Both plots show a steady increase in absorbance until the metal–ligand ratio reaches approximately 2:1. Further increases in the ligand concentration do not alter the absorbance appreciably. The observed discontinuity occurs at a metal: ligand ratio of 2.10 in the case of the DTPA complex and at 1.94 for the TTHA complex. The plots indicate that binuclear molybdenum complexes of DTPA and TTHA are formed.

Crystalline binuclear molybdenum(V) complexes of DTPA and TTHA were synthesized and their infrared spectra examined. As seen in Table I, the spectra show peaks which are indicative of uncoördinated –COOH groups. The ratio of coördinated to uncoördinated carboxyl groups appears to be large in both cases.

Since uncoördinated carboxyl groups were detected in the DTPA complex, a tridentate–quinquedentate structural arrangement for this compound (similar to that shown for Ni in X) is eliminated from consideration. The best structural choices appear to be those in which DTPA functions either as a tridentate–quadridentate or as a tridentate–tridentate ligand.

Similar structures may be proposed for the binuclear Mo(V)–TTHA complex. Structures in which one or both ends of the TTHA group function in a quinquedentate manner are considered unlikely in view of the infrared spectral evidence for the presence of at least one uncoördinated carboxylic acid group. A quadridentate–quadridentate or tridentate–quadridentate structural arrangement appears to be likely for this complex.

Potentiometric titration curves were obtained for the binuclear molybdenum(V) complexes of DTPA and TTHA. The curves showed that each of the complexes contains three acidic protons per molecule. The complexes are tentatively formulated as $H_3[Mo_2O_2(OH)_4(DTPA)]$ and $H_3[Mo_2O_2(OH)_3(TTHA)]\cdot 4H_2O$. Since the coördination number of Mo(V) is not well established, the number of oxo and hydroxo groups coördinated to the metal ion is uncertain.

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Notes

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Six-Coördinate Mercury(II)

By Richard L. Carlin, James Roitman, Mary Dankleff, and John O. Edwards

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We wish to report the synthesis of four new complexes of mercury(II), all of which exhibit the unusually high coördination number of six. These complexes also are unusual in that, in each case, the donor atom is oxygen; the low stability of most oxygen donors to mercury(II) is well-known. The complexes, all of them white, are of the form $[HgL_6](ClO_4)_2$, where L is one of the following: pyridine N-oxide,[1] dimethyl sulfoxide, tetrahydrothiophene oxide, and thioxane oxide. The complexes of several of these ligands with salts of the transition metals have been reported earlier.[1–4]

The structure of each of these complexes involves either octahedral or distorted octahedral[5] coördination about the central mercury atom; earlier workers[6] have suggested that mercury(II) has the coördination number of six in aqueous solution. The fact that four different ligands form compounds of the correct stoichiometry $Hg(ClO_4)_2\cdot 6L$ is indicative of the fact that the complexes are not of the form $[HgL_n](ClO_4)_2$, where n is less than six and with the remaining $6-n$ ligands uncoördinated but in the lattice, for we would not expect this behavior to be general for such varied ligands.

Comparison of X-ray powder patterns of [Ni-

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(1) R. L. Carlin, *J. Am. Chem. Soc.*, **83**, 3773 (1961).

(2) F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

(3) D. W. Meek, D. K. Straub, and R. S. Drago, *ibid.*, **82**, 6013 (1960).

(4) R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).

(5) L. E. Orgel, *ibid.*, 4186 (1958).

(6) (a) C. L. van Panthaleon van Eck, Thesis, Leiden, 1958. (b) P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.*, **82**, 3510 (1960).

$(C_5H_5NO)_6](ClO_4)_2$ and $[Co(C_5H_5NO)_6](ClO_4)_2$[1] show that they are isomorphous, as expected, and the configurations of these compounds involve octahedral coördination as indicated by their visible spectra.[1] The powder pattern of $[Hg(C_5H_5NO)_6](ClO_4)_2$ is the same, except for minor intensity variations, as those of the nickel and cobalt compounds, showing that all three are isomorphous. Octahedral coördination about mercury therefore is proved.

Further information about the bonding in complexes of this type has been obtained by comparing the S–O[7] and P–O[8] stretching vibrations between the various complexes and the free ligands, respectively dimethyl sulfoxide[7] and triphenylphosphine oxide.[8] Because of the strong absorption by perchlorate in the 1000–1200 cm.$^{-1}$ region, we have been unable to identify with certainty the (shifted from the free ligand) N–O and S–O stretching frequencies. The N-oxide must coördinate through the oxygen atom, which would cause a decrease in the N–O stretching frequency, and for this reason we believe that the sulfoxides as well coördinate through the oxygen atom. This result is substantiated by the infrared spectrum[9] of $HgCl_2\cdot(CH_3)_2SO$, which indicates donation through the oxygen atom.[10]

Earlier investigations[2,3,9] of dimethylsulfoxide as a ligand toward mercury(II) resulted in compounds such as $HgCl_2\cdot(CH_3)_2SO$, $(HgCl_2)_2\cdot(CH_3)_2SO$, and $Hg(SCN)_2\cdot 2(CH_3)_2SO$. It now is obvious that mercury(II) in the presence of the non-coordinating anion, perchlorate, will form well-defined octahedral complexes. It is interesting to note that we also have prepared the compound $[Hg(C_5H_5NO)_2(NO_3)_2]$, where nitrate functions as a ligand. This compound is analogous to the copper(II) and nickel(II) compounds.[1]

The factors involved in forming mercury(II) complexes with coördination number six are several. All of the ligands reported here involve minimal steric interaction in the complex. We have attempted to prepare complexes of triphenylphosphine oxide, diphenyl sulfoxide, and trimethylamine oxide with mercuric perchlorate and

TABLE I

NEW SIX-COÖRDINATE COMPLEXES

Compound	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Sulfur (%)		Metal (%)		Chlorine (%)	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[Hg(C_5H_5NO)_6](ClO_4)_2$	37.14	37.58	3.09	2.92	8.66	8.96					7.32	7.41
$[Hg(CH_3SOCH_3)_6](ClO_4)_2$	16.60	16.25	4.18	4.26			22.15	22.24			8.17	8.37
$\{Hg[(CH_2CH_2)_2SO]_6\}(ClO_4)_2$	28.14	28.04	4.72	4.89			18.78	18.57	19.58	19.46	6.92	6.65
$\{Hg[O(CH_2CH_2)_2SO]_6\}(ClO_4)_2$	25.70	25.87	4.31	4.59			17.15	17.21	17.89	17.60	6.41	6.32
$[Hg(C_5H_5NO)_2(NO_3)_2]$	23.29	23.82	1.95	2.15	10.86	10.71			38.89	39.13		
$\{Ni[O(CH_2CH_2)SO]_6\}(ClO_4)_2$	29.46	29.66	4.91	5.44			19.64	19.51	6.01	6.03	7.26	7.27
$[Co(4\text{-}CH_3C_5H_4NO)_6](ClO_4)_2$	47.38	47.22	4.64	4.71	9.21	9.29			6.46	6.51	7.77	7.80
$[Ni(4\text{-}CH_3C_5H_4NO)_6](ClO_4)_2$	47.39	47.25	4.64	4.57	9.21	9.49			6.43	6.55	7.77	7.76

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[7] F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

[8] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

[9] J. Selbin, W. E. Bull, and L. H. Holmes, Jr., *J. Inorg. & Nuclear Chem.*, **16**, 219 (1961).

[10] E. L. McGandy and K. Eriks (American Crystallographic Association Meeting, Boulder, Colorado, July, 1961) have reported the crystal structure of BF_3–$OS(CH_3)_2$. Coördination occurs through the oxygen atom and the S–O bond length is 1.52 Å. (1.47 Å. in the free molecule) and the O–B bond length is 1.54 Å.

have had little success; certainly steric factors are important in forming those complexes we report. In order to coördinate to mercury(II) these ligands have struck a fine balance in the electronegativity of the donor oxygen atom and the charge on it. A major factor also may be that oxygen in these covalent molecular oxides cannot π-bond with the metal in the manner discussed by Leden and Chatt.[11]

We now are investigating other post-transition metal perchlorates in an attempt to make complexes with high coördination numbers.

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Experimental[12]

Preparation of the Complexes.—Interaction of either a methanol or ethanol solution of the appropriate ligand with a similar solution of hydrated mercuric(II) perchlorate results in the precipitation of white crystals. These can be recrystallized from the same solvent. Each complex was dried *in vacuo* at 60°. Several attempts to prepare a six-coördinate mercury complex of 4-methyl-pyridine N-oxide were unsuccessful. The basic ligand precipitated mercuric oxide, whereupon a small amount of perchloric acid was added to prevent hydrolysis. A solid compound of indeterminate analysis then was obtained by evaporation of solvent. New cobalt(II) and nickel(II) complexes of this ligand were prepared easily, and they are listed in Table I, along with the mercury compounds.

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[11] I. Leden and J. Chatt, *J. Chem. Soc.*, 2936 (1955).

[12] Microanalyses by Schwarzkopf Microanalytical Laboratory.

CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AMHERST, MASSACHUSETTS

Sulfone Ligands in Cobalt(II) Complexes

BY C. H. LANGFORD AND P. O. LANGFORD

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Tetramethylene sulfone[1] has attracted recent attention as a dipolar aprotic solvent of interesting properties.[2] The complexing power of sulfones with transition metal ions usually is assumed to be low; preliminary attempts to isolate sulfone complexes have failed.[3] However, sulfone complexes with antimony trichloride have been reported[4] and a number of complexes with the related solvent tetramethylene sulfoxide are known.[5] In the course of an investigation in this Laboratory using tetramethylene sulfone as a solvent, two *unstable* complexes consistent with the formulas $[Co(C_4H_8SO_2)Cl_2]$ and $[Co(C_4H_8SO_2)_3](ClO_4)_2$ have been isolated.

Cobalt (II) Chloride–Tetramethylene Sulfone Adduct.—Tetramethylene sulfone, purified as previously described,[2] was used to dissolve anhydrous cobalt chloride. When two volumes of benzene were added to one volume of the deep blue solution, a fine blue precipitate formed which had the empirical formula $CoCl_2 \cdot C_4H_8SO_2$. Cobalt was determined by titration with ethylenediaminetetraacetic acid using murexide indicator[6] and carbon by commercial microanalysis in the laboratories of G. Weiler and F. B. Strauss, Oxford. *Anal.* Calcd. for $[Co(C_4H_8SO_2)Cl_2]$: Co, 23.6; C, 19.2. Found: Co, 22.8; C, 20.2.

The blue complex is a non-electrolyte in tetramethylene sulfone. The specific conductance of a solution 4.32×10^{-4} M $CoCl_2$ in the sulfone was less than 4×10^{-7} ohm at 30°. Conductance measurements were made using a conventional Wheatstone bridge and a cell with bright Pt electrodes (cell constant = 0.354). Burwell and Langford[2] reported typical ionic salts with conductances 10 to 100 times the limit given here. Despite difficulties in excluding moisture, a crude molecular weight for the blue complex was determined using a simple Beckmann cryoscopic apparatus and the sulfone as solvent. A value of 300 was obtained. The calculated molecular weight for $[Co(C_4H_8SO_2)Cl_2]$ is 250.

It is concluded that the blue complex is a monomeric non-electrolyte consistent with the formula given above. The visible spectrum of this complex shows peaks at 687 and 590 mμ, with log ϵ values of 2.49 and 2.19, respectively. The spectrum is unlike that of $CoCl_4^{=}$, which shows peaks at 690, 672, and 640 in the sulfone solvent. Addition of two equivalents of chloride to the sulfone complex in solution converts it to the tetrachloro anion.

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[1] Tetramethylene sulfone is known commercially as sulfolane and is available from the Phillips Petroleum Company, Bartlesville, Okla.

[2] R. L. Burwell, Jr., and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959).

[3] F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960).

[4] I. Lindquist and P. Einarsson, *Acta Chem. Scand.*, **13**, 420 (1959).

[5] R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1961).

[6] F. J. Welcher, "Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Princeton, N. J., 1958, p. 230.