3. μ-Amido-μ-superoxo-dichlorodiamminecobalttetraamminecobalt(2+). This was prepared from $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$ by Werner's procedure;[5] we were only able to prepare the chloride salt $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_2(Cl)_2]Cl_2$, which was reprecipitated from H_2O by addition of concentrated HCl. *Anal.* Calcd for $Co_2H_{20}N_7O_2Cl_4$: 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 $[(NH_3)_4Co(NH_2)_2(O_2)Co(NH_3)_2(H_2O)_2]^{4+}$. This was reversed by addition of concentrated HCl, when the chloride of **2** was precipitated, but irreversible changes were rapid, leading to cobalt(III)–pentaammine derivatives. Heating of the chloride of **2** in HCl gave $[Co(NH_3)_5(Cl)]^{2+}$ 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 $[(NH_3)_3(Cl)Co(NH_2)(O_2)Co(NH_3)_3(Cl)]^{2+}$ and $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_2(Cl)_2]^{2+}$ to $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4]^{4+}$. 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°, 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 $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](SO_4)_2$ was removed by filtration and converted to the corresponding nitrate.[5] From the chloride of **2** was obtained a 41% yield of octaammine 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 octaammine nitrate, but only in 19% yield, and samples we obtained contained other binuclear cobalt ammines.

5. Photochemistry of $[Co(NH_3)_4(Cl)(H_2O)]^{2+}$. Unlike most cobalt(III) ammines and other Co^{III} products of μ-superoxo-dicobalt ammine photochemistry we have studied, $[Co(NH_3)_4(Cl)(H_2O)]^{2+}$ 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 $[Co(NH_3)_4(Cl)(H_2O)]^{2+}$ was converted not only to Co^{2+} but also to $[Co(NH_3)_4(H_2O)_2]^{3+}$. We have confirmed and extended these findings as summarized below.

$$[Co(NH_3)_4(Cl)(H_2O)]^{2+} \xrightarrow[\text{dilute } HClO_4]{h\nu} Co^{2+} + [Co(NH_3)_4(H_2O)_2]^{3+}$$

Quantum Yields		
Co^{2+}	$[Co(NH_3)_4(H_2O)_2]^{3+}$	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. $[(NH_3)_3Co(NH_2)(O_2)Co(OH)(NH_3)_3](ClO_4)_3$, 37339-54-1; $[(Cl)(NH_3)_3Co(NH_2)(O_2)Co(NH_3)_3Cl](NO_3)_2$, 37339-56-3; $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_2(Cl)_2]Cl_2$, 37339-55-2; $[(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4](NO_3)_4$, 12139-90-1; $[Co(NH_3)_4(Cl)(H_2O)]^{2+}$, 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.

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Metal Complexes of Amino Acids and Derivatives. VI. Donor Properties of *S*-Methylcysteine and Methionine. A Comparison[1]

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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 Nolan[6] synthesized quite a large number of complexes of *S*-methyl-L-cysteine (SmcH): the polymeric six-coordinate $[M(Smc)_2]_n$ (M = Co, Ni, Cu, Zn, Cd) which involve coordination *via* the amino and bidentate, bridging carboxylato groups; the planar $[M(SmcH)X_2]$ (M = Pd, Pt; X = Cl, Br) in which the ligand donors are thioether and amino groups; and $[Cu(Smc)_2Ag]NO_3$, 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 Vallarino[7] on the amino acid DL-methionine, a ligand which differs from *S*-methylcysteine in possessing an extra $-CH_2-$ 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. $[Cu(Smc)(NO_3)]$. *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 $Cu(NO_3)_2 \cdot 3H_2O$ (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%.

$Na[Cu(Smc)_3]$. A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (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%.

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Table I. Physical Properties and Analytical Data of the Metal Complexes

Complex	Color	Mp, °C	μ_{eff}, BM	Analyses,[a] %			
				C	H	N	Metal
$[Cu(Smc)(NO_3)]$	Pale blue	220	2.21	18.0 (18.5)	3.1 (3.1)	10.3 (10.8)	25.0 (24.5)
$Na[Cu(Smc)_3]$	Blue	220	2.27	28.8 (29.5)	4.9 (5.0)	8.7 (8.6)	13.1 (13.0)
$[Pd(SmtH)_2][PdCl_4]$	Yellow	186		11.8 (12.0)	2.3 (2.3)	3.5 (3.5)	
$[Co(Smc)_2Ag]NO_3 \cdot H_2O$	Purple	108	4.87	18.8 (18.6)	3.5 (3.5)	8.0 (8.2)	

[a] Found (calcd).

Table II. Infrared[a,b] and Electronic[c] Spectra of the Metal Complexes

Complex	$\nu(NH_2)$, cm^{-1}	$\nu(COO)_{asym}$, cm^{-1}	$\nu(COO)_{sym}$, cm^{-1}	Visible bands, kK
$[Cu(Smc)(NO_3)]$	3290, 3230 m, 3120 w	1615 s	1420 s	12.5, 15.2
$Na[Cu(Smc)_3]$	3290 m, 3230 m, 3120 w	1615 s	1390 s	16.3
$[Pd(SmcH)_2][PdCl_4]$	3200 m, br	1725 s	1415 s	20.2–20.9, 25.8, 26.5
$[Co(Smc)_2Ag]NO_3 \cdot H_2O$[d]	3290 m, 3240 m	1590 s	1382 s	9.1, 20.0, 34.7

[a] Assignments made by comparison with the deuterated complexes. [b] In KBr disks. [c] Solid reflectance spectra. [d] Broad absorption at ~3500 cm^{-1} assignable to $\nu(OH)$.

$[Pd(SmcH)_2][PdCl_4]$. *S*-Methyl-L-cysteine (0.405 g, 0.003 mol) was added to a stirred solution of Na_2PdCl_4 (1.03 g, 0.0035 mol) in water (8 ml), and the resulting mixture was warmed to 40° for 30 min. Upon cooling the resulting yellow solution to room temperature, dropwise addition of ethanol (25 ml) resulted in the deposition of a yellow precipitate. This was filtered, washed with methanol (10 ml), and dried *in vacuo* over P_4O_{10}; yield 45%.

$[Co(Smc)_2Ag]NO_3 \cdot H_2O$. To a stirred suspension of $[Co(Smc)_2]$[6] (0.5 g, 0.0053 mol) in water (8 ml) was added a solution of $AgNO_3$ (0.26 g, 0.0053 mol) in water (5 ml). An immediate gray precipitate formed. This was filtered, and upon washing with ethanol (20 ml) the gray color changed to purple. The purple solid was dried *in vacuo* over P_4O_{10}; yield 80%.

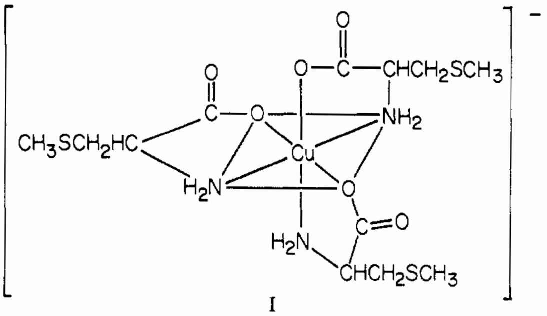
Measurements. Metal analyses were determined using EDTA;[8] carbon, hydrogen, and nitrogen were determined by the microanalytical laboratory of this department. Magnetic measurements, infrared and electronic spectra, and conductivity measurements were obtained as previously described.[9]

Results and Discussion

All the complexes reported by Livingstone and Nolan[6] have also been prepared and examined in this study, and essential agreement with their results was found.

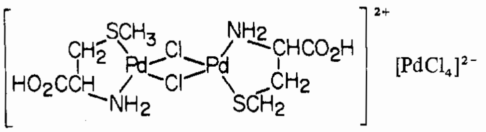
In general, amino acids complex as monoanionic species and with divalent metals form complexes of type $[ML_2]$. In the methionine work[7] an attempt was made to isolate complexes of different stoichiometry, and, in addition to $[MMt_2]$ (M = Mn, Co, Ni, Cu, Zn; Mt = anion of DL-methionine), complexes of type $[MMt]ClO_4$ (M = Ni, Cu) and $Li[NiMt_3]$ were isolated; no $[CuMt_3]^-$ complex could be obtained. In this study with *S*-methylcysteine no complex of nickel(II), other than that of $[Ni(Smc)_2]$, could be obtained. However, with copper(II) salts a tris-ligand complex $Na[Cu(Smc)_3]$ was isolated but no $[Cu(Smc)]ClO_4$ was isolable, $[Cu(Smc)_2]$ being formed in every attempt. However, using an anion of better coordinating ability than perchlorate did lead to a 1:1 derivative, $[Cu(Smc)(NO_3)]$, Table I.

It is difficult to postulate a structure for $[Cu(Smc)(NO_3)]$. Infrared spectra (Table II) indicate that the COO^- and NH_2 groups are coordinated, and bands at 1382 and 815 cm^{-1} can be assigned to monodentate nitrate.[10] There are no bands attributable to Cu–S bonding, and so it is likely that this complex is polymeric and involves bridging carboxylato groups. A comparison of the infrared spectra of $Li[NiMt_3]$ and $Na[Cu(Smc)_3]$ suggests that both complexes have similar structures, and thus the latter can also be assigned a six-coordinate pseudooctahedral configuration (I). (It is emphasized that only one possible geometrical isomer is shown.)



I

The method of Volshtein and Mogilevkina[11] was used by McAuliffe[12] to prepare $[Pd(MtH)Cl_2]$. However, although Livingstone and Nolan[6] have prepared $[Pd(SmcH)Cl_2]H_2O$, the reaction of Na_2PdCl_4 and *S*-methylcysteine by a method analogous to that used to prepare $[Pd(MtH)Cl_2]$ leads to the isolation of a complex the analysis of which corresponds to the formula $Pd_3(SmcH)_2Cl_6$ (Table I). Coordinated amino groups are indicated by infrared absorptions at 3200 cm^{-1}, $\nu(NH_2)$, and 1573 cm^{-1}, $\delta(NH_2)$. The $\nu(COO)_{asym}$ mode occurs at 1725 cm^{-1}, indicative of free non-hydrogen-bonded $-CO_2H$ groups.[6,12] Bands due to ν(Pd–S) at 385 cm^{-1} and ν(Pd–Cl) at 330 cm^{-1} can also be distinguished. These results suggest that the most plausible structure for $Pd_3(SmcH)_2Cl_6$ is II. Additional evidence is obtained for



II

this formulation by the appearance of two major absorptions at 25.8 and 26.5 kK in the visible reflectance spectrum. The band at 25.8 kK has been assigned to the $[PdCl_4]^{2-}$ by Gray.[13] The conductivity of this complex in water (Λ_{1000} = 97 mhos at 24°) is also consistent with the above formulation.

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A mixed-metal complex, $[Co(Smc)_2Ag]NO_3 \cdot H_2O$, was obtained by treating $[Co(Smc)_2]$ with silver nitrate in water. The visible spectrum of the $[Co(Smc)_2Ag]NO_3 \cdot H_2O$ complex differs very little from that of $[Cd(Smc)_2]$, suggesting that in the former the coordination about the Co(II) atom is still $[CoN_2O_4]$. The appearance of a weak absorption in the infrared spectrum of $[Co(Smc)_2Ag]NO_3 \cdot H_2O$ at 380 cm^{-1}, assigned to ν(Ag-S),[6] is evidence of the formation of bonds between the originally uncoordinated thioethers and silver ion.

It should also be mentioned that no complex of the type $Li[Ag(Smc)_2]$ could be prepared. Numerous attempts were made to isolate such a derivative, both in daylight and in the dark. This contrasts sharply with the ready availability of $Li[AgMt_2]$.[7]

A closer examination of the results obtained from this work and previous work on DL-methionine[7,12] and *S*-methylcysteine[6] complexes indicates that there are, as expected and as has already been realized, similarities between the donor properties of these two ligands. However, the present work has shown some significant differences. The similarities and differences can be summarized as follows. Similarities: (a) isostructural $[ML_2]_n$ complexes (M = Co, Ni, Cu, Zn; L = Mt, Smc) containing the $[MN_2O_4]$ donor set; (b) the existence of similar mixed-metal complexes. Differences: (a) the existence of complexes $[ML_3]^-$ (when L = Mt, for Ni but not for Cu; when L = Smc, for Cu but not for Ni); (b) exactly similar reaction conditions produce $[Pd(MtH)Cl_2]$ and $[Pd_2(SmcH)_2Cl_2][PdCl_4]$; (c) the existence in the solid state of $Li[AgMt_2]$ but not of $Li[Ag(Smc)_2]$.

Registry No. $[Cu(Smc)(NO_3)]$, 39532-20-2; $Na[Cu(Smc)_3]$, 39494-99-0; $Pd_3(SmcH)_2Cl_6$, 39495-00-6; $[Co(Smc)_2Ag]NO_3 \cdot H_2O$, 37339-69-8.

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Reaction between *trans*-Carbonylchlorobis(triphenylphosphine)iridium and Some Bidentate Group Vb Chelates

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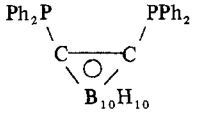
Since Vaska showed that *trans*-$Ir(CO)Cl(PPh_3)_2$ reversibly binds oxygen,[1] interest in synthetic oxygen carriers has grown rapidly. Work published recently has examined differing aspects of these systems: the O-O distance in the complexes,[2] oxygen uptake as a function of ligand,[3] and the effect of differing d^8 metal ions.[4] As part of a program aimed at studying synthetic oxygen carriers involving multidentate ligands, which may relate to natural oxygen transporters, we have begun, and wish to report here on, the reaction of a series of bidentate group Vb ligands with Vaska's compound.

Table I. Analytical and Infrared Data of the Complexes

	% carbon		% hydrogen		Ir spectra, cm^{-1}	
	Calcd	Found	Calcd	Found	ν(CO)	$\nu(O_2)$
$[Ir(CO)(dpp)_2]Cl$	61.1	61.0	4.8	4.6	1910	
$[Ir(dpp)_2]Cl$	61.5	61.3	4.9	4.7		
$[Ir(dpp)_2(O_2)]Cl$	59.6	59.7	4.8	4.8		830
$[Ir(CO)(vpa)_2]Cl$	55.9	56.0	3.9	3.6	1950	
$[Ir(vpa)_2]Cl$	56.3	56.5	3.9	3.9		
$[Ir(vpa)_2(O_2)]Cl$	54.6	54.8	3.9	3.7		840

The ligands employed in this study were 1,3-bis(diphenylphosphino)propane (dpp), 1,2-bis(diphenylarsino)ethane (dae), *cis*-1,2-bis(diphenylarsino)ethylene (vaa), *cis*-1-diphenylphosphino(2-diphenylarsino)ethylene (vpa), 1-diphenylphosphino(2-diphenylarsino)ethane (pae), and bis(diphenylphosphino)-*o*-carborane (dpc). We also used *cis*-1,2-bis(diphenylphosphino)ethylene (vpp), but while our work was in progress, Doronzo and Bianco published the results of a similar study.[5] Our results are in agreement with theirs.

dpc =



Experimental Section

The Ligands. These were prepared by literature methods[6] or by methods to be published shortly.[7]

The Complexes. The method used in complex synthesis was similar to that of Vaska and Catone[8] and involved the steps

$$Ir(CO)Cl(PPh_3)_2 \xrightarrow[C_6H_6,\ \text{cold}]{L\frown L} [Ir(CO)(L\frown L)_2]Cl \xrightarrow[\text{toluene, 1-propanol}]{\text{reflux}}$$

$$[Ir(L\frown L)_2]Cl \xrightarrow[C_6H_6]{O_2} [Ir(L\frown L)_2(O_2)]Cl$$

Analyses were determined by the Microanalytical Laboratory of this department (see Table I). Infrared spectra were obtained as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer.

Results and Discussion

With the ligands dae, vaa, pae, and dpc no reaction occurred upon mixing with Vaska's compound in benzene; even after reflux both the ligand and $Ir(CO)Cl(PPh_3)_2$ appeared to be unchanged. However, reaction did occur with the ligands dpp, vpp, and vpa. In the infrared spectra of the $[Ir(CO)(L\frown L)_2]Cl$ complexes ν(CO) bands were observed at 1910 cm^{-1} (dpp) and 1950 cm^{-1} (vpa). These frequencies may be compared with that of the analogous complex $[Ir(CO)(dpe)_2]Cl$ (dpe = 1,2-bis(diphenylphosphino)ethane), which exhibits ν(CO) at 1933 cm^{-1}.[8] Although there is some risk involved in speculating the extent of back-bonding in complexes which have not been proved to be isostructural, it may nonetheless be mentioned that the low frequency of the dpp adduct compared with that of dpe may indicate a lower CO bond order in the dpp complex because of decreased back-donation from the metal to the phosphine. This rather surprising result may be explained as due to the increased steric

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