-bonded $RCONH_2$ complexes of $(NH_3)_5Co^{III}$.

Reactivity of N- and O-Bonded Isomers. When a red aqueous solution of $[(NH_3)_5CoNHSOCH_3](ClO_4)_2$ is acidified, it instantaneously turns yellow; later it becomes pink. The yellow intermediate is $[(NH_3)_5CoNH_2SOCH_3]^{3+}$. In acidic Me_2SO-d_6 two low-field ^1H NMR signals (6.40, 6.97 ppm; 1 H, 1 H) have been detected, and the absolute chemical shift of each resonance is independent of $[H^+]$ above 1 stoichiometric equiv. Because of the chiral sulfur atom, the NH_2 protons are inherently diastereotopic, and restricted rotation about the sulfinamide S–N bond is not required to explain their inequivalence; indeed restricted rotation is impossible because the lone pair on nitrogen is bound to the metal ion. For free sulfinamides, the apparent restricted rotation about the N–S bond has been ascribed to restricted nitrogen inversion, due to the presence of an adjacent heteroatom, rather than to the influence of p–d π-bonding.[20]

The alternatives to protonation at nitrogen—O- or S-protonation—are much less likely since both –OH and –SH protons would be expected to exchange rapidly with free H^+ and give rise to an average proton signal of variable chemical shift and intensity. This is not observed. To our knowledge the site of protonation of free sulfinamides is unknown, although sulfonamides are known to protonate on nitrogen.[21]

The yellow to pink transformation was found to follow first-order kinetics ($t_{1/2}$ ca. 40 s, 0.1 M $HClO_4$, 25.0 °C) with a rate essentially independent of $[H^+]$ above 0.1 M. However, the plot (not shown) of k(obsd) vs $[H^+]$ in the low acid region (data in Table II) shows the hyperbolic behavour expected for an acid–base preequilibrium involving a weak acid, the deprotonated form of which is unreactive:

$$[(NH_3)_5Co\text{–}NH_2SOCH_3]^{3+} \underset{}{\overset{K'}{\rightleftharpoons}} [(NH_3)_5Co\text{–}NHSOCH_3]^{2+} + H^+$$

$$[(NH_3)_5Co\text{–}NH_2SOCH_3]^{3+} \xrightarrow{k} \begin{cases} [(NH_3)_5Co\text{–}OS(NH_2)CH_3]^{3+} & 95\% \\ [(NH_3)_5Co\text{–}OH_2]^{3+} & 5\% \end{cases}$$

The data were used to fit the parameters to the function appropriate to this scheme by nonlinear regression: $k(\text{obsd}) = kK'[H^+]/(1 + K'[H^+])$, yielding $k = 1.74 \pm 0.08) \times 10^{-2}$ s^{-1} and $K' = 258 \pm 23$ ($K'_a = 1/K'$; $pK'_a = 2.41 \pm 0.04$). The slight increase in k(obsd) above 0.1 M acid and beyond the region of complete protonation is considered to be a medium effect in changing from 1 M $NaClO_4$ to 1 M $HClO_4$ as the supporting electrolyte. A larger and not unexpected medium effect is seen in the results for 1 M KCl as the supporting electrolyte (Table III). The data were again used to fit the parameters to the function above, giving $k = (1.30 \pm 0.03) \times 10^{-2}$ s^{-1} and $K' = 804 \pm 41$ ($pK'_a = 2.91 \pm 0.03$). An independent estimation of the pK'_a came from the substantial acid dependence of the molar absorptivity for the reactant at 290 nm (Table IV, supplementary material). This was measured by extrapolation of the changing absorbance to zero reaction time, and the data were used to fit the relationship $\epsilon(\text{obsd}) = (\epsilon_B + \epsilon_{BH}K'[H^+])/(1 + K'[H^+])$, to give $K' = 669 \pm 56$ ($pK'_a = 2.83 \pm 0.04$), in reasonable agreement with that determined kinetically for the same medium ($pK'_a = 2.91$, 1.0 M KCl, 25 °C). The pK'_a is therefore similar to the values (2–3) for protonated urea-*N* and amide-*N* complexes.[3-5]

The same color changes occur in acidic Me_2SO, and the yellow intermediate decays at a similar rate compared to that in aqueous media (Table V). ^1H NMR studies in D_2O/DCl and Me_2SO-d_6/CF_3CO_2H indicated that $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ was the only immediate product in either solvent system; after several hours at 35 °C $[(NH_3)_5CoOD_2]^{3+}$ or $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ and $OS(CH_3)NH_2$) were ultimately formed.

To confirm these observations of a facile N- to O-linkage isomerization succeeded by a much slower solvolysis of the O-bonded isomer, weighed samples of $[(NH_3)_5CoNHSOCH_3](ClO_4)_2$ were reacted in 1.0 M $HClO_4$ at 25 °C for 7 min (ca.

Table II. Specific Rates of Isomerization[a] for $[(NH_3)_5Co\text{–}NH_2SOCH_3]^{3+}$ in Aqueous Acid (I = 1.0 M, $NaClO_4$) at 25 °C

$[HClO_4]$, M	10^3k(obsd), s^{-1} [b]	$[HClO_4]$, M	10^3k(obsd), s^{-1} [b]
0.991	17.9 ± 0.3	0.0076	14.7 ± 0.4
0.496	18.3 ± 0.3	0.0056	14.6 ± 0.5
0.099	17.8 ± 0.3	0.0036	9.8 ± 0.4
0.0099	14.9 ± 0.3	0.0016	5.1 ± 0.1

[a] Strictly, rates of disappearance (95% linkage isomerization, 5% hydrolysis)—refer to text. [b] Mean (≥3 determinations); mean deviations.

Table III. Specific Rates of Isomerization[a] for $[(NH_3)_5Co\text{–}NH_2SOCH_3]^{3+}$ in Aqueous Buffers (I = 1.0 M, KCl) at 25 °C

p[H$^+$][b]	10^3k(obsd), s^{-1}	p[H$^+$][b]	10^3k(obsd), s^{-1}
4.40[d]	0.50 ± 0.05	2.02[c]	11.3 ± 0.6
3.94[d]	1.12 ± 0.03	2.02[e]	11.0 ± 0.6
3.06[c]	5.07 ± 0.2	2.00[e]	11.9 ± 0.2
2.66[c]	7.09 ± 0.5	1.00[e]	12.8 ± 0.3

[a] Strictly, total rates of disappearance (95% linkage isomerization, 5% hydrolysis)—refer to text. [b] pH scale calibrated against [HCl] (I = 1.0, KCl) standards. [c] Glycine/HCl; $\Sigma([gly] + [glyH^+]) = 0.1$ M. [d] Acetic acid/acetate; $\Sigma([MeCO_2H] + [MeCO_2^-]) = 0.1$ M. [e] HCl/KCl.

(20) Raban, M. *Chem. Commun.* **1967**, 1017.

(21) N-Protonation of *N,N*-dimethyl-*p*-toluenesulfonamide in FSO_3H has been claimed (Birchall, T.; Gillespie, R. J. *Can. J. Chem.* **1963**, *41*, 2642) but is not unequivocal on the basis of the observed ^1H NMR inequivalence of N–Me groups. More convincing is the ^1H NMR spectrum of the cyclic sulfonamide, *N*-methyl-5-chloro-1,2-benzisothiazoline 1,1-dioxide, in FSO_3H, where variable-temperature observations of the coupling of NH to N–Me and methylene protons establishes N-protonation (Menger, F. M.; Mandell, L. *J. Am. Chem. Soc.* **1967**, *89*, 4424).

Table V. Kinetic and Product Distribution Data for Reactions of $[(NH_3)_5CoNH_2SOCH_3]^{3+}$ and $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ at 25 °C

N-Bonded Isomer[a]

	k(obsd), s^{-1}	% O-bonded isomer	% $[Co(NH_3)_5OH_2]^{3+}$
0.1 M $HClO_4$[b]	1.74 (±0.08) × 10^{-2}	95.2[e]	4.8[e]
Me_2SO/CF_3SO_3H[c]	1.47 (±0.02) × 10^{-2}		

O-Bonded Isomer[a]

	k(obsd), s^{-1}	% N-bonded isomer	% $[Co(NH_3)_5OH_2]^{3+}$
0.1 M $HClO_4$[b]	1.20 (±0.01) × 10^{-5}		
1.0 M $HClO_4$[b]		0	100
2.0 M $HClO_4$	1.02 (±0.01) × 10^{-5}		
3.0 M HCl[d]	3.4 (±0.1) × 10^{-3}		
0.1 M NaOH		8.5[e]	91.5[e]
0.1 M NaMES buffer[b] (pH 6.2)		23.7[e]	76.3[e]

[a] Perchlorate salts. [b] I = 1.0 M, $NaClO_4$. [c] 3 molar equiv. [d] T = 35 °C. [e] Normalized for 100% reaction; see Experimental Section.

$10t_{1/2}$). The solutions were then chromatographed and products identified and quantitated spectrophotometrically. The O-bonded isomer $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ was obtained in ca. 95% yield (together with ca. 5% $[Co(NH_3)_5OH_2]^{3+}$), and thus it is evident that the N- to O-linkage isomerization is the primary reaction of the N-bonded isomer in aqueous solution (Table V). This is a convenient synthesis of the O-bonded isomer commencing with the deprotonated N-bonded form (see Experimental Section).

The method of synthesizing $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ from the kinetically labile $[(NH_3)_5CoOSO_2CF_3]^{2+}$ ion showed that the methanesulfinamide-*O* isomer is the kinetically preferred form, and now this N- to O-rearrangement establishes that the O-bonded isomer is also the thermodynamically preferred isomer. Furthermore, since the subsequent and much slower solvolysis of the O-bonded isomer (discussed ahead) leads ultimately to $[(NH_3)_5Co(solvent)]^{3+}$ and free ligand, the N- to O-rearrangement must be an intramolecular process in which the methanesulfinamide ligand never leaves the metal ion.

In 0.1 M $HClO_4$, the O-bonded isomer aquates slowly (k(obsd) = 1.20 × 10^{-5} s^{-1}, 25 °C), yielding exclusively $[Co(NH_3)_5OH_2]^{3+}$ and free sulfinamide (Table V). In contrast, there is exclusive S–N cleavage for $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ in 3 M HCl (Table V), where acid-catalyzed hydrolysis of the ligand ($t_{1/2}$ = 3.4 min, 35 °C) yields initially $[(NH_3)_5CoOSOCH_3]^{2+}$ and NH_4^+. This is a two stage process

$$[(NH_3)_5Co\text{–}OS(NH_2)CH_3]^{3+} \xrightarrow[HCl]{k_1} [(NH_3)_5Co\text{–}OS(O)CH_3]^{3+} + NH_4^+$$

$$[(NH_3)_5Co\text{–}OS(O)CH_3]^{3+} \xrightarrow[HCl]{k_2} [(NH_3)_5Co\text{–}S(O)_2CH_3]^{2+} \quad [(NH_3)_5Co\text{–}OH_2]^{3+} + CH_3SO_2H$$

with $k_1 = 20k_2$ for 3 M HCl. The second step is also acid catalyzed, and this reaction will be dealt with separately elsewhere.[22] For the primary stage reaction no catalysis was observed for either 0–2 M $HClO_4$, 3 M CF_3SO_3H (k = 2.2 × 10^{-5} s^{-1}, 35 °C; 100% aqua product), or acidified Me_2SO (Table V). Clearly both H^+ and Cl^- are required for effective catalyzed hydrolysis. Dramatic specific anion effects in acid-catalyzed reactions have been documented previously for ligands such as N_3^-,[23] but there are few examples for hydrolysis of the ligand while bound to a metal ion. The rate of S–N cleavage in CH_3SONH_2 is evidently greatly accelerated by O-coordination to the $(NH_3)_5Co^{3+}$ moiety, since the reaction is complete in 60 min at 25 °C whereas the free ligand remains intact (>95%) in 3 M HCl even after 60 h at the same temperature. Interestingly, no such catalysis was observed for the structurally related amide complex $[(NH_3)_5CoOC(NH_2)CH_3]^{3+}$ under similar conditions, suggesting that the sulfur analogue may be activated by nucleophilic addition to the sulfur center (by Cl^-) with an increase in coordination number to 5.

The O-bonded isomer was also reacted in 1 M $HClO_4$ or CF_3SO_3H with an excess of $NaNO_2$ (>1 equiv.). After several minutes, $NaClO_4$ was added and a good yield of $[(NH_3)_5CoOS(O)CH_3](ClO_4)_2$ obtained. A portion of the reaction mixture prior to the addition of $NaClO_4$ was chromatographed on Sephadex; only the O-bonded sulfinate complex was observed. The inability of perchloric or triflic acid itself to effect ligand hydrolysis on the time scale of this nitrosation process indicates that NO^+ rather than H^+ is effective here. Although the nitrosation reaction is reasonably rapid, it is qualitatively much slower than the corresponding process for 2+ ions such as $[(NH_3)_5CoN_3]^{2+}$ but faster than for comparable 3+ ions such as $[(NH_3)_5CoOC(NH_2)_2]^{3+}$.[4]

The HCl-catalyzed hydrolysis of the O-bonded sulfinamide complex or the nitrosation reaction provide convenient and high-yield syntheses of the O-bonded sulfinate complex. The more usual synthesis is via the reaction of coordinated OH^- (in $[(NH_3)_5CoOH]^{2+}$) with CH_3SOCl in nonaqueous solution.[22]

In 0.1 M NaOH, hydrolysis of $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ leads to $[Co(NH_3)_5OH]^{2+}$ (91.5%) and $[(NH_3)_5CoNHSOCH_3]^{2+}$ (8.5%). No accompanying S–N cleavage (>0.5%) to form $[(NH_3)_5CoOSOCH_3]^{2+}$ was observed chromatographically. Also, the ^1H NMR spectra of a solution of $[(NH_3)_5CoOS(CH_3)NH_2](ClO_4)_3$ in D_2O/NaOD confirmed the formation of free methanesulfinamide and no $CH_3SO_2^-$. The proportion of N-bonded isomer formed in the reaction may be compared with the amount of N-bonded urea complex (ca. 7%)[4] formed during the base hydrolysis of $[(NH_3)_5CoOC(NH_2)_2]^{3+}$. The driving force for these reactions comes from formation of the thermodynamically stable deprotonated N-bonded isomers. That the O- to N-linkage isomerization of the methanesulfinamide ligand can be considered as a distinctly separate process to aquation is demonstrated by the considerably higher proportion of N-bonded isomer formed (24%) in competition with hydrolysis (76%) from the O-bonded isomer at pH 6.2 (0.1 M NaMES buffer; Table V); this argument has been advanced previously.[4] This greater efficacy of linkage isomerization in the spontaneous versus base-catalyzed hydrolysis has also been witnessed for pentaamminecobalt(III) complexes of O-bonded ureas[4] and O-bonded carbamates.[7]

The relative stabilities of the N- and O-bonded isomers of tripositive [(methanesulfinamide)pentaamminecobalt(III)] are described by an equilibrium constant that is defined by the ratio of the specific rates for N- to O-bonded and O- to N-bonded spontaneous rearrangements. The rate of solvolysis of the O-bonded isomer in dilute aqueous $HClO_4$ is known, and from this and the product distribution for this reaction at pH 6.2, assuming no contribution from the base-catalyzed path, the former can be separated to give the specific rate constants for the linkage isomerization and aquation pathways: k_{ON} = 3.73 × 10^{-6} s^{-1} and k_s = 1.20 × 10^{-5} s^{-1}. Also, the observed rate of decay of the N-bonded isomer in dilute $HClO_4$ (k(obsd) = 1.74 × 10^{-2} s^{-1}) can be separated according to the observed product distribution (Table V) to give k_{NO} = 1.66 × 10^{-2} s^{-1} and k_{H2O} = 8.4 × 10^{-4} s^{-1}. Thus, $K'_{NO} = k_{NO}/k_{ON}$ = 4665. This value can be compared with those for the urea complexes (200–3000)[4] and demonstrates the much greater thermodynamic stability of these O-bonded isomers compared to their corresponding N-bonded forms. However, the observed equilibrium is pH dependent (K'_{NO}(obsd) = $K'_{NO}[H^+]/([H^+] + K'_a)$) due to the selective deprotonation of the much more acidic N-bonded isomer (pK'_a ca. 2–3). Thus, at pH 1, K'_{NO}(obsd) = 4295, whereas at pH 7, K'_{NO}(obsd) = 0.12. The pK'_a of the O-bonded isomer has not been determined, but it is estimated to be ≥ca. 10.

Experimental Section

^1H NMR spectra were recorded for Me_2SO-d_6 solutions containing TMS by using a Varian T60 continuous-wave spectrometer. UV and visible spectra were measured with use of Cary 118 and 210 spectro-

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(23) Staples, P. J. *J. Chem. Soc.* **1967**, 45.

photometers. All reagents were analytical grade. $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$,[24] $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3 \cdot H_2O$,[25] $[Co(NH_3)_6]^{3+}$,[26] and 2,2,6,6-tetramethylpiperidine[27] were prepared by established methods. Measurements of pH were made at 25.0 °C on a Philips PW 9414 instrument with use of a Ross combination electrode and calibrated for slope against standard phthalate and phosphate buffers. pH values were converted to $p[H^+]$ through measurements on 1.00×10^{-2} and 1.00×10^{-3} M HCl (Volucon) solutions made up in the same medium (1.00 M KCl).

CH_3SONH_2. Methanesulfinamide was prepared by a simplification of the published method.[28] Methanesulfinyl chloride was obtained as described in the literature (^1H NMR: δ 3.43, SCH_3; $CDCl_3$); this was purified by fractional distillation until free of its major impurity, methanesulfonyl chloride (^1H NMR: δ 3.73, SCH_3; $CDCl_3$). This material (ca. 10 mL) was *cautiously* added *dropwise* to $NH_3(l)$ (80–100 mL) in a round-bottom 250-mL flask (*very exothermic reaction!*). A white solid formed instantly. The NH_3 was removed by rotary evaporation (15 °C, water-pump pressure), and the residual solid was suspended in diethyl ether; the yellow supernatant liquid was decanted and retained for later work up. The solid product was then extracted with dry acetone (3×), and then the solvent was removed by evaporation. The purified residue was washed with ether and dried over P_2O_5 in vacuo. Yield: ca. 6 g. This was substantially increased by extracting the original yellow filtrate with water. The ^1H NMR spectrum (δ 2.73, 3 H, SCH_3; δ 4.96, 2 H, NH_2 ($CDCl_3$); δ 2.50, 3 H, SCH_3; δ 5.72, 2 H (Me_2SO-d_6)) established the purity of the compound and the absence (>1%) of methanesulfinate.

$[(NH_3)_5CoOS(CH_3)NH_2](ClO_4)_3$. CH_3SONH_2 (4.0 g, 50.6 mmol) and $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (4.0 g, 6.8 mmol) were reacted (20 °C, 7 min) with acetone (30 mL), during which time the solution changed color from pink to slightly orange. Addition of diethyl ether (200 mL) caused precipitation of a pink solid, which was rapidly dissolved in ice water (5–10 mL) and filtered onto solid $NaClO_4$. The resulting pink crystals were recrystallized from ice water (30 mL) by addition of saturated aqueous $NaClO_4$. Yield: ca. 1 g. The purity of the complex was checked chromatographically on Sephadex. Visible spectrum: ϵ_{514}^{max} 63.6, ϵ_{349}^{max} 65.9 (0.1 M $HClO_4$). These molar absorptivities were checked by measuring the product spectra (aged 1 week at 25 °C): $[Co(NH_3)_5OH_2]^{3+}$, ϵ_{492}^{max} 47.7. We note that some samples obtained as above solvolyzed unusually rapidly and with irreproducible specific rates. The best samples were obtained from the N-bonded isomer (below), although recrystallization from dilute Li_nEDTA (pH 7) solutions removed the problem. These difficulties are no doubt associated with catalysis by residual Co(II) in the $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ and have been observed in preparations of analogous $[(NH_3)_5CoOC(NH_2)R]^{3+}$ complexes.[1]

When the original product (ca. 2 °C) was sorbed on SP-Sephadex C25 resin and eluted with 0.2 M NaCl, four bands were observed. The ions were identified by their rate of elution and electronic absorption spectra as yellow-brown $[(NH_3)_5CoSO_2CH_3]^{2+}$ (1%; $\epsilon_{294.5}^{max}$ 13 100, ϵ_{455}^{max} 165.0), pink $[(NH_3)_5CoOSOCH_3]^{2+}$ (9%; $\epsilon_{307.5}^{max}$ 1265, ϵ_{515}^{max} 80.0), a trace of $[Co(NH_3)_5OH_2]^{3+}$, and $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ (90%; ϵ_{514}^{max} 63.6). The O-bonded isomer could also be prepared from the N-bonded isomer as follows. A sample of $(NH_3)_5CoNHSOCH_3](ClO_4)_2 \cdot H_2O$ (1.0 g) was suspended in water (20 mL) and treated with excess CF_3CO_2H (5 mL). After 10 min, sufficient time for the N-bonded isomer to have completely isomerized, cold aqueous $NaClO_4$ (5 M) was added and the mixture cooled on ice. The crystals of $(NH_3)_5CoOS(NH_2)CH_3](ClO_4)_2 \cdot H_2O$ that had deposited were collected, washed, dried, and recrystallized as above. Slow crystallization produced large pink rods, and the kinetics of solvolysis on these samples were reproducible.

$[(NH_3)_5CoNHSOCH_3](ClO_4)_2 \cdot H_2O$. CH_3SONH_2 (3.0 g, 38.1 mmol) and $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3 \cdot H_2O$ (4.0 g, 7.4 mmol) were reacted with 2,2,6,6-tetramethylpiperidine (2.0 g, 14.2 mmol) in Me_2SO (30 mL) for 2 h at 65 °C. An equal volume of butan-2-ol followed by excess diethyl ether caused precipitation on a red oily solid. This product was dissolved in water, and the solution was sorbed onto SP-Sephadex-C25 resin and eluted with 0.2 M $NaClO_4$ (pH 9.5, Tris buffer). A red-crimson (2+) product eluted behind a trace of a yellow (1+) ion and ahead of some (<10%) $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ and $[Co(NH_3)_6]^{3+}$ (ca. 10%). In some preparations the 2+ band was a mixture of $[(NH_3)_5OH]^{2+}$ and $[(NH_3)_5CoNHSOCH_3]^{2+}$, but the latter can be obtained pure by rechromatographing on Biorex (Na^+ form, 200–400 mesh) cation-exchange resin and eluting with 1 M $NaClO_4$ (pH 9.5, Tris). Red crystals, which deposited on cooling the eluted major fraction, were collected by filtration, washed with absolute ethanol and diethyl ether, and air-dried. ^1H NMR analysis revealed the presence of 1.0 molar equiv of lattice water, which was subsequently removed by storage in vacuo over P_2O_5. Yield: 62%. Anal. Calcd: C, 2.85; H, 4.51; N, 19.95; Cl, 16.86. Found: C, 2.81; H, 4.62; N, 19.68; Cl, 16.71. Electronic spectrum: ϵ_{508}^{max} 103.3, ϵ_{285}^{max} 2193 (0.1 M Tris).

In a similar preparation, $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3 \cdot H_2O$ (6.0 g) was reacted with CH_3SONH_2 (2.0 g) and NEt_3 (2.0 g) in Me_2SO (30 mL) for 30 min (65 °C). An equal volume of butan-2-ol and excess diethyl ether were added to precipitate a brown oily residue. This was dissolved in water, the mixture was filtered to remove green cobalt oxide, and the solution was chromatographed as above on Sephadex by using the same eluant. Traces of pink and yellow-brown 1+ ions eluted ahead of a small amount of yellow-brown $[(NH_3)_5CoS(CH_3)O_2]^{2+}$, red $[(NH_3)_5CoNHSOCH_3]^{2+}$, and a trace of an unknown yellow brown 2+ ion. Following these bands, the pink $[(NH_3)_5CoOS(CH_3)NH_2]^{3+}$ and yellow $[Co(NH_3)_6]^{3+}$ were also detected. The 2+ ions were rechromatographed on Biorex resin and eluted as above. The major product, $[(NH_3)_5CoNHSOCH_3]^{2+}$, ran ahead of the other 2+ ions and was isolated as the perchlorate salt following removal of water by evaporation. The unknown yellow-brown 2+ ion, which eluted behind the other 2+ ions on Sephadex and Biorex but well ahead of 3+ ions, may have contained a Co–S linkage, as indicated by an intense absorption maximum at ca. 290 nm, but this was not investigated further.

$[(NH_3)_5CoOSOCH_3](ClO_4)_2$ and $[(NH_3)_5CoS(CH_3)O_2](ClO_4)_2$. These complexes were isolated in small (<10%) yields from the above preparations designed primarily for obtaining the sulfinamide species. They were isolated following chromatography and evaporation to concentrated solutions whence they crystallized. They were characterized by their rate of elution, their known molar absorptivities and wavelength maxima (see above), and NMR spectra (Table I). Anal. Calcd for $[(NH_3)_5CoOSOCH_3](ClO_4)_2 \cdot H_2O$: C, 2.73; H, 4.55; N, 15.91; S, 7.28. Found: C, 2.56; H, 4.72; N, 15.48; S, 7.30. Calcd for $[(NH_3)_5CoS(CH_3)O_2](ClO_4)_2 \cdot H_2O$: as above. Found: C, 2.49; H, 4.86; N, 15.28; S, 7.01.

The O-bonded sulfinate[23] has been prepared in high yield by three alternative routes, two involving the sulfinamide-*O* complex as the reactant. This species (1.0 g) is dissolved in water (30 mL) containing $NaNO_2$ (1.0 g), and CF_3CO_2H (5 mL) is added portionwise. After 15 min, $HClO_4$ (5 mL) is added and the mixture is cooled on ice. The crystals are collected, washed with ethanol and ether, and air-dried. Recrystallization was from water/$NaClO_4$ at ambient temperature. In a different synthesis, the O-bonded sulfinamide complex was dissolved in 3 M HCl (30 mL) and the reaction allowed to proceed for 2 h. The product was worked up as above and the perchlorate salt isolated.

Kinetic Data. Solid complexes were rapidly dissolved in thermally equilibrated solutions (25.0 °C), and spectra were recorded without delay on a Cary 118 spectrophotometer. Spectrophotometric rate data were obtained from absorbance changes at 520 nm, and all reported specific rates represent means of at least three determinations. For reactions of the N-bonded isomer, runs were conducted by the rapid introduction of 50 μL of 2×10^{-2} M Co solution into 2.5 mL of prethermostated acid (I = 1.0 M; $NaClO_4$ or KCl). The A/t data were collected at 290 nm where at this low [Co] there are large changes associated both with protonation and linkage isomerization. Cell temperatures were regulated to ±0.1 °C by water circulating from a Haake bath and monitored (±0.01 °C) by using a properly calibrated glass-housed miniprobe. Some rates were also measured by continuous ^1H NMR spectral monitoring. The rates of acid-catalyzed hydrolysis of $[(NH_3)_5CoOS(NH_2)CH_3]^{3+}$ in 3 M DCl and 3 M CF_3SO_3D (D_2O) were determined exclusively by this technique. The probe temperature was regulated to 35.0 ● 0.2 °C.

pK'_a Determination. For the reactions of the N-bonded sulfinamide complex in buffered KCl (I = 1 M) and in acidified $NaClO_4$ (I = 1 M), the zero-time absorbances were measured as a function of $[H^+]$. These were converted to the equivalent of molar absorbancy indices by dividing by the final absorbance for each particular run (shown to be pH independent), and the $\epsilon(obsd)/[H^+]$ data so obtained were used to fit the parameters in the function describing the protonation by weighted nonlinear least squares: $\epsilon(obsd) = (\epsilon_B + \epsilon_{BH}K'[H^+])/(1 + K'[H^+])$, where ϵ_B is the molar absorbancy index for the deprotonated form of the N-bonded isomer and ϵ_{BH} is the molar absorbancy index for the protonated form. Runs were carried out in triplicate for each $[H^+]$. Similarly, the rate data $k(obsd)$ and $[H^+]$ were used to fit the parameters in the function by weighted nonlinear regression: $k(obsd) = kK'[H^+]/(1 + K'[H^+])$ describing the acid–base preequilibrium and values for the acidity constant K'_a ($=1/K'$) as well as the limiting specific rate k for

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the reaction of the fully protonated N-bonded sulfinamide isomer were obtained.

Product Distribution. In typical experiments, cobalt complexes were dissolved in appropriate media and after specific lengths of time the product solutions were sorbed onto SP-Sephadex C25 cation-exchange resin and eluted with either $NaClO_4$ (pH < 1 or ca. 6), NaCl (pH 7), or 0.23 M Na^+ (0.1 M $H_2PO_4^-$, 0.1 M HPO_4^{2-}, 0.2 M Cl^-; pH 6.88). Products were identified and quantified by absorption spectra, using ϵ and λ values reported.

For the reaction of $[(NH_3)_5CoNHSOCH_3]^{2+}$ in 0.1 M $HClO_4$ (I = 1.0 M, $NaClO_4$), after 93.7% reaction (10 min, 22 °C) recoveries were as follows: N-bonded isomer, 6.3% (R_f = 6.5); $[Co(NH_3)_5OH_2]^{3+}$, 4.5% (R_f = 3.5); O-bonded isomer, 89.2% (R_f = 2.5). For the O-bonded isomer in 0.1 M NaOH (I = 0.1 M) after 72% reaction (60 s, 20 °C), recoveries were as follows: N-bonded isomer, 6.1% (R_f = 5.7); $[Co(NH_3)_5OH_2]^{3+}$, 66.0% (R_f = 3.7); O-bonded isomer, 27.9% (R_f = 1.7). For the reaction of the O-bonded isomer in 0.1 M NaMES buffer (pH 6.2), after 88% reaction (69 h, 25 °C), recoveries were as follows: N-bonded isomer, 19.8% (R_f = 7.5); $[Co(NH_3)_5OH_2]^{3+}$, 63.8% (R_f = 4.5); O-bonded isomer, 12% (R_f = 2.3); $[Co(NH_3)_6]^{3+}$, 4% (R_f = 1.5).

Acknowledgment. This work was supported by a grant from the Australian Research Grants Scheme.

Registry No. II, 18649-16-6; $[(NH_3)_5CoOS(CH_3)NH_2](ClO_4)_3$, 128445-10-3; $[(NH_3)_5CoNHSOCH_3](ClO_4)_2$, 128445-12-5; $[(NH_3)_5CoNH_2SOCH_3](ClO_4)_3$, 128445-14-7; $[(NH_3)_5CoOSOCH_3](ClO_4)_2$, 128445-16-9; $[(NH_3)_5CoS(CH_3)O_2](ClO_4)_2$, 128470-30-4; $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$, 75522-50-8; $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3$, 51667-94-8; MeSOCl, 676-85-7; NH_3, 7664-41-7.

Supplementary Material Available: Table IV, containing spectral data (1 page). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Indiana University-Purdue University at Fort Wayne, Fort Wayne, Indiana 46805

Equilibria and Spectra of Mono- and Polynuclear Bromocuprate(I) Complexes in Aqueous Solution

Kenneth L. Stevenson,* Melissa M. Grush,[1] and Kristine S. Kurtz[2]

Received October 16, 1989

The spectra of $CuBr_2^-$ and $CuBr_3^{2-}$ were resolved in aqueous solution at 1 and 5 M ionic strengths, in neutral and 1 M H^+ concentration. The spectra revealed the presence of CTTS absorption bands centered at about 277 nm for the 5 M ionic strength solutions. The tris complex exhibits a higher molar extinction than does the bis complex in each solution, and increasing ionic strength causes a blue shift in this band. Such spectral behavior bears a very strong resemblance to that of the chlorocuprate(I) complexes. At increasing copper concentrations, spectral and solubility data confirmed that polynuclear complexes form, and freezing-point depression studies indicated that these complexes are $Cu_2Br_5^{3-}$ and $Cu_3Br_7^{4-}$. Concentration stability constants were calculated for these complexes at 5 M ionic strength, yielding $\beta_{25} = 4.80 \times 10^{15}$ and $\beta_{37} = 1.75 \times 10^{24}$. Spectral studies indicated that $Cu_2Br_5^{3-}$ exhibits a maximum at 277 nm, with nearly twice the extinction coefficient of $CuBr_3^{2-}$, while $Cu_3Br_7^{4-}$ showed a red-shift of this band to about 291 nm with almost a 3-fold increase in extinction coefficient compared to that of the monomer.

Introduction

The chlorocuprate(I) complexes in aqueous solution have been extensively studied in terms of equilibria,[3,4] spectra,[5-9] and photochemistry.[5,6,9-11] Such studies have indicated that the monomeric complexes, $CuCl_2^-$ and $CuCl_3^{2-}$, are the primary species in aqueous solutions of 0.01 M CuCl and at ligand concentrations up to 5 M and that the absorption spectra of both complexes, occurring only in the ultraviolet region, exhibit charge-transfer-to-solvent (CTTS) bands at about 274 nm, the intensities of which are higher for the tris- than for the bis-coordinated complex.

On the other hand, the analogous bromocuprate(I) complexes have received much less attention. Several equilibrium studies[3,12] in aqueous solution have shown that the complexes, $CuBr_2^-$ and $CuBr_3^{2-}$, are formed similarly to the chloro complexes, with somewhat higher stability constants, but no published spectra of these complexes are known. A comparison of the spectra of the chloro- and bromocuprates, as well as the analogous iodocuprates, could give some valuable insights into the effects the ligand has on the nature of the CTTS transition. This study, then, considers the equilibria and spectra of these bromocuprate complexes, and a subsequent paper will consider their photochemical properties.

In the course of this investigation, we discovered that, in contrast to the chlorocuprates, the bromocuprates tend to form dimers and trimers at relatively low copper concentrations (ca. 0.01 M), complicating the resolution of the equilibria and spectra. We have been successful, however, in separating the monomer spectra from those of the polynuclear complexes by carrying out the studies at low enough copper concentrations where only monomers exist. The spectra of the polynuclear species were then determined from solutions of higher copper concentrations using stability constants determined from solubility data.

Experimental Section

Materials. Reagent grade NaBr, HBr, $NaClO_4$, and $HClO_4$ were used for preparation of all stock solutions, from which solutions of a given hydrogen ion concentration, ligand concentration, and ionic strength could be prepared. CuBr was prepared from reagent grade copper powder and copper(II) sulfate by the same method described earlier[5] for the preparation of CuCl.

Procedures. For the determination of spectra of monomers, solutions of the desired ionic strength, ligand, and hydrogen ion concentration were prepared and bubble-degassed with argon. Exactly 3.0 mL of this solution was placed in a 1-cm quartz cuvette situated in an HP-8451 photodiode array spectrophotometer and the reference base line recorded. With a micropipet, 30 μL of a stock solution containing 0.01 M CuBr and 5 M NaBr was added so that the final concentration of CuBr was 9.8×10^{-5} M. This was quickly stirred by gently bubbling with He gas and the spectrum taken within 20 s of mixing to minimize oxidation by traces of air in the solutions. In spite of these precautions and because the copper concentrations were so small, occasionally the absorbance

(1) Graduate student, Department of Chemistry, University of California at Berkeley.
(2) Graduate student, Department of Chemistry, Michigan State University.
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0020-1669/90/1329-3150$02.50/0