maximum value for reaction with RI[20] although the precision of the difference is rather small.

Finally, the absence of a major path involving rate-determining homolysis shows that any strain due to the very large $PCy_3$ substituents is not sufficient to induce this process to any extent, although the very minor path might correspond to homolysis. Since the homolysis would probably involve a value of ca. +20 kcal $K^{-1}$ $mol^{-1}$ for $\Delta S^{*}$,[1,3,8] the value of $\Delta H^{*}$ for homolysis must be ≥41 kcal $mol^{-1}$, which is comparable to the lower limit for $Re_2(CO)_{10}$.[22]

**Acknowledgment.** We thank NSERC, Ottawa, Canada, for support, and C.N.S. thanks the CSIR, Pretoria, South Africa, for a postdoctoral fellowship.

**Registry No.** $Re_2(CO)_8(P(C_6H_{11})_3)_2$, 65531-96-6; $C_{16}H_{33}I$, 544-77-4; $P(OPh)_3$, 101-02-0; $P(OEt)_3$, 122-52-1.

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(20) The fact that the rate constants for reaction with P donors and with RI are so close shows that reaction with the latter cannot be due to reaction with HI or $I_2$ formed by decomposition of RI. No decomposition of RI to $I_2$ is evident at the temperatures used, and such decomposition is known to be very slow.[21]

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# Metal Ion Promoted Synthesis of a Monothiocarbamate and Kinetics and Mechanism for Its Oxygen- to Sulfur-Bonded Rearrangement

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The residual nucleophilicity of coordinated $OH^-$ in $(NH_3)_5CoOH^{2+}$ has been utilized in the synthesis of the oxygen-bonded monothiocarbamate complex $(NH_3)_5CoOC(NHCH_3)S^{2+}$, from its reaction with methyl isothiocyanate in trimethyl phosphate solution. In water the O-bonded linkage isomer isomerizes intramolecularly and completely to the inherently more stable S-bonded form, which has been crystallized and characterized. This O to S isomerization reaction occurs by both spontaneous and base-catalyzed pathways; $k_1(\text{obsd}) = k_{1S} + k_{1OH}[OH^-]$, where $k_{1S} = (8.8_1 \pm 0.10) \times 10^{-5}$ $s^{-1}$ and $k_{1OH} = (3.7 \pm 0.3) \times 10^{-2}$ $s^{-1}$ ($\mu = 0.1$ M, $NaClO_4$; 25 °C). Parallel hydrolysis (30 ± 7%) is observed only for the $OH^-$-catalyzed route, and the mechanistic significance of this observation is discussed. A major conclusion is that the spontaneous isomerization process has significant associative character, not generally recognized as characteristic of cobalt(III) substitution processes. The kinetics and course of reaction have also been studied for the slower subsequent reactions of the $(NH_3)_5CoS(NHCH_3)O^{2+}$ isomer. The usual base hydrolysis rate law is observed, $k_2(\text{obsd}) = k_{2S} + k_{2OH}[OH^-]$, although here $k_{2S}$ is negligible ($<10^{-7}$ $s^{-1}$; $k_{2OH} = (1.12 \pm 0.03) \times 10^{-2}$ $M^{-1}$ $s^{-1}$; $\mu = 0.1$ M, $NaClO_4$; 25 °C). Only starting material, colloidal (and ultimately precipitated) cobaltic sulfide, and some $Co^{II}(aq)$ are observed at any stage of this reaction. It is argued that either (i) the expected $(NH_3)_5CoOH^{2+}$ coproduct is decomposed rapidly by liberated $CH_3NHC(O)S^-$ or, alternatively, (ii) $OH^-$ directly attacks the coordinated S-C(O)R group of the $(NH_3)_5CoS(NHCH_3)O^{2+}$ complex, with elimination of $(NH_3)_5CoSH^{2+}$ and $CH_3NHCO_2^-$ as the immediate products, and cobaltic sulfide then results from the reaction of the latter complex in $OH^-$ solution. Evidence is presented to support the second alternative.

## Introduction

The oxygen- and nitrogen-bonded nitrite complexes $(NH_3)_5CoONO^{2+}$ and $(NH_3)_5CoNO_2^{2+}$ remain the classic pair of linkage isomeric complexes in inorganic chemistry.[1] Since their discovery in the late nineteenth century,[2,3] additional examples have been slow to emerge. In the past decade we have set about synthesizing new pairs of linkage isomers in an attempt to understand the detailed mechanism of rearrangement between the isomers. The reader is referred to the most recent review[1] and to a selection of subsequent publications[4-13] for the present status of intramolecular rearrangements of this kind. This article is the first of several further studies from our laboratories dealing with new examples of rearrangement between $(NH_3)_5CoAB^{n+}$ and $(NH_3)_5CoBA^{n+}$ linkage isomers, where the ambidentate ligand AB includes amides $NH_2C(O)R$, ureas $NH_2C(O)NR_2$, urethane $NH_2C(O)OCH_2CH_3$, sulfinamides $NH_2S(O)R$, sulfamide $NH_2S(O)_2NH_2$, sulfonamides $NH_2S(O)_2R$, methanesulfinate $CH_3SO_2^-$, chlorosulfate $ClSO_3^-$, and the monothiocarbamate $CH_3NHC(O)S^-$. Herein we report the synthesis of a pair of *N*-methylmonothiocarbamate complexes with the $(NH_3)_5Co^{III}$ moiety, where the ligand is bound through sulfur or oxygen. The kinetics and product distribution for the spontaneous and base-catalyzed oxygen to sulfur rearrangement are described. We also report on the subsequent and slower base hydrolysis reaction of the S-bonded isomer $(NH_3)_5CoSC(NHCH_3)O^{2+}$.

## Discussion

**Synthesis.** Monothiocarbamates are uncommon (and unstable) species, and the reaction between $(NH_3)_5CoOH^{2+}$ and $CH_3NCS$ in an inert solvent affords a convenient synthesis of a metal ion stabilized derivative, here the *N*-methylmonothiocarbamate ion (the sodium salt of this species, prepared by conventional methods, was known previously[14]). The residual nucleophilicity of $OH^-$ bound to Co(III) has been demonstrated many times,[15-19] and the

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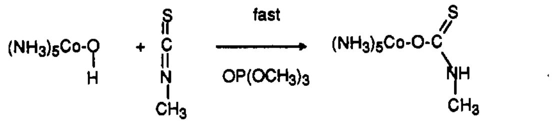
present reaction is clearly an additional example since it is very much faster than can reasonably be attributed to metal ion substitution processes. Moreover, alternative mechanisms are excluded by the observed stereospecificity—the product is essentially all the O-bonded linkage isomer:



At least some of the product formed via free $CH_3NHC(O)S^-$ and a suitable $Co^{III}$ complex, by a substitution process, might be expected to be the S-bonded isomer, especially since the S-isomer is the thermodynamically preferred form, and also because sulfur appears to be a better nucleophile toward $Co^{III}$ than is oxygen.[10,20,21] Also, a substitution process whereby $OH^-$ is displaced from $(NH_3)_5CoOH^{2+}$ by $CH_3NCS$ to give $(NH_3)_5CoSCNCH_3^{3+}$ is unreasonable on two grounds. First, $OH^-$ is lost from $Co^{III}$ far too slowly,[22] and second, subsequent $OH^-$ attack on the $(NH_3)_5CoSCNCH_3^{3+}$ complex must give the S-isomer.

Balahura et al. have published the synthesis and structure of the phenylmonothiocarbamate analogue of our S-bonded methyl derivative.[23] They failed to observe the initial formation of the O-bonded form but postulated a mechanism for the synthesis similar to ours, and which now can be regarded as firm.

An important result is that this synthesis affords an example of a facile kinetic route to a thermodyamically unstable species. The rapid nitrosation of $(NH_3)_5CoOH_2^{3+}$ to yield $(NH_3)_5CoONO^{2+}$ [2,24] and the capture of $SCN^-$ to yield $(NH_3)_5CoSCN^{2+}$ during both the induced and base-catalyzed substitution reactions of $(NH_3)_5CoX^{n+}$ in $SCN^-$ media are other examples.[20,21]

As synthesized, the O-isomer $(NH_3)_5CoOC(NHCH_3)S^{2+}$ contained a little of the S-bonded form, which arises from subsequent isomerization ($t_{1/2}$ = ca. 2.2 h, 25 °C). It also contained some unreacted aqua complex, which could be removed by ion-exchange chromatography at 0 °C. Later it was found that $S_2O_6^{2-}$ selectively crystallizes the O-isomer, which renders the chromatographic purification step redundant. The S-form $(NH_3)_5CoSC(NHCH_3)O^{2+}$ was prepared simply by allowing the O-isomer to isomerize completely in solution, and after a chromatographic step it was crystallized with the addition of $HClO_4$ or $NaClO_4$.

The $^1H$ NMR spectra of $(NH_3)_5CoX^{n+}$ complexes can be diagnostic of the donor atom X.[25] The chemical shift difference between the cis- and trans-$NH_3$ signals is typically $\Delta\delta = 1$ to 1.5 for oxygen donors, the trans signal being at higher field, while for sulfur-bonded ligands this shift difference is much smaller and is in the opposite sense $\Delta\delta = 0$ to $-0.5$.[10,11,13] The absolute chemical shifts are also diagnostic, especially for the trans-$NH_3$ signal. These patterns are followed for the O- and S-bonded linkage isomers of the $CH_3NHC(O)S^-$ ambidentate ligand (see Experimental Section), confirming the isomer assignments that followed directly from their mode of synthesis. The NMR spectra also showed separate resonances for the NH and $CH_3$ protons for each isomer, serving to confirm their isomeric purity.

The possibility that the rearranged O-isomer is N- rather than S-bonded warranted consideration. The spacing of the cis- and trans-$NH_3$ $^1H$ NMR signals for the $(NH_3)_5Co$–N skeleton is typically narrow ($\Delta\delta \sim 0$) and occasionally inverted ($\Delta\delta < 0$).[4,11,13] Thus N-bonding is not inconsistent with the observed NMR spectrum. Also $CH_3NHC(O)S^-$ is similar to the carbamate ion $NH_2CO_2^-$, for which both O- and N-bonded pentaamminecobalt(III) forms are known.[13,26] However, our experience with the N- and O-bonded amides, ureas, and similar ligands dictates that, unless deprotonated at nitrogen, the N-bonded form for the monothiocarbamate would be thermodynamically unstable with respect to the O-isomer. Furthermore, the stoichiometry $[(NH_3)_5CoN(CH_3)C(O)S]ClO_4$ is not that established, and moreover, N-bonded N-alkylated derivatives of this kind have yet to be synthesized.

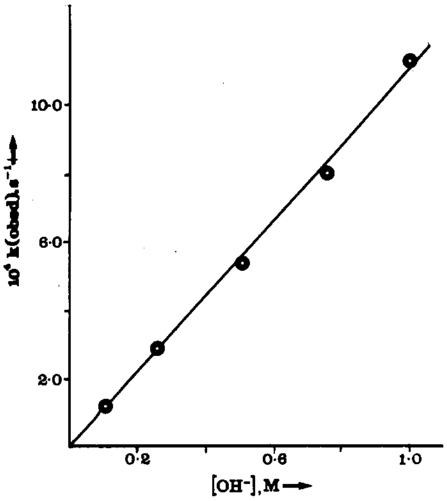


**Figure 1.** Hydroxide ion dependence of the specific rate of hydrolysis of $(NH_3)_5CoSC(NHCH_3)O^{2+}$ at 25 °C and 0.1 M ionic strength ($NaClO_4$).

The visible/ultraviolet spectra positively confirm S- and O-bonding. The S-isomer shows very strong UV absorption characteristic[27] of the $Co^{III}$–S linkage (295 nm, $\epsilon$ 7895; 252 nm, $\epsilon$ 8967), although interestingly the intensity is spread in two well-spaced bands, whereas usually a single absorption is observed, at ca. 290 nm, and this is about twice as strong.[10,20,27] The O-bonded isomer is devoid of this strong near-UV band, and its visible spectrum, which shows $\epsilon$(max) 108.5 at 518 nm for the first ligand field band, is typical. The S-isomer absorbs at slightly higher energy (510 nm, $\epsilon$ 88.5), which is atypical, but this ligand field band is characteristically broader.

The spectroscopic data reported[23] for the analogous derivative $(NH_3)_5CoSC(NHC_6H_5)O^{2+}$ is very similar to ours, and it is noted that S-bonding is established for the phenyl complex by a single-crystal X-ray structure.[23]

**Hydrolysis of $(NH_3)_5CoSC(NHCH_3)O^{2+}$.** The S-bonded isomer is completely stable for at least 24 h in water or dilute $HClO_4$ at ca. 25 °C. Over several days however it decomposes with the deposition of black cobaltic sulfide (and $Co^{II}$), and this reaction is catalyzed by light. Base also catalyzes the reaction, and surprisingly good (reproducible) first-order kinetics were observed over 2–3 half-lives, despite the development of colloidal cobaltic sulfide (which is ultimately precipitated). A good isosbestic point was observed at 233 nm for ca. 2 half-lives; this represents the crossing point in the absorption curve for the S-isomer and the apparent absorption (light scattering) curve for the colloidally dispersed product. Ion-exchange chromatographic analysis of the reaction mixture revealed starting material, the insoluble cobaltic sulfide, and some $Co^{II}(aq)$; $(NH_3)_5CoOH^{2+}$ was never observed. The observed specific rate $k_2$(obsd) showed a linear dependence on $[OH^-]$ in the range investigated, with a zero intercept (Figure 1; Table I, supplementary material). Thus, $k_2(\text{obsd}) = k_{2OH}[OH]^-$,

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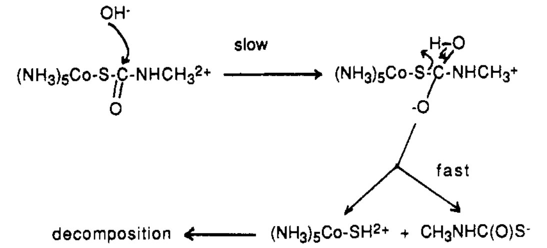
(27) Deutsch, E.; Root, M. J.; Nosco, D. L. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 269–389.

with $k_{2OH} = (1.12 \pm 0.03) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ at 25 °C and $\mu = 0.1$ M ($NaClO_4$). Even for 0.1 M $OH^-$, there was no evidence of net deprotonation at the $-NH(CH_3)$ center.

These results may be interpreted in one of two ways. The first is normal base hydrolysis of $(NH_3)_5CoS(NHCH_3)O^{2+}$ via the $S_N1CB$ mechanism,[1] yielding $(NH_3)_5CoOH^{2+}$ and the free ligand $CH_3NHC(O)S^-$. This can accomodate the observed rate law, provided the subsequent decomposition reaction is fast. The magnitude of $k_{OH}$ for this 2+ S-bonded complex is not unreasonable for such a mechanism, and moreover, rapid decomposition of $(NH_3)_5CoOH^{2+}$ in basic solutions of anionic S ligands such as $CH_3S^-$ is our common experience.

The second possibility is rate-determining $OH^-$ attack at the ligand, activated by coordination to $Co^{III}$, and there is also ample precedence for this kind of reaction:[19]



Species such as Co–S–R are known[28] to be stable in acid as well as in basic solution, but the proposed $(NH_3)_5CoSH^{2+}$ ion with a potentially ionizable proton could provide a route to redox decomposition. These considerations alone do not lead to a clear decision, but the results described in the next section, where it is found that $(NH_3)_5CoOH^{2+}$ and free $CH_3NHC(O)S^-$ can coexist on the time scales involved, suggest that this second mechanism is operative.

**The Oxygen to Sulfur Rearrangement.** In neutral aqueous solution, this rearrangement is characterized by a sharp isospestic point at 246 nm (ϵ 8805), and the reaction goes to completion with no parallel or subsequent hydrolysis path. Good first-order kinetics were observed, $k_{1S} = (9.60 \pm 0.23) \times 10^{-5}$ $s^{-1}$ for $H_2O$ and $k_{1S} = (8.81 \pm 0.10) \times 10^{-5}$ $s^{-1}$ for 0.1 M $NaClO_4$, both at 25 °C and for data obtained at several λ's where there were reasonable absorbance changes. The reaction is catalyzed by base, and a different but sharp isosbestic point is observed initially, the position of which is $[OH^-]$-dependent at low concentrations. Above ca. 0.04 M $OH^-$, its initial position is fixed. These observations are consistent with the appearance of a new pathway leading to base hydrolysis in parallel with base-catalyzed linkage isomerization. Kinetic studies confirm that the $[OH^-]$ path dominates (≥95%) above ca. 0.04 M $OH^-$. The reaction was studied at several wavelengths, 295 and 307 nm providing the most convenient absorbance changes, and reasonable pseudo-first-order kinetics were observed up to ca. 2 half-lives at each $[OH^-]$. The specific first-order rates calcuated in the usual way from the 307-nm data obeyed the relation $k_1(\text{obsd}) = k_{1S} + k_{1OH}[OH^-]$, with $k_{1S}$ as above and $k_{1OH} = (3.15 \pm 0.088) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ for 0–0.1 M $OH^-$ and $\mu = 0.1$ M ($NaClO_4$) (Figure 2; Table II, supplementary material). A somewhat higher result was obtained from the 295-nm data, $k_{1OH} = (5.05 \pm 0.10) \times 10^{-2}$ $M^{-1}$ $s^{-1}$, although a good linear $[OH^-]$ dependence was still found. Note that this reaction is not that much faster than the subsequent base hydrolysis reaction of $(NH_3)_5CoSC(NHCH_3)O^{2+}$ under the same conditions ($k_{2OH} = 0.0112$ $M^{-1}$ $s^{-1}$), and the intrusion of the latter could be expected to interfere in the data analysis beyond ca. 2 half-lives of the primary reaction of the O-isomer. Indeed, it is easily shown that the secondary reaction *does* interfere, even within just the 2 half-lives of data. The rates are in error by about 10% for the present conditions, and for the 295-nm data they are over- rather than underestimated because the absorbance changes for the second step oppose those for the first. For the 307-nm data sets, $k_1$(obsd) values so obtained proved to be *under*estimated because both reactions entailed absorbance increases. Finally, data collected at the isosbestic point for the second step (233 nm) should have been free of the difficulty raised, but the proportional changes in primary absorbance were not large enough to be useful.

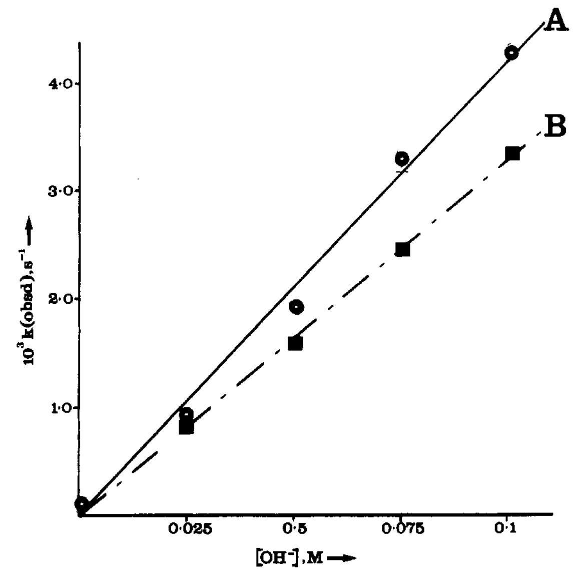


Figure 2. Hydroxide ion dependence of the specific rate of linkage isomerization/hydrolysis of $(NH_3)_5CoOC(NHCH_3)S^{2+}$ at 25 °C and 0.1 M ionic strength ($NaClO_4$): (A) data (295 nm) corrected for secondary reaction; (B) data (307 nm; $\leq 2t_{1/2}$) uncorrected for secondary reaction.

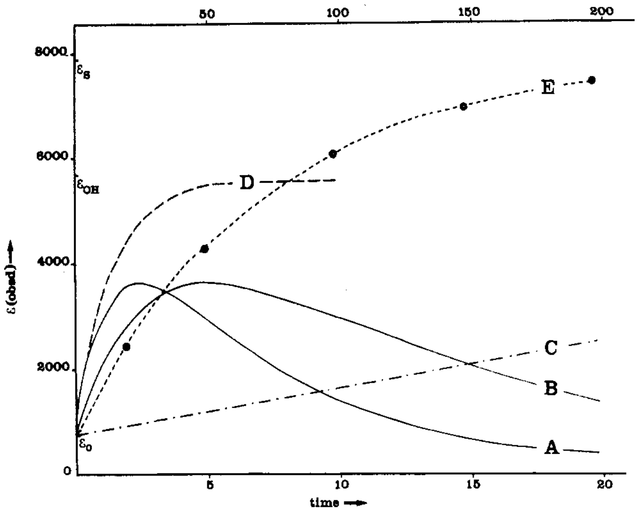


Figure 3. Changes in absorbance (295 nm) with time, for the sequential hydrolysis reactions of $(NH_3)_5CoOC(NHCH_3)S^{2+}$: (A) 0.1 M NaOH; (B) 0.5 M NaOH; (C) 0.1 M $NaClO_4$, pH 5; (D) 0.1 M NaOH, data corrected for subsequent reaction of the S-bonded isomer; (E) 0.1 M $NaClO_4$, pH 5. Curves A–D refer to the bottom time axis; curve E refers to the top axis. Units of time are half-lives (156 s) for the primary reaction in 0.1 M $OH^-$. The molar extinction coefficients $\epsilon_S$, $\epsilon_O$, and $\epsilon_{OH}$ refer to pure S-bonded isomer, pure O-bonded isomer, and the first-formed base hydrolysis product mixture (which is 70% S-isomer/30% $(NH_3)_5CoOH^{2+}$), respectively.

The absorbance-time traces shown schematically in Figure 3 illustrate the points above. They reveal clearly the consecutive reactions, and they also indicate the change in product distribution on going from the spontaneous to the base-catalyzed process. Since both the primary and secondary reactions are first order in $[OH^-]$ (vide infra), it was not possible to eliminate the effect of the second reaction by varying the $[OH^-]$. Therefore the data covering almost the entire two-step reaction were reanalyzed in terms of the complete reaction scheme by using a two-exponential function. The results of nonlinear least-squares data fits were essentially identical for the cases, (i) $k_1$(obsd) and $k_2$(obsd) used as parameters and (ii) $k_2$(obsd) fixed at its independently determined values.

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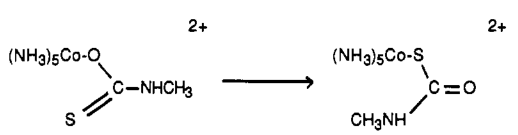
The results so obtained for $k_1$(obsd) are plotted in Figure 2 to show the linear [$OH^-$] dependnece; $k_1(\text{obsd}) = k_{1S} + k_{1OH}[OH^-]$ where $k_{1S} = (8.81 \pm 0.10) \times 10^{-5}$ s$^{-1}$ and $k_{1OH} = (3.73 \pm 0.30) \times 10^{-2}$ M$^{-1}$ s$^{-1}$ at 25.0 °C and $\mu$ = 0.1 M ($NaClO_4$). The results also show the magnitude of the inaccuracy (as opposed to lack of precision) introduced by adopting the simpler approach in data analysis. This is also evident from Figure 3 (compare curves A and D). Finally it is noted that the linear [$OH^-$] dependence up to 0.1 M requires no net deprotonation of the $-NH(CH_3)$ group.

In 0.1 M $OH^-$ the reaction proceeds very largely via the base-catalyzed path, and the first-formed products, corrected for secondary reaction, were found to be $(NH_3)_5CoSC(NHCH_3)O^{2+}$ (70 ± 7%) and $(NH_3)_5CoOH^{2+}$ (30 ± 7%). We have noted previously[10,29] that base accelerates the hydrolysis pathway more so than the linkage isomerization reaction, and the monothiocarbamate system provides yet another example. The trend is accommodated by recognizing the partly associative nature of the spontaneous linkage isomerization reaction. For this pathway, which lacks the dissociative labilization afforded by $NH_2^-$ of the conjugate-base route, nucleophilic assistance from the pendant S atom of the ambidentate ligand should be more prominant. Indeed, as is usual, the S center wins out over water, whereas in free (external) competition,[1,30] water is usually the superior "nucleophile". The associative character coupled with the location of the incoming group with respect to the metal ion in the ground state conformation[31] accommodates the observation of a reasonably rapid ($t_{1/2}$ = 2.2 h, 25 °C) and clean rearrangement:



A similar scheme can be drawn for the base-catalyzed reaction, except that the immediate precursor is deprotonated at a bound $NH_3$ and that water and the ligand terminus are now competitive entering groups.

Finally, some comment on the relative stability of the linkage isomers can be made. There are now several pentaamminecobalt(III) systems involving ambidentate sulfur/oxygen ligands in addition to monothiocarbamate, among which are thiocyanate $SCN^-$, sulfite $SO_3^{2-}$, thiosulfate $S_2O_3^{2-}$, sulfenate $RSO^-$ and sulfinate $RSO_2^-$, sulfinyl halide RS(Cl)O, and sulfoxide RR′SO.[1,10,12] Of these, all except the last two are anionic ligands, and S is preferred. In contrast, the neutral sulfur/oxygen ligands appear to bind oxygen better.[1,12]

## Experimental Section

Visible and ultraviolet spectra ($\epsilon$, M$^{-1}$ cm$^{-1}$; $\lambda$, nm) were recorded in matched silica cells on a Cary 210 instrument thermostated to 25.00 ± 0.05 °C by circulation of water from a Lauda bath. Temperature control and measurement were as previously described.[4,11,31] Proton NMR spectra were recorded for dry $Me_2SO$-$d_6$ solutions by using a Varian T60 spectrometer (35 °C) and tetramethylsilane as the internal reference. All chemicals were AnalaR grade or the equivalent. The cation-exchange resin was SP Sephadex C-25 (Pharmacia; $Na^+$ form). Chromatography at low temperature was carried out with jacketed columns cooled by circulated ice-cold water. Pentaamminehydroxocobalt(III) perchlorate was obtained from the aqua complex recrystallized from a saturated solution in 0.1 M tris(hydroxymethyl)methylamine by using $NaClO_4$ as the precipitant.

**Pentaammine(*N*-methylmonothiocarbamato-*O*)cobalt(III) Dithionate Dihydrate.** Methyl isothiocyanate (0.9 g, 12.3 mmol; Fluka) was added to a solution of pentaamminehydroxocobalt(III) perchlorate (4.0 g, 11.1 mmol) in trimethyl phosphate (50 mL) at 0 °C in an ice bath. The solution was stirred for 2.5 h at ice temperature, after which the product was precipitated as an oily solid by the addition of diethyl ether (500 mL). The residue after decantation was dissolved in ice-cold acidified water (pH ~2; $HClO_4$) and sorbed onto a cold column (ca. 5 °C, 5 × 15 cm) of Sephadex in reduced light. Elution with cold 0.25 M $NaClO_4$ (pH ~ 2) was continued until a clear separation between $(NH_3)_5CoOH_2^{3+}$ and the desired faster moving $(NH_3)_5CoOC(NHCH_3)S^{2+}$ ions was achieved. Each band was then physically removed from the column, and that containing the monothiocarbamato complex was transferred to the top of a smaller column of Sephadex. After the product was washed well with water, elution with cold 0.1 M $Ba(ClO_4)_2$ yielded a concentrated solution of the perchlorate salt, which was maintained at ca. 5 °C. After filtration, the addition of an equal volume of a saturated solution of $Li_2S_2O_6$ in methanol resulted in the slow deposition (several hours, 0 °C) of pink pearlescent needles. These were collected by filtration, washed with methanol and ether, and air-dried. Yield: 0.50 g, 23%. The product was stored over silica gel under dry $N_2$ in the freezer, but nonetheless slowly decomposed, yielding black cobaltic sulfide. The material was always used freshly synthesized. Anal. Calcd. for $C_2H_{23}N_6CoS_3O_9$: C, 5.58, H, 5.39; N, 19.53; Co, 13.69; S, 22.35. Found: C, 5.51; H, 4.90; N, 19.79; Co, 13.86; S, 22.63. Visible/ultraviolet spectrum [$\lambda$ (nm), $\epsilon$]: 518, 108.5; 227, 16 800; 0.1 M $HClO_4$. $^1H$ NMR spectrum, $\delta$: 7.62, br, 1 H, NH; 4.13, br, 12 H, cis $NH_3$; 3.30, s, 3 H, $CH_3$; 3.30, s, 2 H, $H_2O$; 2.75, br, 3 H, trans $NH_3$; $Me_2SO$-$d_6$/$Me_4Si$.

**Pentaammine(*N*-methylmonothiocarbamato-*S*)cobalt(III) Perchlorate.** Methyl isothiocyanate (0.42 g, 5.75 mmol; Fluka) was added to a solution of pentaamminehydroxocobalt(III) perchlorate (2.0 g, 5.56 mmol) in trimethyl phosphate (25 mL) at ambient temperature and the mixture stirred for 3 h. The crude product was obtained as an oil by the addition of ether (500 mL), and after decantation the residue in acidified water (400 mL; pH ~2, $HClO_4$) was sorbed onto a column (5 × 25 cm) of Sephadex ion-exchange resin. The desired product $(NH_3)_5CoSC(NHCH_3)O^{2+}$ was eluted clear of unreacted $(NH_3)_5CoOH_2^{3+}$ with 0.25 M $NaClO_4$ (pH ~ 2) as the eluent. This red band was collected, filtered, and carefully rota-evaporated to a concentrate (~$^1/_2$ volume). After the addition of saturated $NaClO_4$ (5 mL) and a suitable period in the refrigerator, the deposited red-brown crystals were collected, washed with ethanol and ether, and dried over $P_2O_5$ in vacuo. The recrystallized product ($H_2O/NaClO_4$) is stable only for a modest period in a freezer; it decomposes slowly to cobaltic sulfide. Yield: 0.8 g, 33%. Anal. Calcd for $C_2H_{19}N_6CoCl_2O_9S$: C, 5.55; H, 4.42; N, 19.41; Co, 13.61; Cl, 16.37; S, 7.40. Found: C, 5.65; H, 4.44; N, 19.48; Co, 13.82; Cl, 16.38; S, 7.51. Visible/ultraviolet spectrum [$\lambda$ (nm), $\epsilon$] 510, 88.5; 295, 7895; 252, 8967; 227 (sh), 6406; 0.1 M $HClO_4$. $^1H$ NMR spectrum, $\delta$: 7.96, br, 1 H, NH; 3.90, br, 3 H, trans $NH_3$; 3.35, s, 3 H, $CH_3$; 3.20, br, 12 H, cis $NH_3$; $Me_2SO$-$d_6$/$Me_4Si$.

**Isomerization and Hydrolysis Kinetics.** All reactions were followed spectrophotometrically on the Cary instrument at 25.00 °C. Solutions of AnalaR $NaClO_4 \cdot H_2O$ (0.1 M) and Volucon NaOH (0.1 M) were mixed as appropriate to provide the 0.1 M ionic strength media. Reacting mixtures were scanned to locate isosbestic points for both neutral and NaOH solutions. For the kinetics, a judicious amount of complex was dissolved rapidly in the neutral or base solution prethermostated in the spectrophotometer. Absorbance–time traces at a preselected wavelength were commenced almost immediately thereafter, and for the hydrolysis of the S-bonded complex studied at 295 nm, the data were handled in the usual way to provide pseudo-first-order specific rates, $k$(obsd). All runs were performed at least three times, and reported values are means and mean deviations. For the reactions of the O-bonded isomer in water or 0.1 M $NaClO_4$, the method was as described above, but consecutive reactions were observed for basic solution. At 295 nm, the absorbance rises sharply only to later decay back toward zero. Care was taken to ensure the recording of absolute reaction times since these are important for the proper analysis of consecutive first-order reactions.[32] Three approaches were adopted. In the first, absorbance–time data covering just the first 2 half-lives of reaction were fitted to a single exponential function. In the second and third, the entire absorbance–time data sets were used, and fitted to a two-exponential function in either of two ways—both $k_1$(obsd) and $k_2$(obsd) were used as parameters or $k_2$(obsd) was confined to its independently determined value(s). The results were essentially identical, save for the expected higher uncertainties in $k_1$(obsd) evaluated by the first approach.

**Product Analyses.** For the reaction of the O-isomer in neutral to acid solution, the identity of the final visible/ultraviolet spectrum with that of an authentic specimen of the S-isomer indicated the lack of competitive hydrolysis and the irreversibility of the rearrangement. This was confirmed by ion-exchange chromatographic analysis of the product; no aqua complex (<0.5%) was detected. For reactions in basic solution, weighed amounts of $[(NH_3)_5CoOC(NHCH_3)S]S_2O_6 \cdot 2H_2O$ or $[(NH_3)_5CoSC(NHCH_3)O](ClO_4)_2$ were allowed to react in 0.100 M NaOH at 25.00 °C

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for 1–2 half-lives. After being quenched with cold 1 M $HClO_4$, the product mixtures were separately chromatographed on chilled Sephadex columns, with acidified 0.25 M $NaClO_4$ as the eluent. The O- and S-bonded monothiocarbamate isomers eluted together, followed by the aqua complex. The individual isomer concentrations for mixtures were determined from the absorbances at 295 and 227 nm by using the following data: $(NH_3)_5CoOC(NHCH_3)S^{2+}$, $\epsilon(295) = 812$, $\epsilon(227) = 16800$; $(NH_3)_5CoSC(NHCH_3)O^{2+}$, $\epsilon(295) = 7895$, $\epsilon(227) = 6406$. The aqua complex was determined by using $\epsilon(492) = 47.7$. Experiments were performed in duplicate. Cobalt recoveries never exceeded about 95% because of the production of black cobaltic sulfide, which remained at the top of the column. The coproduction of $Co^{II}$ was detected and determined by using the Kitsen method. In one set of experiments, the S-isomer was reacted for 570 s in 0.1 M NaOH at 25 °C. The only $Co^{III}$ species recovered was starting material (37.9%; corresponding to $k_2$(obsd) = $1.7 \times 10^{-3}$ s$^{-1}$ (cf. direct spectrophotometric value, $1.1 \times 10^{-3}$ s$^{-1}$, Table I, supplementary material). When reaction proceeded for shorter or longer periods, a similar result was obtained, i.e., no aqua product. In a corresponding set of experiments starting with the O-isomer, for reaction at 25 °C for 302 s in 0.1 M NaOH, recovered O-isomer was determined as 26.1%, S-isomer as 38.5%, and aqua complex as 16.6%; the balance (19.5%) was $Co^{II}$ and cobaltic sulfide. The percent consumed O-isomer corresponds to $k_1$(obsd) = $4.4 \times 10^{-3}$ s$^{-1}$ (cf. direct spectrophotometric value, $4.45 \times 10^{-3}$ s$^{-1}$, Table II, supplementary material), while the amount of S-isomer observed, corrected for its secondary reaction as well as for incomplete reaction of the O-isomer, corresponds to an initial product ratio of 36% aqua complex/64% S-isomer. Another calculation, based on the observed proportion of aqua complex, gave a product distribution of 23% aqua complex/77% S-isomer. A mean distribution of 70 ± 7% S-isomer/30 ± 7% aqua complex accommodates both sets of results.

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**Registry No.** $[(NH_3)_5CoSC(NHCH_3)O](ClO_4)_2$, 106782-09-6; $[(NH_3)_5CoOC(NHCH_3)S]S_2O_6$, 106782-11-0; $[(NH_3)_5CoOH](ClO_4)_2$, 18885-27-3; $CH_3NCS$, 556-61-6; $OP(OCH_3)_3$, 512-56-1.

**Supplementary Material Available:** Tables I and II, giving kinetic data (3 pages). Ordering information is given on any current masthead page.

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# Preparation and Reactivity of Tricarbonyl($\eta^5$-cyclopentadienyl)(organothiolato)tungsten Complexes with Potentially Chelating Thiolate Ligands

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The photochemical reaction of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ with the organic disulfides bis(2-pyridyl) disulfide, bis(2-benzothiazolyl) disulfide, and bis(*o*-aminophenyl) disulfide, using visible irradiation, produces mononuclear tungsten carbonyl complexes containing monodentate thiolate ligands. Disappearance quantum yields for the tungsten dimer in the formation reaction are >0.4 and are higher with 546-nm irradiation than with 366-nm light. Carbonyl loss from $(\eta^5\text{-}C_5H_5)(CO)_3WSR$, R = 2-pyridyl or 2-benzothiazolyl, can be induced thermally, or photochemically with ultraviolet light, to yield dicarbonyl complexes with chelated thiolate ligands. Quantum yields for the chelation reaction are higher with 366-nm than with 436-nm irradiation; values of $\Phi$ at 366 nm are ≥0.6 for both benzothiazole- and pyridinethiolates. Similar reactions where $R$ = *o*-aminophenyl do not result in a chelated product, but instead may form oligomers. The monodentate nature of the benzothiazolethiolate ligand in $(\eta^5\text{-}C_5H_5)W(CO)_3S\text{-}(CNC_6H_4S)$ has been validated by X-ray crystallography. The molecule crystallizes in space group $C2/c$, with unit cell parameters $a = 24.03\ (3)$ Å, $b = 10.236\ (3)$ Å, $c = 12.526\ (4)$ Å, $\beta = 95.63\ (4)°$, and $Z = 8$.

Photolysis of metal–metal-bonded carbonyl dimers is known to produce reactive metal carbonyl radicals.[1,2] These photogenerated radicals react with organic disulfides to produce metal carbonyl thiolate complexes, e.g.[3-5]

$$(\eta^5\text{-}C_5H_5)_2M_2(CO)_6 + RSSR \xrightarrow{h\nu} 2(\eta^5\text{-}C_5H_5)(CO)_3MSR \quad (1)$$

$$M = Mo, W$$

Reactions of metal carbonyl dimers with organic disulfides can also form metal thiolate complexes via thermal routes.[6,7] In cases where subsequent chelation reactions are possible, thermal routes form only bidentate compounds.[8]

The loss of CO from metal carbonyl compounds has been observed to occur by both photochemical and thermal pathways. Photochemical reactions of metal carbonyls result in the dissociative loss of a carbonyl ligand,[2,9] and thermal substitutions proceed by a dissociative mechanism with the loss of CO as the rate-determining step.[10] The resulting coordinatively unsaturated compound may recombine with CO or react with another two-electron-donor ligand. Intramolecular substitution is easily brought about with $\pi$- or $\sigma$-donor systems linked to $\sigma$-bonded ligands.[4,5,11,12] $\sigma$-to-$\pi$ rearrangements as a consequence of CO lability have been observed for several organometallic compounds.[11]

Previous work has shown the photoreaction of $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ with a thiuram disulfide to be an efficient method to prepare a mononuclear tungsten complex containing a monodentate dithiocarbamate ligand,[4,5] whereas previous thermal routes only resulted in chelated complexes.[8] The results presented below confirm the usefulness of this method for the production of mononuclear tungsten complexes with monodentate thiolate ligands regardless of the type of potentially chelating ligand used. We also report a detailed investigation of the subsequent photochemical and thermal reactivity of these products containing monodentate thiolate ligands.

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