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Linkage Isomerization, Acid and Base Hydrolysis, and Oxidation Reactions of Coordinated Methanesulfinate: Oxygen- and Sulfur-Bonded Isomers of $[(NH_3)_5Co(CH_3SO_2)]^{2+}$ [1]

W. Gregory Jackson,* Silvia S. Jurisson, and Margaret A. O'Leary

Department of Chemistry, University College (NSW), Australian Defence Force Academy,
Northcott Dr., Campbell, ACT, Australia 2600

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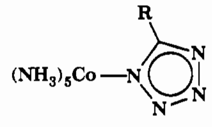
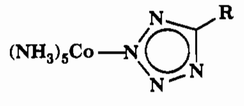
Alkanesulfinates (RSO_2^-) can bind to a metal ion through either the sulfur or oxygen atom. Herein are described the synthesis of both linkage isomeric pentaamminecobalt(III) complexes containing $CH_3SO_2^-$ so bonded. The $[(NH_3)_5CoOH]^{2+}$ complex reacts with CH_3SOCl in $PO(OCH_3)_3$ solvent to give the O-bonded isomer, while photoisomerization of this isomer gives the more stable S-bonded form. The reaction between $[(NH_3)_5CoO_3SCF_3]^{2+}$ and free $CH_3SO_2^-$ in acetone gives a mixture of the S- and O-bonded isomers, which are readily separated, while the O-bonded isomer is also obtained from the corresponding sulfinamide species $[(NH_3)_5CoOS(NH_2)CH_3]^{2+}$ by either acid-catalyzed hydrolysis or nitrosation of the amine function. The O-bonded isomer assignment follows unambiguously from its optical resolution and also from each of two independent methods of synthesis. The S-bonded isomer has characteristic ^1H NMR (trans-NH_3 shift) and UV spectra (Co–S charge transfer). The $[(NH_3)_5CoOS(O)CH_3]^{2+}$ isomer is slowly alkylated by MeI in Me_2SO to generate the solvent complex $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ and free Me_2SO_2. Further, it is rapidly oxidized by H_2O_2 to the known $[(NH_3)_5CoOS(O)_2CH_3]^{2+}$ complex (for which only oxygen bonding is possible), and by Cl_2 (or *N*-chlorosuccinimide) to generate $[(NH_3)_5CoOS(Cl)(O)CH_3]^{3+}$, which then hydrolyzes extremely rapidly to $[(NH_3)_5CoOH_2]^{3+}$ and free CH_3SO_2Cl (which is ultimately hydrolyzed to CH_3SO_3H and HCl); only a little $[(NH_3)_5CoOS(O)_2CH_3]^{2+}$ (6%, $I \sim 0$ M, 25 °C) is produced in the Cl_2 oxidation route, and no $[(NH_3)_5CoCl]^{2+}$ (<0.5%) by linkage isomerization of $[(NH_3)_5CoOS(Cl)(O)CH_3]^{3+}$ by a route akin to that reported for $[(NH_3)_5CoOS(O)_2F]^{2+}$. In NO_3^-, HSO_4^-, or Cl^- media, significant anion competition is observed for the Cl_2-induced hydrolysis (consistent with Co–O rather than O–S cleavage), but the extent is generally less than by the classic induced aquation routes. In all these reactions the resolved complex loses its activity. Also, as expected the sulfur-bonded isomer undergoes none of these reactions, nor does it readily lose its trans-NH_3 (through labilization by S), contrary to reports for other and closely related S-bonded sulfinate complexes. The $[(NH_3)_5CoOS(O)CH_3]^{2+}$ isomer is less stable than $[(NH_3)_5CoSO_2CH_3]^{2+}$, isomerizing slowly but completely in solution ($k_s^{OS} = 6.0 \times 10^{-7}$ s^{-1}) and even more slowly in the solid state. A base-catalyzed path has been detected, $k(\text{obsd}) = k_s^{OS} + k_{OH}(\text{obsd})[OH^-]$, with $k_{OH}(\text{obsd}) = k_{OH} + k_{OH}^{OS} = 0.033$ M^{-1} s^{-1}, 25 °C, $I = 0.1$ M, $NaClO_4$. Base hydrolysis (75%, $k_{OH} = 0.024$ M^{-1} s^{-1}) accompanies the OH^--catalyzed O- to S-rearrangement (26%, $k_{OH}^{OS} = 0.0085$ M^{-1} s^{-1}); above 0.01 M the product distribution is independent of $[OH^-]$, confirming that both parallel reactions are first-order in $[OH^-]$. More competitive hydrolysis by the base-catalyzed route is now the norm for linkage isomerization. Azide ion competition accompanies base hydrolysis, and the extent (6.9% for 1 M NaN_3) is lower than that usually observed for a 2+ $[(NH_3)_5CoX]^{n+}$ complex, consistent with its low reactivity and the emerging correlation between the two. The O-bonded isomer also undergoes acid-catalyzed reaction ($k(\text{obsd}) = 1.5 \times 10^{-4}$ s^{-1}, 3 M DCl), and the product is $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ and free ligand $MeSO_2H$; only the Co–O cleavage path leading to hydrolysis appears to be acid-catalyzed; linkage isomerization is not competitive in strong acid. Finally, the racemization rate for (+)-$[(NH_3)_5CoOS(O)CH_3]^{2+}$, which is a measure of the oxygen scrambling plus O- to S-bonded rates, is very small, but attempts to quantify it were consistently thwarted by Co(II) catalysis.

Introduction

In the last decade a number of new linkage isomeric pairs and intramolecular rearrangements have been discovered, especially for $[(NH_3)_5CoX]^{n+}$,[2-8] largely through concerted efforts to synthesize the less stable linkage isomers. For example $[(NH_3)_5CoOC(S)NHMe]^{2+}$, which isomerizes irreversibly to $[(NH_3)_5CoSC(O)NHMe]^{2+}$, is obtained by reacting $[(NH_3)_5CoOH]^{2+}$ with SCNMe;[3] initial oxygen bonding is assured because the reaction does not involve Co–O cleavage. Similarly, the N1 (adjacent R) linkage isomers of the tetrazoles


N1 isomer


N2 isomer

are unstable with respect to the N2 (remote R) forms but can be synthesized by N_3^- addition to the coordinated nitrile in $[(NH_3)_5Co\text{–}NCR]^{2+}$.[9] Sulfinates RSO_2^- are potentially ambidentate ligands (O- or S-), but only S-bonded forms $[(NH_3)_5CoSO_2R]^{n+}$ are known.[10] We anticipated that the O-bonded forms

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(1) Paper presented at the 11th Coordination and Organometallic Chemistry Conference (Royal Australian Chemical Institute), Australian National University, Aug 1982; Abstracts XI COMO, P62.

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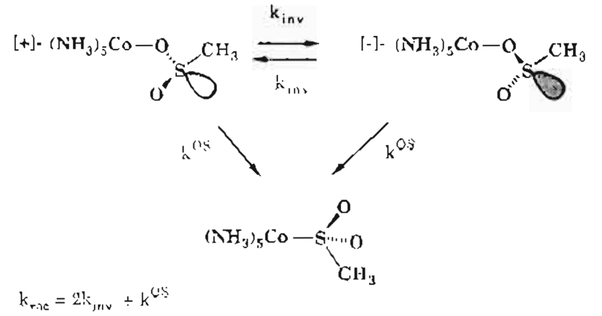
might be synthesized from $[(NH_3)_5CoOH]^{2+}$ and $RS(O)OR'$[2] or RSOCl under the appropriate conditions again utilizing the residual nucleophilicity of coordinated OH^-, and this hope has now been realized. Further, RSO_2^- is chiral when O-bonded but achiral when S-bonded, by analogy with sulfinic acid esters and sulfones, respectively. The resolved O-bonded isomer is of special interest because its racemization is a measure of oxygen scrambling, akin to oxygen scrambling in ions such as $[(NH_3)_5Co{-}^{17}ONO]^{2+}$[11,12] or $[(NH_3)_5Co{-}^{18}OC(O)Me]^{2+}$.[13] Also, we were interested in the O- to S-bonded rate, which could be independently measured, to assess the relative efficacies of O- and S-capture.



Similar rearrangements processes have been probed for sulfinate as part of a chelate in $[Co(en)_2(NH_2CH_2CH_2OSO)]^{2+}$.[14,15] Here O scrambling amounts to a mutarotation and optical resolution is not required; as it happens, however, the resolved epimers were used to probe O- to O-bonded rearrangement by CD spectroscopy,[15] although independently ^{13}C and ^1H NMR have been used.[16] The oxygen scrambling appears to be faster than O- to S-bonded rearrangement,[17] and we were interested in knowing the restriction on these rates imposed by the chelate ring, especially as scrambling does not involve a change in ring size whereas O- to S-bonded rearrangement involves a ring contraction. The $[(NH_3)_5Co(CH_3SO_2)]^{2+}$ system seemed ideal in this regard.

Finally, oxidation and alkylation at sulfur in the O-bonded (but not the S-bonded) isomer seemed a good way not only to distinguish the isomers but also to generate very good leaving groups such as CH_3SO_2Cl and the sulfone $(CH_3)_2SO_2$, work which is relevant to substitution mechanisms.

Results and Discussion

Syntheses. The O- and S-bonded $CH_3SO_2^-$ complexes can be made in one synthesis by reaction of the triflato complex $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$ in acetone at ambient temperature with a $CH_3SO_2^-$ salt or CH_3SO_2H—they are separated by fractional crystallization or by ion-exchange chromatography. Previously only S-bonded arenesulfinate complexes (benzene- and toluenesulfinates) have been obtained by reaction of $[(NH_3)_5CoOSMe_2]^{3+}$ with RSO_2^- in Me_2SO.[10] From our results (vide infra) it seems likely that any O-bonded isomer formed would be isomerized to the more stable S-bonded form under these conditions, whereas a kinetic isomer distribution is found in our rapid triflate preparation, which is carried out under very mild conditions.

The $[(NH_3)_5CoOH]^{2+}$ ion reacts with MeSOCl in an inert solvent containing a noncoordinating base to give the O-bonded isomer exclusively. The S-bonded isomer is simply obtained by isomerization of the O-form in Me_2SO; isomerization is complete.

Other routes to the O- and S-bonded forms have been described recently[7] in connection with the chemistry of the related ligand methanesulfinamide. The neutral $MeSONH_2$ ligand prefers to bind through O rather than S or N, and the O-bonded isomer can be deaminated by H^+ or NO^+ to generate the O-bonded sulfinate:

$$[(NH_3)_5Co\text{-}OS(Me)NH_2]^{3+} \xrightarrow[\text{or } NO^+]{HCl} [(NH_3)_5Co\text{-}OS(Me)O]^{2+} + NH_4^+ \text{ or } N_2$$

Characterization. The isomer assignment for the O-bonded isomer follows from the synthetic routes. The Co–O bond is retained when $[(NH_3)_5CoOH]^{2+}$ attacks MeSOCl, and this method of synthesis is analogous to that used to prepare, e.g. $[(NH_3)_5CoOS(O)_2R]^{2+}$.[19] Similarly the Co–O bond is retained when the S–N bond is cleaved in $[(NH_3)_5CoOS(Me)NH_2]^{3+}$.[7] Further, H_2O_2 oxidation yields the known[19] $[(NH_3)_5CoOS(O)_2Me]^{2+}$, clearly identifying the Co–O–S–Me fragment in the reactant.

The O-bonded form was successfully resolved using the hydrogen dibenzoyl-L-tartrate anion. The resolved ion completely racemized on conversion to the achiral S-bonded form; it can of course racemize without going via the S-bonded isomer (vide infra). These observations constitute unambiguous proof of O-bonding.

The ^1H NMR spectrum is typical of the $Co(NH_3)_5$–O fragment,[20] with cis- and trans-NH_3 signals separated by 1.07 ppm and a trans-NH_3 signal at δ 2.78 ppm in Me_2SO-d_6. The vis/UV spectrum is also characteristic of the CoN_5O chromophore (ϵ_{515}(max) 80.0), and the strong (ϵ 1265) as distinct from very strong absorption at 308 nm in the UV is typical[21,22] of Co–O–S– (i.e., the S is β rather than α to the metal ion); cf. Co–S, with ϵ ca. 10 000–20 000.[22]

The yellow isomer of composition $[(NH_3)_5Co(CH_3SO_2)]Z_2$ is clearly linkage isomeric with $[(NH_3)_5CoOS(O)CH_3]Z_2$; it is obtained from the former by heating, either in solution or in the solid state. Its vis/UV spectrum is analogous to those of $[(NH_3)_5CoSO_2R]^{2+}$, where R = aryl, and all these ions exhibit characteristic Co–S charge-transfer absorption,[10] with ϵ_{295}(max) 13 100 for R = Me. One of the aryl derivatives has been characterized by single-crystal X-ray crystallography.[10] The ^1H NMR spectrum is also typical, exhibiting "reversed" cis- (δ 3.00 ppm) and trans-NH_3 (δ 3.65 ppm) signals; the cis peak is usually to lower field, except for S-bonded ligands and others such as CN^-.[7,20]

Elder et al. report that the trans-NH_3 group is readily lost from the $[(NH_3)_5CoSO_2R]^{2+}$ salts in solution, evidenced by a reduced trans-NH_3 proton count and in one case the appearance of an additional signal (δ ca. 3.6 ppm) attributable to released NH_3.[10] However, in dry Me_2SO-d_6 free NH_3 gives a broad signal much closer to $SiMe_4$, ca. 1.0 ppm, and on addition of sufficient acid (CF_3CO_2H), a characteristic 1:1:1 sharp triplet (J_{NH} = 51 Hz) for the NH_4^+ ion is observed centered at δ 7.33 ppm. Our Me derivative gives the correct proton intensities and does not show the additional signal, even in the presence of excess H^+.

Reactions of the Coordinated Ligand. Sulfolane is a poor ligand,[13,23-25] and dimethyl sulfone should also be. However the

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[17] From the activation parameters given in ref 14, $k = 6.6 \times 10^{-8}$ s^{-1} for the O- to S-bonded rearrangement of $[Co(en)_2(NH_2CH_2CH_2OSO)]^{2+}$, corresponding to a half-life of 2923 h at 25 °C (not 600 h as quoted in ref 14). We obtain $k = 2.46 \times 10^{-6}$ s^{-1} for the O- to O-bonded rearrangement at 19 °C from the CD data published in ref 15; this is the sum of forward and reverse specific rates.

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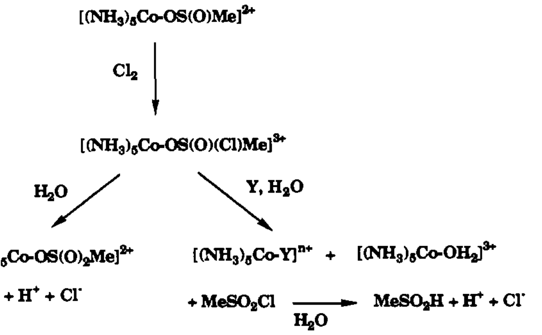
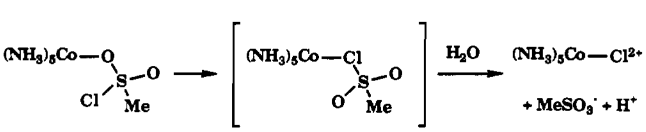
sulfur in $[(NH_3)_5CoOS(O)Me]^{3+}$ is only alkylated very slowly by MeI in Me_2SO, and thus the Me_2SO_2 so generated appears as free ligand together with solvent complex $[(NH_3)_5CoOSMe_2]^{3+}$—$[(NH_3)_5CoOS(O)Me_2]^{3+}$ was never observed.

Oxidation of the unsaturated sulfur was also anticipated. H_2O_2, or more rapidly H_2O_2/H^+, generates $[(NH_3)_5CoOS(O)_2Me]^{2+}$ faster than the latter ion hydrolyzes ($t_{1/2}$ ca. 58 min, 25 °C[19]). Oxidation by Cl_2 (or *N*-chlorosuccinnimide, NCS) was even more rapid, yielding $[(NH_3)_5CoOH_2]^{3+}$ and free $MeSO_2Cl$ which could be easily detected and identified (^1H NMR) before it hydrolyzed ultimately to $MeSO_2H$ and Cl^-. Neutral methanesulfinyl chloride is evidently a very good leaving group. The transient existence of $[(NH_3)_5CoOS(Cl)Me]^{3+}$ was not detected by ^1H NMR, but considerable anion competition accompanied the hydrolysis reaction in 1 M NO_3^-, HSO_4^-, and Cl^- media (~38%, 14%, and 13.5%, respectively; Table II (supplementary material)). For HSO_4^- and Cl^- the amounts are less and for NO_3^- the amount more than the limits achieved in the so-called induced aquation. Nitrosation of $[(NH_3)_5CoN_3]^{2+}$ yields 31%, 21%, and 18%, respectively, for the three nucleophiles NO_3^-, HSO_4^-, and Cl^-.[26] The observation establishes Co–O rather than S–O cleavage, and this now seems to be usual.[19,27] There appears to be a correlation between lability and the extent of anion competition,[28] and the present competition results confirm that $MeSO_2Cl$ is an excellent leaving group.

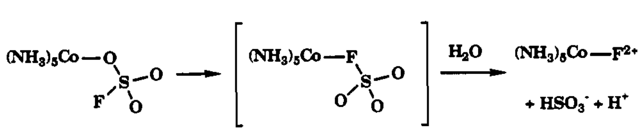
Some competitive hydrolysis (5–15%) of the ligand accompanies Co–O cleavage, but the % anion capture corrected for this pathway is insufficient to raise the *R* values[26] for Cl^- and HSO_4^- anion competition to the induced aquation limits:



Curiously, the amount is medium dependent (Table II (supplementary material)). Clearly this S–Cl cleavage reaction is rapid also, much more rapid than for the free ligand, and an independent study proposes to quantify this.[29] Furthermore, some $[(NH_3)_5CoCl]^{2+}$ might have been anticipated by intramolecular rearrangement



akin to that observed for $[(NH_3)_5CoOS(O)_2X]^{2+}$ (X = F, Cl):[27,30]



None (<0.5%) was found.

There are parallels to the chemistry of coordinated thiols and to organic sulfur chemistry. For example the residue Co–S–R is oxidized by H_2O_2 stepwise to Co–SO–R and then Co–SO_2–R, and these reactions are acid-catalyzed.[22] For Cl_2 or NCS as oxidant, Co–SO–R adds Cl^+ to give Co–S(Cl)O–R but then cleaves the Co–S bond with capture of the oxygen, yielding Co–OS(Cl)–R which goes on to Co–OS(O)$_2$–R with further hydrolysis and Cl^+ addition steps.[31] There is a little Co–O cleavage in this second phase, and this involves ring-opening. Contrast $[(NH_3)_5$Co–OS(O)–R$]^{2+}$, which after adding Cl^+ to give Co–OS(O)-Cl–R then reacts predominantly by cleavage of Co–O. Only a little (5–15%) Co–OS(O)$_2$–R is ultimately formed, and this can be understood because the functional group is now no longer part of a ring system.

Chlorine oxidation of $[(NH_3)_5CoOSMe_2]^{3+}$ in water gives $[(NH_3)_5CoOH_2]^{3+}$ and free Me_2SO_2.[23] The presumed intermediate $[(NH_3)_5CoOS(Cl)Me_2]^{4+}$ is never observed. In the light of the present work it seems likely that this ion cleaves Co–O rather than hydrolyzes at the ligand to generate $[(NH_3)_5CoOS(O)Me_2]^{3+}$, which then cleaves Co–O. Such an explanation is also consistent with the abnormally high anion competition observed for this reaction,[23,32] indicative of a 4+ rather than 3+ precursor.[18]

Rearrangement in Acid and Base. In water or Me_2SO, the O-bonded isomer isomerizes very slowly but completely to the S-bonded form; $k_s^{OS} = (6.00 \pm 0.09) \times 10^{-7}\ s^{-1}$, 25 °C, H_2O. The reaction can be subject to Co(II)-mediated electron-transfer catalysis unless special precautions are taken (cf. SO_3^{2-} and RSO_2^- reactions),[33] although reproducible rates for spontaneous isomerization in water could be obtained. After about a half-life, and characteristically irreproducibly, the reaction got faster, and this is consistent with autocatalysis. In Me_2SO the situation was similar, and the autocatalysis is triggered by sunlight. This is probably a photoreduction with catalytic Co(II) generation rather than true photocatalysis; for the chelated sulfinate analog $[(en)_2Co(SO_2(CH_2)_2NH_2)]^{2+}$, which is no doubt more resistant to reduction, photoisomerization is from the S- and O-bonded form, not vice versa.[14,15]

The reaction of the O-bonded isomer is appreciably acid-catalyzed, $k = 9 \times 10^{-5}\ s^{-1}$ in 3 M CF_3SO_3D and $1.5 \times 10^{-4}\ s^{-1}$ in 3.0 M DCl at 35 °C, as determined by ^1H NMR. Correcting for the 10 °C temperature difference (corresponding to a 5-fold rate difference), the acceleration factors are 40 and 60, respectively, relative to spontaneous reaction. The product in acid is $[(NH_3)_5CoOH_2]^{3+}$ plus free $MeSO_2H$ rather than $[(NH_3)_5CoSO_2Me]^{2+}$ (<5%); H^+ has accelerated hydrolysis but not linkage isomerization. Since hydrolysis does not compete with linkage isomerization at zero $[H^+]$, the acceleration of hydrolysis must be substantially greater than the factor of 50 observed for the reaction, and the hydrolysis rate enhancement is estimated to be $\geq 10^3$. The specific rates are not greatly different in Cl^- or $CF_3SO_3^-$ media, in contrast to hydrolysis of the *ligand* in $[(NH_3)_5CoOS(NH_2)Me]^{3+}$, which is greatly accelerated by the specific combination H^+ plus Cl^-.[7]

As regards the specific effect of H^+ on the rate of linkage isomerization, one could expect this reaction to represent only $100 \times (6 \times 10^{-7})/(3 \times 10^{-5}) = 2\%$ of the total reaction in 1 M HCl, and this would be difficult to detect by ^1H NMR. Thus, since the acid dependence of the product ratio is actually indeterminate, the prospect that H^+ adds to the S and blocks linkage isomerization cannot be decided from our results. Certainly if it adds to oxygen it does not promote the O to S rearrangement. This observation is consistent with the decreased requirement for bond making by the incoming nucleophile when dissociative activation is promoted,[6] such as the case here where the leaving group is improved by protonation. Acid-catalyzed reactions for O-bonded methyl monothiocarbamate[34] and O-

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bonded succinimide[35] are analogous—the hydrolysis pathway is accelerated by H^+ much more so than is the O- to S- or O- to N-bonded linkage isomerization process.

For the reaction in base both hydrolysis (75%) and linkage isomerization (25%) were observed, independent of $[OH^-]$ in the range 0.025–0.1 M ($I = 0.1$ M, $NaClO_4$) (Table II (supplementary material)). The increased relative importance of hydrolysis vis-a-vis linkage isomerization in base-catalyzed reaction has been noted several times previously,[3,6–8] and it now can be considered the norm. This general result is consistent with significant associative activation for the spontaneous linkage isomerization reaction. The rate data (Table I and Figure 1 (supplementary material)) are consistent with the rate law $k(\text{obsd}) = k_{OH}(\text{obsd})[OH^-]$, where $k_{OH}(\text{obsd}) = 0.0326 \pm 0.0005\ M^{-1}\ s^{-1}$ ($I = 0.1$ M, $NaClO_4$, 25 °C). The product distribution leads to the division $k_{OH} = 0.0245\ M^{-1}\ s^{-1}$ for base hydrolysis and $k_{OH}^{OS} = 0.0082\ M^{-1}\ s^{-1}$ for base-catalyzed linkage isomerization.

Base-catalyzed reaction via Co–O cleavage is expected to lead to anion competition.[36] In N_3^- media, for example, an azido as well as a hydroxo product results. For $MeSO_2^-$ (O-bonded) as a leaving group, the azido product for reaction in 1 M NaN_3 and corrected for the linkage isomerization pathway (29%) was 6.9%, a result to be compared with a range of 5–13% azido product depending upon not only the charge of the leaving group but also the intrinsic reactivity.[28] The present result coupled with the observed reactivity serves to confirm a correlation between reactivity and extent of anion competition first noted for the corresponding substitution in acid solution;[18] indeed the anion competition for $MeSO_2^-$ (6.9%) as a leaving group is between that for $[(NH_3)_5CoF]^{2+}$ (5.4%) and $[(NH_3)_5CoOPO(O^nC_4H_{10})_2]^{2+}$ (7.4%) of comparable reactivity.

The racemization rate for (+)-$[(NH_3)_5CoOS(O)Me]^{2+}$, which is a measure of the oxygen scrambling plus O- to S-bonded rates, is very small, but attempts to quantify it were plagued by Co(II) catalysis. Thus we cannot comment on the relative rates of O- to O- and O- to S-bonded rearrangements, other than to note that the O- to O- is not overwhelmingly greater than the O- to S-bonded rate. Similar rearrangements processes have been probed for sulfinate as part of a chelate in $[Co(en)_2(NH_2CH_2CH_2OSO)]^{2+}$, and the oxygen scrambling appears to be faster than O- to S-bonded rearrangement by a factor of about 60 at 25 °C.[17] Clearly there are restrictions on these rates imposed by the sulfinate being part of a chelate ring; O-scrambling does not involve a change in ring size whereas O- to S-bonded rearrangement involves a ring contraction which is more sterically demanding. This nicely accords with the fact that the O- to S-bonded rate for $[Co(en)_2(NH_2CH_2CH_2OSO)]^{2+}$ ($6.6 \times 10^{-8}\ s^{-1}$) is about 10-fold slower than that for $[(NH_3)_5CoOS(O)Me]^{2+}$, whereas the reverse might have been expected because $[Co(en)_2(NH_3)X]^{2+}$ complexes generally dissociate X somewhat faster than $[Co(NH_3)_5X]$, and the linkage isomerization reaction involves, as a major component, dissociation of X (oxygen in this case).

Experimental Section

UV–visible absorption spectra were monitored with a Cary 210 or 118C spectrophotometer. The same instruments thermostated to 25.0 ± 0.05 °C by water circulation from a Lauda bath (±0.02 °C) were used for kinetic studies by operating in the absorbance–time mode for several preselected wavelengths; a 5-cell turret was used on the Cary 210 instrument. Optical rotations were measured with use of a Perkin-Elmer Model 241 spectropolarimeter also thermostated at 25 °C. ^1H NMR spectra were measured on a Varian 60 MHz spectrometer at 35 °C. All ^1H chemical shifts are reported as positive downfield from DSS for D_2O and TMS for Me_2SO-d_6 and $CDCl_3$. Common chemicals were AnalaR or an equivalent grade. Me_2SO_2 and Me_2S_2 were purchased from Aldrich, and Me_2S_2 was used to synthesize MeSOCl and $MeSONH_2$ by published procedures (^1H NMR ($CDCl_3$): Me, δ 3.43 and 2.73, respectively).[37,38] $MeSO_2H$ was generated in situ by hydrolysis of MeSOCl in H_2O or D_2O as monitored by ^1H NMR. Known complexes $[(NH_3)_5CoOS(O)_2Me](ClO_4)_2$,[19,25] $[(NH_3)_5CoOS(NH_2)Me](ClO_4)_2$,[7] $[(NH_3)_5CoOH](ClO_4)_2$,[3] and $[(NH_3)_5CoOH_2](ClO_4)_3$ were from batches used in concurrent work[7] or were synthesized freshly and characterized by comparison of their spectroscopic properties (^1H NMR in Me_2SO-d_6 and vis/UV) with literature values. Elemental analyses were satisfactory for all complexes used in this work. SP-Sephadex C25 (Pharmacia) and Dowex 50W-X2 (200–400 mesh) (Biorad) were used routinely for the separation of complexes for characterization purposes and product analyses.

$[(NH_3)_5CoOS(O)Me](ClO_4)_2$. $[(NH_3)_5CoOH_2](ClO_4)_3$ (10 g, 22 mmol) was dissolved in $OP(OMe)_3$ (100 mL) containing 2,6-lutidine (4.6 mL, 40 mmol), and the stirred mixture was cooled on an ice bath. MeSOCl (1.5 mL) was added dropwise, and the reaction was left for 3 h before warming back to ambient temperature. The addition of diethyl ether (0.8–1 L) oiled out the product, which after decantation of the ethereal layer was induced to form a gum and finally a fine pink powder by the addition of ethanol (300 mL) and stirring. This was crystallized by dissolution in H_2O (100–150 mL) and addition of $NaClO_4$ (4 g) and prolonged cooling. The crude product (5.0 g, 55%) was filtered off, washed with ethanol and ether, and when dry recrystallized from water (100 mL) by addition of $NaClO_4$ (3 g), filtration, and cooling overnight. Yield: 2.8 g, 31%. Alternatively, the total product could be chromatographed on Dowex and eluted with 2 M $NaClO_4$ (pH 3) to separate the pink O-bonded isomer from orange-red $[(NH_3)_5CoOH_2]^{3+}$; rotary evaporation of the pink 2+ band (<40 °C) to a small volume and cooling gave the pure O-bonded isomer in good yield. ^1H NMR (Me_2SO-d_6): δ 3.85 (s, 12H, cis-NH_3), 2.78 (s, 3H, trans-NH_3), 2.35 (s, 3H, Me). Vis/UV (0.01 M $HClO_4$): ϵ_{515}(max) 80.0, $\epsilon_{307.5}$(max) 1265.

The compound is relatively stable in the solid state in the dark, but in the sun or under laboratory lighting it becomes golden-brown (S-bonded isomer). It was stored in a freezer.

$[(NH_3)_5CoSO_2Me](ClO_4)_2$. A sample of $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ (2.8 g) was dissolved in a small volume of Me_2SO (5–10 mL) and the viscous solution placed in direct sunlight. When conversion from red O-bonded to golden-brown S-bonded isomer was visibly complete (several hours), diethyl ether (300 mL) was added to oil out the product. After settling and decantation, ethanol (200 mL) was added to the oily residue to produce on prolonged agitation and stirring a yellow-brown powder. To this material dissolved in a minimum of water (50–100 mL) was added, after filtration, 20 mL of 10 M $NaClO_4$, and the product was recrystallized from $H_2O/NaClO_4$. On cooling overnight, fine golden-brown crystals were produced. These were collected and washed and dried as described for the O-bonded isomer. Yield: 1.1 g, 39%. ^1H NMR (Me_2SO-d_6): δ 3.65 (s, 3H, trans-NH_3), 3.0 (s, 3H, Me), 2.8 (s, 12H, cis-NH_3). Vis/UV (0.01 M $HClO_4$): ϵ_{455}(max) 146.0, $\epsilon_{294.5}$(max) 13 100.

Optical Resolution of $[(NH_3)_5CoOS(O)Me]^{2+}$. To a concentrated solution of $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ (0.68 g) in water (20 mL) was added a fine suspension of dibenzoyl-L-tartaric acid (1.21 g, 2 equiv) which had been treated with 1 equiv of $NaHCO_3$ (0.135 g) in water (20 mL). After a few minutes of stirring the mixture thickened with a pink precipitate. After 30 min, this was removed by filtration, washed with a little water, and pumped dry. This diastereomer is ethanol and acetone soluble but only sparingly water soluble. The ^1H NMR (Me_2SO-d_6) of this presumed bis(hydrogen benzoyltartrate) salt revealed resonances due to the O-bonded cation and the hydrogen benzoyltartrate anion. The solid was dissolved in an ethanol/water mixture and absorbed onto a short Sephadex ion-exchange column, washed with ethanol/water and then water, and finally eluted with 0.5 M $NaClO_4$. Concentration by freeze drying or rotary evaporation (<40 °C) of the red 2+ band yielded crystals. Two reresolutions as above increased the specific rotation to +35° at 589 nm ([Co], 2 mg/mL; 20 °C). The filtrates from the resolutions were also recovered from Sephadex. After washing to remove excess resolving agent, the eluate on concentration yielded crystals in fractions; the first crops were racemic, but later crops were appreciably levorotatory. The best results were as follows for the ClO_4^- salt derived from the less soluble diastereomer: $[M]_{589}$ + 148, $[M]_{578}$ + 138, and $[M]_{436}$ + 328°. The magnitude of the rotations suggest substantial if not complete resolution.

Chlorine Oxidation. A sample of freshly recrystallized $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ (0.15–0.25 g) was dissolved in water or 1.00 M HX or

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1.00 M $NaNO_3$ (50 mL; X = Cl^-, $^1/_2\ SO_4^{2-}$), and Cl_2 gas was passed through the solution at a moderate rate for 5 min (the reason is visibly complete in less than 1 min). The solution was degassed of excess Cl_2 by the brief passage of N_2 and then diluted with water and loaded onto an ice-jacketed column of Dowex. After washing (H_2O) and elution, the separated bands of $[(NH_3)_5CoOSO_3]^+$ (1 M $NaClO_4$, pH 3), $[(NH_3)_5CoX]^{2+}$ (X = NO_3^- or Cl^- plus X = O_3SMe^-; 2 M $NaClO_4$), and $[(NH_3)_5CoOH_2]^{3+}$ (3 M HCl) were collected and their volumes and vis/UV recorded. Cobalt concentrations were determined using ϵ_{515} 63.9 for $[(NH_3)_5CoOSO_3]^+$, ϵ_{500} 56.5 for $[(NH_3)_5CoONO_2]^{2+}$, ϵ_{532} 50.9 for $[(NH_3)_5CoCl]^{2+}$, and ϵ_{490} 47.7 for $[(NH_3)_5CoOH_2]^{3+}$. For reaction in Cl^- and NO_3^- media, the mixtures of $[(NH_3)_5CoX]^{2+}$ plus $[(NH_3)_5CoOS(O)_2Me]^{2+}$ were treated with OH^- (0.1 M) for a time sufficient to hydrolyze both ions to $[(NH_3)_5CoOH]^{2+}$ and reacidified (HCl), and the total [Co] was determined as $[(NH_3)_5CoOH_2]^{3+}$. Also, for reaction in water containing no added anion, in a larger scale experiment the 2+ band $[(NH_3)_5CoOSO_2Me]^{2+}$ was checked for the presence of $[(NH_3)_5CoCl]^{2+}$ by allowing the $[(NH_3)_5CoOSO_2Me]^{2+}$ component to selectively aquate ($5t_{1/2}$ = 5 h, 25 °C); the product was rechromatographed, and no $[(NH_3)_5CoCl]^{2+}$ (<0.5%) was detected, only $[(NH_3)_5CoOH_2]^{3+}$. Independently, the two-component mixture after hydrolysis but prior to chromatography was analyzed spectrophotometrically at two wavelengths, 536 nm (ϵ 32.0 and 50.5 for the aqua and chloro ions, respectively) and 490 nm (ϵ 47.7 and 41.8, respectively). The results were in essential agreement (Table II, supplementary material). For the chlorination reaction in 1 M $NaNO_3$, the 2+ band comprising $[(NH_3)_5CoONO_2]^{2+}$ and $[(NH_3)_5CoOS(O)_2Me]^{2+}$ could not be accurately analyzed as a two-component mixture in this manner, nor could the components be cleanly separated by selective hydrolysis and rechromatography because some of the nitrato ion ($t_{1/2}$ = 8.0 h, 25 °C) is lost in the time required to completely destroy the $MeSO_3^-$ complex (5 h, ca. $5t_{1/2}$; $t_{1/2}$ = 58 min). Nonetheless, estimates were made by this latter technique. The sum $[(NH_3)_5CoOSO_2Me]^{2+}$ plus $[(NH_3)_5CoONO_2]^{2+}$ was determined as above by OH^-/H^+ treatment and then one-component spectrophotometric analysis. The results were 43% for the total and 37% for the amount of nitrato complex alone.

Azide Ion Competition. A sample of freshly recrystallized $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ (0.2–0.3 g) was reacted 80 min in 1.00 M NaX/0.1 M NaOH (50 mL; X = N_3^- or ClO_4^-) thermostated at 25.0 °C in reduced light. The product mixture was diluted to 600 mL with water and absorbed onto, washed on (H_2O then pH 2 H_2O), and eluted (0.20, 0.25, and 0.5 M $NaClO_4$, pH 3) from a Sephadex column (15 × 4 cm). The 2+ and 3+ bands were directly analyzed spectrophotometrically using $\epsilon_{294.5}$ 13 100 for $[(NH_3)_5CoSO_2Me]^{3+}$ and ϵ_{490} 47.7 for $[(NH_3)_5CoOH_2]^{3+}$ in these media, except for X = N_3^-, in which case the 2+ band was treated further as follows. Sufficient $HClO_4$ (2 M) was added to make $[H^+]$ ca. 0.1 M, and $NaNO_2$ was added (0.1 g) to convert the azido ion into the aqua complex (5 min). NaN_3 (0.1 g) was added to destroy excess HNO_2, and the mixture was reloaded onto an ion-exchange column, this time Dowex (15 × 4 cm). After rinsing, $NaClO_4$ (2 M) and HCl (3 M) were used to elute from the column $[(NH_3)_5CoSO_2Me]^{2+}$ and $[(NH_3)_5CoOH_2]^{3+}$, respectively. These bands were analyzed both by direct spectrophotometry (ϵ_{295}(max) 13 100 for $[(NH_3)_5CoSO_2Me]^{2+}$ and ϵ_{490}(max) 47.7 for $[(NH_3)_5CoOH_2]^{3+}$) and by a modified Kitson analysis[39] for [Co] as follows: A 5.00-mL aliquot of ca. 5×10^{-3} M Co(III) solution was pipetted into a 25-mL Erlenmeyer flask and the pH adjusted to ca. 3 with $HClO_4$. Potassium persulfate (0.1 g) was added, and the covered (watch glass) solution was boiled gently for 3 h, the volume being replenished at intervals with H_2O as necessary. The solution was then transferred to a 50.00-mL volumetric flask, and 50% w/w NH_4SCN (5 mL) solution was added. After acidification (0.1 mL, HCl, 11 M), addition of acetone (25 mL), and making up the volume to 50.00 mL when cool, the absorbance at 622.5 nm was read (ϵ 1480).

Other Product Distributions. The isomerization/solvolysis reactions of $[(NH_3)_5CoOS(O)Me]^{2+}$ (0.5 g) in H_2O, Me_2SO, or H_2O/NaOH (0.05 and 0.1 M, I = 0.1 M, $NaClO_4$, 50 mL) at 25 °C were allowed to proceed ca. $10t_{1/2}$ and then quenched with water (400 mL) containing sufficient $HClO_4$ to neutralize any OH^-, and the mixture was absorbed onto an ice-jacketed column of Sephadex. Washing and elution with cold 0.2 M NaCl (pH 3) easily separated $[(NH_3)_5CoSO_2Me]^{2+}$ from $[(NH_3)_5CoOH_2]^{3+}$ and just separated $[(NH_3)_5CoOS(O)Me]^{2+}$ from $[(NH_3)_5CoSO_2Me]^{2+}$ (elution order implied). The volumes of eluates were recorded, and vis/UV were measured in a 10-cm silica cell after Millipore filtration. Cobalt analyses were made using the molar extinction coefficients recorded above. Product analyses for the photoinitiated isomerization of $[(NH_3)_5CoOS(O)Me]^{2+}$ in water and Me_2SO (a few hours for the reaction times, 25 °C) were also determined in the above manner. Experiments were carried out at least in duplicate, and all cobalt recoveries from the columns were 100 ± 2% (Table II (supplementary material)).

The reaction of $[(NH_3)_5CoOS(O)Me]^{2+}$ with MeI (10-fold excess) in Me_2SO-d_6 was followed by ^1H NMR at 35 °C. Alkylation was very slow, and Me signals for only the substrates and products Me_2SO_2 (δ 3.00) were observed at any time; the intermediate $[(NH_3)_5CoOS(O)Me_2]^{3+}$ was formed too slowly to be observed.

The H_2O_2, H^+-catalyzed H_2O_2, N-chlorosuccinimide, and Cl_2 oxidation reactions were followed by ^1H NMR in D_2O as well as by chromatography. A sample of $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ (ca. 50 mg) in D_2O (0.5 mL) was treated with H_2O_2 (2 M, in D_2O or in 1 M DCl), N-chlorosuccinimide (NCS, 1.05 equiv), or briefly with Cl_2 gas, and the spectra were promptly recorded. Using only 0.5 equiv of NCS left 50% of the O-bonded isomer unreacted (δ 2.48), and 0.5 equiv of product succinimide (δ 2.75) was observed, confirming that only one Cl^+ is involved in the oxidation. All these solutions were monitored over a period of time to follow the decay of the immediately formed products. In separate experiments products were identified by the addition of authentic specimens. $MeSO_2Cl$ (δ 3.92) was observed to hydrolyze to $MeSO_3H$ (δ 2.83) over a period of several hours.

In one experiment a saturated solution of $[(NH_3)_5CoOS(O)Me](ClO_4)_2$ in HCl (0.1 M) was treated with H_2O_2 (30% w/w, $^1/_{10}$ volume) and after 5 min the mixture was ice-cooled and cold $HClO_4$ (70%, another $^1/_{10}$ volume) was added to crystallize the product. It was filtered out, washed with ethanol and ether, and air dried. Yield: 80%, shown from its ^1H NMR in Me_2SO-d_6 to be pure $[(NH_3)_5CoOS(O)_2Me](ClO_4)_2$ (free of $[(NH_3)_5CoOH_2](ClO_4)_3$) by comparison with an authentic specimen.[19,25]

Kinetics. The O- to S-bonded isomerization rate was determined on both of the Cary instruments by collecting D,t traces at 294.5 nm at 25.0 °C. Reactions were followed for several $t_{1/2}$ periods, but only the first half-life of data (for which absorbance changes were substantial) were reproducible and fitted a first-order rate law. To ensure accuracy, calculated infinity absorbances were used (0.010 20 g/50 mL of O-bonded complex, [Co] = 4.84×10^{-4} M, $\epsilon_{294.5}$ 1150 for $[(NH_3)_5CoOSOMe]^{2+}$ and $\epsilon_{294.5}$(max) 13 100 for $[(NH_3)_5CoSO_2Me]^{2+}$). Specific rates were determined using Kincal (a program facilitating weighted nonlinear least-squares analysis).[33] All rates were determined at least in triplicate, and the results were averaged appropriately (weights $1/\sigma^2$). The kinetics for the base-catalyzed reaction were followed similarly except using λ = 307.5 nm. Absorbance changes were reasonable but smaller because much less S-bonded isomer is formed, but runs were complete in relatively short times and there was no problem with the autocatalysis experienced with the spontaneous reaction. Thus, specific rates were determined in the usual ways[33] from data covering at least $3t_{1/2}$.

The acid-catalyzed reactions for $[(NH_3)_5CoOS(O)Me]^{2+}$ in 3 M CF_3SO_3D/D_2O and in 3 M DCl were followed by ^1H NMR at 35 °C by monitoring normalized CH_3 peak heights for reactant and product(s) as a function of time, and the specific rates were determined in the usual way.[40]

Reactions of $[(NH_3)_5CoSO_2Me](ClO_4)_2$. All the reactions described for the O-bonded isomer were carried out on the S-bonded form, and in all cases the starting material was recovered quantitatively (Sephadex). Predictably, attempts at optical resolution failed. The only reaction relevant to the present work is the slow loss of NH_3 induced by acid;[29] it generates yellow-brown $[(NH_3)_4(OH_2)CoSO_2Me]^{2+}$, which elutes close to $[(NH_3)_5CoSO_2Me]^{2+}$ on Sephadex.

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Supplementary Material Available: Rate data (Table I, Figure 1) and product distribution data (Table II) (4 pages). Ordering information is given on any current masthead page.

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