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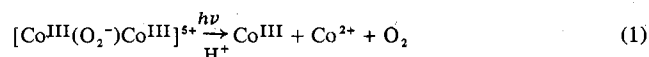
Contribution from the Chemistry Department of Princeton University, Princeton, New Jersey 08540

Preparation and Photochemical Decompositions of Acido-Substituted μ -Superoxo-dicobalt-Ammine Derivatives

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Received April 21, 1971

We reported before on the photochemical decompositions of several μ -superoxo-dicobalt amines according to reaction 1,^{2,3} where Co^{III} is a cobaltic-amine derivative. This

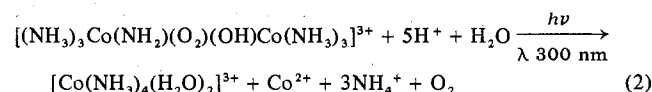


work has been extended to include photochemical decompositions of 1-3, which have other coordinated acido groups in addition to superoxide. We sought to discover if additional acido ligands and consequent low-lying ligand-to-metal electron-transfer transitions would change the course of photochemical decomposition of the $[\text{Co}^{\text{III}}(\text{O}_2^-)\text{Co}^{\text{III}}]$ chromophore and if the acido-substituted μ -superoxo-dicobalt-amine chromophores would undergo photoaquation reactions as reported recently for a variety of $[\text{Co}(\text{NH}_3)_5(\text{X})]^{2+}$ and $[\text{Co}(\text{NH}_3)_4(\text{X})(\text{Y})]^{+ \text{ or } 2+}$ derivatives.⁴

Preparations and interconversions of 1-3 as shown in Scheme I were carried out as described by Werner.⁵ These reactions appear to establish the gross chemical structures of 1-3.⁶ The compounds are paramagnetic⁷ and their electronic absorption spectra exhibit strong absorption (ϵ 200-400) near 700 nm as found for other μ -superoxo-dicobalt amines.^{2,3} Attempts to provide further evidence for the presence of the $[\text{Co}^{\text{III}}\text{O}_2^-\text{Co}^{\text{III}}]$ chromophore by esr measurements were successful with 1 which gave the characteristic 15-line signal⁸ for $[\text{Co}^{\text{III}}\text{O}_2^-\text{Co}^{\text{III}}]$, (^{59}Co , $I = 7/2$), with two equivalent Co centers. Fresh solutions of 2 in either 0.1 M HClO_4 or 25% H_3PO_4 solution did not give a detectable esr spectrum, perhaps because of rapid exchange of ammine hydrogens with environment. Aged solutions of 2 in 0.1 M HClO_4 gave a 15-line spectrum we attributed to 1, produced by thermal aquation of chloride.⁹ Solutions

of 3 in 0.1 M HClO_4 or 25% H_3PO_4 were too unstable for esr studies.¹⁰

Irradiations of solutions of the perchlorate of 1, the nitrate of 2, and the chloride of 3 in 0.1 M HClO_4 with $\lambda > 345$ -nm light proceeded with gas evolution and gave mixtures of amines of Co^{2+} and Co^{III} which could be separated by ion-exchange chromatography. Complex 1 gave 0.96 ± 0.02 mol of gas and stoichiometric amounts of Co^{2+} and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ as the only products. Visible absorption spectra of photolyzed solutions of 1 taken immediately after irradiation had λ_{max} 505 nm (ϵ 50.1).¹¹ This visible maximum changed over 4-6 hr after photolysis was completed to λ_{max} 506-507 nm (ϵ 48),⁹ values similar to those reported¹² for thermally equilibrated mixtures of *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$. There were other small changes in position and intensity of absorbance in the 300-500-nm range over the same period. These changes were not precisely reproducible from experiment to experiment but their time scale at 25° was quite constant and we believe they were due to chemical transformations subsequent to photolysis. The exact nature of the chemistry is unknown. We thought at first that the *cis*-diaquo isomer might be our major photolysis product and that the observed spectral changes were due to a *cis* to *trans* isomerization to bring about thermal equilibrium. This explanation was made unattractive by the report¹³ that at equilibrium under conditions similar to ours, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ exists almost entirely in the *cis* form. Consequently, we suspect the spectral changes we observe are due to side reaction products produced in small amounts not detected by our chromatography experiments. Whatever the origin of the extra absorbance,¹⁴ it is clear that the only important stoichiometry for photochemical decomposition of 1 is reaction 2, which was observed from pH 0 to pH 3, at various ionic



strengths, and with $\lambda > 480$, > 345 , and > 310 nm light sources.

The kinetics of 1 photodecompositions in dilute HClO_4 proved to be quite similar to those observed before for other μ -superoxo-dicobalt amines.^{2,3} For reaction 2 we found the quantum yield for disappearance of 1 to be $\phi_{320} = 0.50 \pm 0.05$ and $\phi_{350} = 0.42 \pm 0.04$ and to be independent of complex concentration and absorbed intensity in optically dense solutions. Electronic absorption spectra on partially decomposed solutions of 1 in the 300-700-nm region were consistent with the sole presence of the reactants and prod-

(10) A solution of 3 in 85% H_3PO_4 was stable as described by Y. Ohyagi, *Bull. Chem. Soc. Jap.*, **15**, 186 (1940), and gave a single broad esr signal. Either an 8- or a 64-line spectrum could be expected from 3, depending on the relative magnitudes of $J_{\text{Co}(1)}$ and $J_{\text{Co}(2)}$. The nature of cationic species formed from the chloride of 3 in 85% H_3PO_4 is unclear in any case.

(11) Corrected for absorbance due to Co^{2+} .

(12) R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, **59**, 298 (1955).

(13) J. D. White and T. G. Newton, *J. Phys. Chem.*, **75**, 2117 (1971).

(14) R. Davies and A. G. Sykes, *J. Chem. Soc. A*, 2237 (1968), also reported unidentifiable absorption between 250 and 350 nm in photolyzed solutions of 1. However, these authors used the nitrate salt of 1. Nitrate ion is well known to absorb in this spectral region.

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(3) J. S. Valentine and D. Valentine, Jr., *Inorg. Chem.*, **10**, 393 (1971).

(4) For a recent review see D. Valentine, Jr., *Mol. Photochem.*, **3**, 89 (1971).

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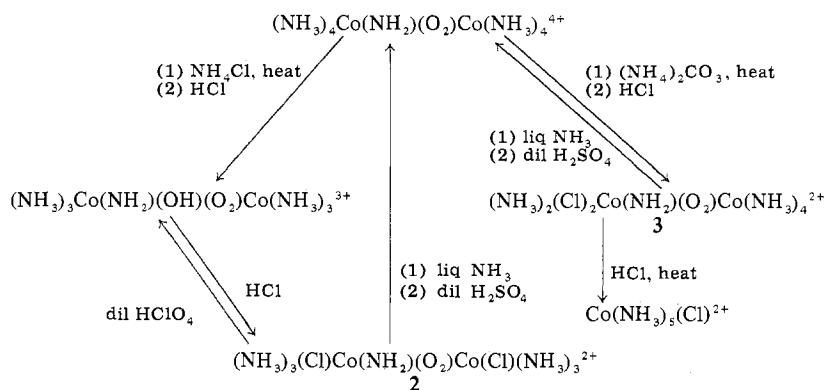
(6) A. G. Sykes and J. A. Weil, "Inorganic Reaction Mechanisms," J. A. Edwards, Ed., Interscience, New York, N. Y., 1970, provided a recent review of μ -superoxo-dicobalt ammine structures and chemistry.

(7) R. W. Asmussen, "Magnetokemiske undersøgelser over uorganiske Kompleksforbindelser," Copenhagen, 1944, p 193.

(8) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

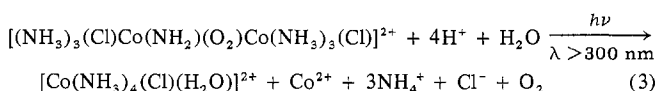
(9) This aquation followed roughly first-order kinetics with $k(25^\circ) = 0.001 \text{ min}^{-1}$ in 0.1 M HClO_4 and gave ca. 0.96 mol of 1 for each mole of 2 decomposed. Other products were not identified and the presence of intermediates, e.g., $[(\text{NH}_3)_3(\text{H}_2\text{O})\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{Cl})(\text{NH}_3)_3]^{3+}$, while not detected, cannot be excluded.

Scheme I. Preparations, Interconversions, and Decompositions of 1-3



ucts required by reaction 2. All of these data are strikingly similar to those observed earlier for $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4]^{4+}$ for which we found for reaction 1: ϕ_{320} (disappearance) = 0.48 ± 0.04 and $\phi_{350} = 0.40 \pm 0.04$; these parameters are also independent of pH, complex concentration, and light intensity.¹⁵

Photochemical decompositions of solutions of the nitrate of **2** in 0.1 M HClO₄ gave the Co²⁺ ion together with mixtures of $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$, and gas was evolved. Results depended on irradiating wavelength as follows: (a) $\lambda \geq 480$ nm, $[\text{Co}^{2+}] = [\text{Co}^{\text{III}}]$, which was about 1:1 mixture of chloroaquo and diaquo complexes; (b) $\lambda \geq 350$ nm, $[\text{Co}^{2+}] = [\text{Co}^{\text{III}}]$, which was mostly chloroaquo with some diaquo; (c) $\lambda \geq 300$ nm, $[\text{Co}^{2+}] \geq 1.2[\text{Co}^{\text{III}}]$, which was now mostly diaquo with some chloroaquo. The dependence of stoichiometry of **2** photodecomposition on irradiating wavelength was found to be due to two experimental artifacts. Photolysis of **2** with $\lambda > 480$ nm light is very slow, allowing formation of **1** by thermal aquation to compete with photolysis of **2**. Subsequent photolysis of **1** produces $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ which is observed. In the $\lambda > 350$ and > 300 nm cases, $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ is formed by secondary photolysis of $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$, whose photolysis at 365 nm gives $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ and whose photolysis at 310 nm yields both Co²⁺ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. Correcting our data for $\lambda > 300$, > 350 , and > 480 nm irradiations for competing thermal aquation of **2** and secondary photolysis of $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$ shows that the stoichiometry for photodecomposition of **2** under all three sets of irradiation conditions is that demanded by reaction 3. Photoaquation of **2** was not detected.



The quantum yield for disappearance of **2** on 320-nm irradiations was $\phi_{320} = 0.75 \pm 0.10$ when $I_a = 5.4 \times 10^{-4}$ einstein/min l. and decreased somewhat at lower intensities. Difference spectra taken on partially photolyzed samples of **2** in 0.1 M HClO₄ were not explainable solely in terms of the reactants and products required by reaction 3. This suggests formation of metastable photolysis intermediates which are later destroyed thermally or photochemically. Given the clean stoichiometry of reaction 3 for the photolysis and the mechanism we proposed earlier^{2,3} to account for reaction 1 occurring in other systems, it is difficult to

(15) It is somewhat curious that **1** and $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4]^{4+}$ should be such similar photochemical substrates when changing from NH₃ to ethylenediamine; i.e., $[(\text{en})_2\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{en})_2]^{4+}$, produced a dramatic decrease in the quantum yield of photochemical decomposition of $[\text{Co}^{\text{III}}\text{O}_2\text{Co}^{\text{III}}]$.³

write plausible metastable intermediates in the photolysis. It is easy, however, to imagine that in side reactions some oxidized halogen or amine species may be formed and the decay of these systems conceivably could lead to the weak dependence of ϕ_{320} on I_a .

Photochemical decompositions of **3** in 0.1 M HClO₄ solutions were briefly studied. Such solutions are very unstable thermally and this hindered analysis. Nevertheless, we found that more Co²⁺ than Co^{III} was formed and all of the Co^{III} was $\text{Co}(\text{NH}_3)_5\text{X}^{n+}$ derivatives where X = Cl or H₂O. In this unsymmetrical system, therefore, the Co center with the more acido groups is the one which is reduced.

Our original intention in studying chromophores of the $[\text{Co}^{\text{III}}\text{O}_2\text{Co}^{\text{III}}]$ type was to demonstrate that inorganic chromophores could be found whose properties might be varied and studied in a systematic way so as to permit study of those factors which influence the rates of photochemical reactions of inorganic chromophores. This paper concludes our work in this area. We have found that reaction 1 provides the only major photochemical decomposition pathway for $[\text{Co}^{\text{III}}\text{O}_2\text{Co}^{\text{III}}]$ substituted with a variety of acido and ammine ligands. Although not all of the systems studied have been treated in detail, our data indicate that the same basic mechanism² probably obtains in all cases.^{2,3} This has enabled us to study effects of different bridging^{2,3} and peripheral ligands on the magnitude and wavelength dependencies of quantum yields for $[\text{CoO}_2\text{Co}]^{5+}$ photodecompositions^{2,3} and to make use of our knowledge of $[\text{CoO}_2\text{Co}]^{5+}$ photochemistry as an analytical tool.³

Experimental Section

I. Preparations. **1.** μ -Amido- μ -hydroxy- μ -superoxo-bis(triamminecobalt)(1+). Samples of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{O}_2)(\text{OH})\text{Co}(\text{NH}_3)_3](\text{NO}_3)_3$ were prepared from $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$ as described by Werner⁵ and then converted to $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{O}_2)(\text{OH})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ by successive precipitations from 0.1 M HClO₄ with NaClO₄. Electron spin resonance spectra in both H₂O and 0.1 M HClO₄: $g = 2.025$, $A_{\text{Co}} = 12$ Oe, 15 lines; electronic absorption: in H₂O, $\lambda_{\text{max}} 703$ nm ($\epsilon 203$) and $\lambda_{\text{sh}} 460$ nm ($\epsilon 261$); in 0.1 M HClO₄, $\lambda_{\text{max}} 703$ nm ($\epsilon 205$) and $\lambda_{\text{sh}} 460$ nm ($\epsilon 256$); in 10 M HClO₄, $\lambda_{\text{max}} 700$ nm ($\epsilon 176$) and $\lambda_{\text{max}} 460$ nm ($\epsilon 254$). *Anal.* Calcd for Co₂H₂₇N₇O₈Cl₃: Co, 18.5; N, 15.4; H, 4.24; Cl, 16.7. Found: Co, 18.5; N, 15.0; H, 4.01; Cl, 17.01.

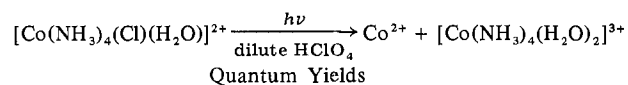
2. μ -Amido- μ -superoxo-bis(chlorotriamminecobalt)(2+). Addition of HCl to the nitrate of **1** in 0.1 M HClO₄ gave $[(\text{Cl})(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_3(\text{Cl})\text{Cl}_2]^{5+}$ which was converted to the nitrate by successive reprecipitations from aqueous solution with NH₄NO₃. We could not obtain a perchlorate salt. No esr signal was observable from solutions of the nitrate of **2** in 0.1 M HClO₄, 25% H₃PO₄, or 85% H₃PO₄ except that in the first solvent the spectrum of **1** gradually appeared due to hydrolytic conversion **2** → **1**. Electronic absorption spectra of **2** in 0.1 M HClO₄: $\lambda_{\text{max}} 700$ nm ($\epsilon 177$); $\lambda_{\text{max}} 460$ nm ($\epsilon 265$). *Anal.* Calcd for Co₂H₂₆N₇O₈Cl₂: Co, 25.5; N, 27.3; H, 4.30; Cl, 15.4. Found: Co, 25.5; N, 27.5; H, 4.24; Cl, 17.1.

3. μ -Amido- μ -superoxo-dichlorodiamminocobalttetraammine-cobalt(2+). This was prepared from $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4]-(\text{NO}_3)_4$ by Werner's procedure;⁵ we were only able to prepare the chloride salt $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_2(\text{Cl})_2]\text{Cl}_2$, which was reprecipitated from H_2O by addition of concentrated HCl. *Anal.* Calcd for $\text{Co}_2\text{H}_{26}\text{N}_7\text{O}_2\text{Cl}_4$: Co, 28.8; N, 23.5; H, 4.88; Cl, 34.7. Found: Co, 29.0; N, 24.3; H, 4.78; Cl, 34.9. Solutions of the chloride of 3 in 0.1 M HClO_4 rapidly became grayish green, probably due to replacement of coordinated chloride by H_2O , giving $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{4+}$. This was reversed by addition of concentrated HCl, when the chloride of 2 was precipitated, but irreversible changes were rapid, leading to cobalt(III)-pentaamine derivatives. Heating of the chloride of 2 in HCl gave $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$ as reported by Werner.⁵

In fresh 0.1 M HClO_4 solutions, we find λ_{max} 720 nm (ϵ 140), λ_{sh} 590 nm (ϵ 131), and λ_{max} 476 nm (ϵ 271).

4. Conversions of $[(\text{NH}_3)_5(\text{Cl})\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_3(\text{Cl})]^{2+}$ and $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_2(\text{Cl})_2]^{2+}$ to $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4]^{4+}$. Following the general outline of the Werner procedure,⁵ 1.0 g of the chloride of 2 (or 3) was added to 50 ml of liquid NH_3 at -33° . The mixture was stirred vigorously and allowed to warm slowly to 0° . When complete solution of the chloride of 2 had occurred, 25 ml of distilled water was added and, with the solution temperature kept below $+10^\circ$, the solution was cautiously acidified with 6 N H_2SO_4 to pH 2. The solution was placed in the dark at 25° for 2 days, and then the finely divided precipitate of gray $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4](\text{SO}_4)_2$ was removed by filtration and converted to the corresponding nitrate.⁵ From the chloride of 2 was obtained a 41% yield of octaamine nitrate, whose high purity was indicated by electronic absorption spectroscopy [λ_{max} 700 nm (ϵ 305), λ_{max} 477 nm (ϵ 368)] and by photolysis in 0.1 M HClO_4 .² Complex 3 gave the octaamine nitrate, but only in 19% yield, and samples we obtained contained other binuclear cobalt ammines.

5. Photochemistry of $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$. Unlike most cobalt(III) ammines and other Co^{III} products of μ -superoxo-dicobalt ammine photochemistry we have studied, $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$ is quite unstable when irradiated with near-ultraviolet light and we corrected for this in photochemical studies of 2. Moggi, *et al.*,¹⁶ reported recently that on 254- and 313-nm irradiation $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$ was converted not only to Co^{2+} but also to $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$. We have confirmed and extended these findings as summarized below.



Co^{2+}	$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$	λ
0.24	0.10	254 nm
Both aquation and reduction observed		313 nm
<0.001	~0.01	365 nm
<0.0001	<0.001	>480 nm

II. Photochemical and Analytical Procedures. These have been described in our previous papers.^{2,3} Gas analyses were done with the aid of Dr. James White.

Registry No. $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{OH})(\text{NH}_3)_3](\text{ClO}_4)_3$, 37339-54-1; $[(\text{Cl})(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_3\text{Cl}](\text{NO}_3)_2$, 37339-56-3; $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_2(\text{Cl})_2]\text{Cl}_2$, 37339-55-2; $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{O}_2)\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$, 12139-90-1; $[\text{Co}(\text{NH}_3)_4(\text{Cl})(\text{H}_2\text{O})]^{2+}$, 39262-43-6.

Acknowledgment. We are grateful to Professor H. Taube for helpful discussions and to the Petroleum Research Fund administered by the American Chemical Society for support of this work through Grants 928 G2 and 3620 A3. Use of analytical facilities of Hoffmann-La Roche, Inc., is also gratefully acknowledged. We are grateful to Mrs. Claudette Liptak for typing the manuscript.

(16) Photoaquation and reduction to Co^{2+} of $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{Cl})]^{2+}$ was studied previously by L. Moggi, N. Sabbatini, and V. Balzani, *Gazz. chim. Ital.*, **97**, 980 (1967).

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Metal Complexes of Amino Acids and Derivatives. VI. Donor Properties of S-Methylcysteine and Methionine. A Comparison¹

C. A. McAuliffe

Received November 17, 1972

The study of coordination complexes has recently received added impetus with the discovery that some possess anticancer activity.^{2,3} In addition to the well-publicized platinum-amine complexes,^{2,3} for which antitumor properties have been demonstrated, a number of transition metal complexes of amino acids are now undergoing laboratory tests as anticancer agents;^{4,5} among these are complexes derived from the amino acid S-methyl-L-cysteine.^{5,6}

Livingstone and Nolan⁶ synthesized quite a large number of complexes of S-methyl-L-cysteine (SmcH): the polymeric six-coordinate $[\text{M}(\text{Smc})_2]_n$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$) which involve coordination *via* the amino and bidentate, bridging carboxylate groups; the planar $[\text{M}(\text{SmcH})\text{X}_2]$ ($\text{M} = \text{Pd}, \text{Pt}; \text{X} = \text{Cl}, \text{Br}$) in which the ligand donors are thioether and amino groups; and $[\text{Cu}(\text{Smc})_2\text{Ag}]\text{NO}_3$, which involves ligand coordination to copper *via* oxygen and nitrogen donors and to silver *via* the sulfur atom. The work of Livingstone and Nolan had been preceded by the work of McAuliffe, Quagliano, and Vallarino⁷ on the amino acid DL-methionine, a ligand which differs from S-methylcysteine in possessing an extra $-\text{CH}_2-$ group in the carbon chain. The results in these two papers^{5,6} lead to the conclusion that the donor properties of these two ligands are very similar. In fact, work carried out in this laboratory, as well as adding to the number of complexes of S-methylcysteine, shows that there are some significant differences in the complexing properties of these ligands.

Experimental Section

Starting Materials. S-Methyl-L-cysteine (Nutritional Biochemicals Corp.) and analytical grade metal salts were used without further purification.

Preparation of the Complexes. $[\text{Cu}(\text{Smc})(\text{NO}_3)]$. S-Methyl-L-cysteine (0.68 g, 0.005 mol) and Na_2CO_3 (0.27 g, 0.0025 mol) in water (10 ml) were added dropwise to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.42 g, 0.010 mol) in water (10 ml). Precipitation of a light blue solid occurred immediately. The solid was filtered, washed with methanol (10 ml) and water (10 ml), and dried *in vacuo* over P_4O_{10} ; yield 85%.

$\text{Na}[\text{Cu}(\text{Smc})_3]$. A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.60 g, 0.0025 mol) in water (10 ml) was added to a solution of S-methyl-L-cysteine (1.35 g, 0.010 mol) and Na_2CO_3 (0.53 g, 0.005 mol) in water (10 ml). Immediate precipitation of a blue complex occurred. The solid was filtered, washed with methanol (10 ml) and ethanol (10 ml), and dried *in vacuo* over P_4O_{10} ; yield 75%.

(1) Part V: C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta*, in press.

(2) B. Rosenberg, L. Van Camp, J. E. Trosko, and V. H. Mansour, *Nature (London)*, **222**, 385 (1969); B. Rosenberg and L. Van Camp, *Cancer Res.*, **30**, 799 (1970).

(3) J. J. Roberts and J. M. Pascoe, *Nature (London)*, **235**, 282 (1972).

(4) D. R. Williams and P. A. Yeo, *J. Chem. Soc., Dalton Trans.*, **1988** (1972).

(5) The complexes reported here are currently being tested at the laboratories of the Imperial Cancer Research Fund.

(6) S. E. Livingstone and J. D. Nolan, *Inorg. Chem.*, **7**, 1447 (1968).

(7) C. A. McAuliffe, J. V. Quagliano, and L. M. Vallarino, *Inorg. Chem.*, **5**, 1996 (1966).