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# Mercury(I) Complexes

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The following new complexes of mercury(I) with oxygen-donor ligands have been prepared and characterized: $Hg_2[(C_6H_5)_3PO]_4(ClO_4)_2$, $Hg_2SiF_6 \cdot 5(C_6H_5)_3PO$, $Hg_2(C_5H_5NO)_4(ClO_4)_2$, $Hg_2SiF_6 \cdot 5(C_5H_5NO)$, $Hg_2[(CH_3)_2SO]_{3.4}(ClO_4)_2$, $Hg_2[(CH_3)_2SO]SiF_6 \cdot xH_2O$, $Hg_2[(C_6H_5)_2SO]_{2.6}(ClO_4)_2$, and $Hg_2[(CH_3CH_2CH_2)_2SO]_4(ClO_4)_2$. Anhydrous mercury(I) nitrate was isolated and investigated. The formation of complexes of mercury(I) and criteria for their stability are discussed. A correlation was observed between the stability of mercury(I) compounds and the position of the ligands in the spectrochemical series.

## Introduction

The number of recognized mercury(I) complexes is small owing to the instability of mercury(I) toward disproportionation with common ligands, including ammonia, many amines, cyanide ion, hydroxide ion, thiocyanate ion, sulfides, and acetylacetone. Many texts report that mercury(I) either forms no complexes or has very little tendency to form complexes.

A claim was made for the formation of an addition compound between hydrazine and mercury(I) nitrate.[2] The compound $[HO-CH_2CH_2-S-Hg]_2$[3] and a soluble complex of mercury(I) with triethanolamine[4] have been mentioned.

Grdenić[5,6] in determining the crystal structure of mercury(I) nitrate dihydrate found that the mercury to oxygen (water) distance is 2.15 A. The approximately linear aquo complex $[H_2O-Hg-Hg-OH_2]^{2+}$ was suggested for this compound and for aqueous solutions of mercury(I).

Sillén and co-workers[7,8] using potentiometric data found evidence for weak complexes between mercury(I) and the nitrate, sulfate, and perchlorate anions and also found that mercury(I) forms a stronger complex with the perchlorate anion than does mercury(II).

Yamane and Davidson[9] using potentiometric methods discovered mercury(I) complexes in solution with polyphosphate and dicarboxylate anions. They suggest that mercury(I) is unstable toward disproportionation with ligands which form strong covalent bonds but is stable with strong "ionic" ligands which complex by virtue of their charge and chelating character.

The compound, mercury(I) diacetylhydrazide, is a linear polymer containing the chain –Hg–Hg–N–N–.[10] Wirth and Davidson[11] detected the first soluble mercury(I)–nitrogen complex, aniline–mercury(I) perchlorate, with potentiometric and spectrophotometric methods. The stability constant for this complex and also those for the mercury(II), silver(I), and nickel(II) complexes were found to be: $5.1 \times 10^3$ $M^{-1}$, $C_6H_5NH_2Hg_2^{2+}$; $4.0 \times 10^4$ $M^{-1}$, $C_6H_5NH_2Hg^{2+}$; 27.6 $M^{-1}$, $C_6H_5NH_2Ag^+$; 1.2 $M^{-1}$, $C_6H_5NH_2Ni^{2+}$. These constants show that although the mercury(I) complex is not so stable as the mercury(II) complex, both are much more stable than the other two metal complexes. This study reaffirms the idea that the scarcity of mercury(I) complexes results not from the weak complexing ability of mercury(I) but from the very strong complexing ability of mercury(II). The suggestion was also made that mercury(I) may form stable complexes with other amines of low basicity.

The goals of the current research included (A) an investigation of the factors which influence the stability of the mercury–mercury bond and perhaps of metal–metal bonds in general and (B) the preparation and characterization of new compounds of mercury(I).

## Experimental Section

**Materials.**—Mercury(I) nitrate dihydrate,[5] mercury(I) perchlorate dihydrate and tetrahydrate,[12] and mercury(I) hexafluorosilicate dihydrate[13] were prepared by a general method outlined for the preparation of the perchlorate compounds.[12] Mercury(II) perchlorate hexahydrate[14] was prepared by dissolving mercury(II) oxide in dilute perchloric acid and concentrating the solution to form crystals.

The following chemicals were purchased: triphenylphosphine oxide (Chemical Procurement Laboratories) which was recrystallized from a water–alcohol mixture, mp 156–158°; pyridine N-oxide (Aldrich Chemical Co.) which was recrystallized from toluene in a dry nitrogen atmosphere; dimethyl sulfoxide (Matheson Coleman and Bell); diphenyl sulfoxide (Aldrich Chemical Co.) which was recrystallized from heptane, mp 70°; di-*n*-butyl and di-*n*-propyl sulfoxides (Aldrich Chemical Co.) which were purified by vacuum distillation; triphenylarsine oxide (Chemical Procurement Laboratories), mp 194–196°; triphenylphosphine sulfide (Chemical Procurement Laboratories), mp 162–163°; triphenylphosphine (Matheson Coleman and Bell), mp 79–80°; triphenyl phosphite (Matheson Coleman and Bell), mp 22–24°; triphenyl phosphate (Matheson Coleman and Bell), mp 49–50°; triphenylstibine (Matheson Coleman and Bell), mp 50–52°; diethyldithiophosphate (Aldrich Chemical Co.); sodium dimethyldithiocarbamate (Aldrich Chemical Co.); hydrazine (Distillation Products Industries); 2,2′,4,4′,6,6′-hexanitrodiphenylamine (Distillation Products Industries); *as*-diphenylhydrazine hydrochloride (Distillation Products Industries); diphenyl-

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amine (Matheson Coleman and Bell) which was recrystallized from a water–alcohol mixture, mp 52–53°; and mercury(I) sulfate (J. T. Baker Chemical Co.). 2,4,6-Trinitrohydrazobenzene was on hand.[15]

**Preparation of Compounds. A. Preparation of Mercury(I) Oxalate.**—Mercury(I) oxalate was prepared by the method given by Larson and Tomsicek.[16]

**B. Preparation of Anhydrous Mercury(I) Nitrate.**—This compound was prepared by dehydration of mercury(I) nitrate dihydrate under vacuum. The weight loss of dihydrate crystals, whose stoichiometry had been ensured by equilibration in a vacuum desiccator, corresponded to 2 moles of water/mole of compound.

The anhydrous compound decomposes to a yellow solid with the evolution of a brown gas when heated above 100°. An attempt to sublime anhydrous mercury(I) nitrate at a pressure of $10^{-6}$ mm and temperatures up to 95° for a period of 24 hr was unsuccessful. *Anal.* Calcd for $Hg_2N_2O_6$: O, 18.29; N, 5.33. Found: O, 17.81; N, 5.36.

**C. Attempted Preparation of Mercury(I) Nitrite.**—This compound was reported by Rây,[17] and an attempt was made to prepare it by his method. The described yellow crystals were obtained, but they slowly decomposed with an odor of nitrogen dioxide over them, leaving an unidentified solid. The reaction of mercury(I) with sodium nitrite in dilute acetic acid was also tried, but only disproportionation resulted.

**D. Preparation of Tetrakis(triphenylphosphine oxide)mercury(I) Perchlorate.**—The method given here for the preparation of this complex is illustrative of the methods used to prepare many other complexes reported below.

A solution of mercury(I) perchlorate tetrahydrate (4.7 g, 7.0 mmoles) in absolute methanol (50 ml) was added to a solution of triphenylphosphine oxide (7.8 g, 28.1 mmoles) in absolute methanol (50 ml). Colorless crystals formed when the solution was concentrated by evaporation under vacuum. The crystals were filtered, washed with absolute methanol (20 ml), and dried under vacuum (mp 190–192° dec). *Anal.* Calcd for $C_{72}H_{60}Cl_2Hg_2O_{12}P_4$: C, 50.47; H, 3.54. Found: C, 50.61; H, 3.50.

Recrystallization was achieved with only moderate success from a concentrated nitromethane solution or a diethyl ether–nitromethane mixture. The same complex was also prepared with 2:1 and 3:1 ratios of ligand to metal. The addition of water to an alcoholic solution of the compound immediately precipitates the ligand.

The molar conductivity of this compound in nitrobenzene at 25° was measured with a standard conductance bridge and a Jones-type cell. The nitrobenzene was dried over potassium hydroxide and distilled just before use in a dry nitrogen atmosphere. For a concentration of $8.75 \times 10^{-4}$ *M*, the molar conductance was found to be 46.5 $ohm^{-1}$ $cm^{-1}$ $mole^{-1}$.

**E. Preparation of Tetrakis(triphenylphosphine oxide)mercury(II) Perchlorate.**—This colorless compound was prepared by a method similar to that given in section D (mp 161–164°). *Anal.* Calcd for $C_{72}H_{60}Cl_2HgO_{12}P_4$: C, 57.16; H, 4.01. Found: C, 56.38; H, 4.14.

**F. Preparation of Mercury(I) Hexafluorosilicate Pentakis(triphenylphosphine oxide).**—The white crystals, prepared from mercury(I) hexafluorosilicate dihydrate by procedure D, were purified by washing with benzene and then recrystallizing from a concentrated methanol solution (dec ~130°). *Anal.* Calcd for $C_{90}H_{75}F_6Hg_2O_5P_5Si$: C, 55.86; H, 3.92. Found: C, 55.32; H, 4.02.

**G. Preparation of Tetrakis(pyridine N-oxide)mercury(I) Perchlorate.**—The procedure in section D was again followed. The white precipitate which formed immediately melted over a wide range (140–170°), and only the small amount of colorless crystals which appeared upon evaporation of the solvent under vacuum was analyzed with good results (mp 139–141° dec). *Anal.* Calcd for $C_{20}H_{20}Cl_2Hg_2N_4O_{12}$: C, 24.50; H, 2.06. Found: C, 25.18; H, 2.16.

**H. Preparation of Mercury(I) Hexafluorosilicate Pentakis(pyridine N-oxide).**—The hygroscopic complex, prepared by method G, was handled in a dry nitrogen atmosphere. *Anal.* Calcd for $C_{25}H_{25}F_6Hg_2N_5O_5Si$: C, 29.47; H, 2.48. Found: C, 29.28; H, 2.99.

**I. Reaction of Mercury(I) Perchlorate Tetrahydrate with Dimethyl Sulfoxide.**—The method of preparation of the colorless solid here was similar to that outlined in section D (mp 121–123° dec). *Anal.* Calcd for $C_6H_{18}Cl_2Hg_2O_{11}S_3$: C, 8.63; H, 2.18. Calcd for $C_8H_{24}Cl_2Hg_2O_{12}S_4$: C, 10.53; H, 2.66. Found: C, 9.34; H, 2.44. The reported analysis of this solid is the average of the analysis of five separate preparations where the ratios of ligand to metal were 1:1, 2:1, 4:1, 5:1, and 15:1. The standard deviations of the analyses are 0.13 for carbon and 0.12 for hydrogen. An attempt to recrystallize the solid from methanol yielded products with slightly lower melting points. Both mercury(I) perchlorate tetrahydrate and this complex slowly disproportionate when dissolved in dimethyl sulfoxide.

**J. Reaction of Mercury(I) Hexafluorosilicate Dihydrate with Dimethyl Sulfoxide.**—A solution of mercury(I) hexafluorosilicate dihydrate (3.1 g, 5.36 mmoles) in absolute methanol (50 ml) was mixed with a solution of dimethyl sulfoxide (6.5 g, 83.1 mmoles) in absolute methanol (15 ml). This solution was added to cold benzene (200 ml). A white solid appeared which was filtered and dried under vacuum (dec above 90°). *Anal.* Calcd for $C_2H_8F_6Hg_2O_2SSi$: C, 3.77; H, 1.26. Calcd for $C_2H_{10}F_6Hg_2O_3SSi$: C, 3.65; H, 1.54. Calcd for $C_2H_{12}F_6Hg_2O_4SSi$: C, 3.56; H, 1.79. Found: C, 3.73; H, 1.34. The compound was also prepared by using a 5:1 ratio of ligand to metal with similar results. When an attempt was made to prepare the compound by concentrating the alcoholic solution, disproportionation resulted.

**K. Reaction of Mercury(I) Perchlorate Tetrahydrate with Diphenyl Sulfoxide.**—A solution of mercury(I) perchlorate tetrahydrate (1.4 g, 2.08 mmoles) in absolute methanol (25 ml) was added to a solution of diphenyl sulfoxide (2.2 g, 10.9 mmoles) in absolute methanol (20 ml). As much solvent as possible was removed by evaporation under vacuum. The remaining oil was poured into cold benzene (100 ml). The white precipitate was collected and dried under vacuum (mp 128–129° dec). *Anal.* Calcd for $C_{24}H_{20}Cl_2Hg_2O_{10}S_2$: C, 28.69; H, 2.01. Calcd for $C_{36}H_{30}Cl_2Hg_2O_{11}S_3$: C, 35.82; H, 2.51. Found: C, 32.64; H, 2.37. The reported analysis of this solid is the average of the analyses of five separate preparations where the ratio of ligand to metal was varied: 4:1, 5:1, 15:1. The standard deviations of the analyses are 0.41 for carbon and 0.10 for hydrogen.

**L. Reaction of Mercury(I) Hexafluorosilicate Dihydrate with Diphenyl Sulfoxide.**—From a reaction, involving method J except for a 5:1 ratio of ligand to metal, only starting material was recovered.

**M. Preparation of Tetrakis(di-*n*-propyl sulfoxide)mercury(I) Perchlorate.**—A solution of mercury(I) perchlorate dihydrate (2.3 g, 3.42 mmoles) in absolute ethanol (25 ml) was added to a solution of di-*n*-propyl sulfoxide (5.2 g, 38.8 mmoles) in absolute ethanol (20 ml). As much solvent as possible was evaporated under vacuum. The remaining colorless oil was washed five times by adding anhydrous diethyl ether (50 ml) to the flask in an ice bath, cooling the mixture to −78.5°, decanting the ether, and then warming to 0° before the addition of fresh diethyl ether. During the third wash, the oil turned to a white solid which was collected and dried under vacuum after the fifth wash (mp 55–57° dec). *Anal.* Calcd for $C_{24}H_{56}Cl_2Hg_2O_{12}S_4$: C, 25.35; H, 4.97. Found: C, 25.60; H, 4.96. An unsuccessful attempt was made to prepare this compound by method K. Dimethyl, diphenyl, and di-*n*-butyl sulfoxide complexes were not obtainable by the method used for this compound.

**N. Reaction of Mercury(I) Perchlorate Tetrahydrate with Triphenylarsine Oxide.**—From the reaction of these two compounds in an alcoholic solution at −78° is obtained a white precipitate which turns gray on warming.

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TABLE I

INFRARED STRETCHING FREQUENCIES

| Compd | M–X str frequency, cm$^{-1}$ (M = P, N, S, As and X = O, S) |
|---|---|
| $(C_6H_5)_3PO$ | 1192 s |
| $Hg_2[(C_6H_5)_3PO]_4(ClO_4)_2$ | 1193 m, 1176 m, 1137 m |
| $Hg[(C_6H_5)_3PO]_4(ClO_4)_2$ | 1138 s |
| $Hg_2SiF_6 \cdot 5[(C_6H_5)_3PO]$ | 1153 s, 1144 s |
| $C_5H_5NO$ | 1243 s[21] |
| $Hg_2(C_5H_5NO)_4(ClO_4)_2$ | 1208 s |
| $Hg_2SiF_6 \cdot 5(C_5H_5NO)$ | 1218 m, 1200 s |
| $(CH_3)_2SO$ | 1053 s |
| $Hg_2[(CH_3)_2SO]_{3.4}(ClO_4)_2$ | 924 s |
| $Hg_2[(CH_3)_2SO]SiF_6 \cdot xH_2O$ | 925 s |
| $(C_6H_5)_2SO$ | 1038 s |
| $Hg_2[(C_6H_5)_2SO]_{2.6}(ClO_4)_2$ | 904 s |
| $[CH_3CH_2CH_2]_2SO$ | 1020 s |
| $Hg_2[(CH_3CH_2CH_2)_2SO]_4(ClO_4)_2$ | 940 s |
| $(C_6H_5)_3AsO$ | 881 s |
| $Hg[(C_6H_5)_3AsO]_4(ClO_4)_2$ | 845 s |
| $(C_6H_5)_3PS$ | 639 s |
| $Hg[(C_6H_5)_3PS]_4(ClO_4)_2$ | 587 s |

**O. Preparation of Tetrakis(triphenylarsine oxide)mecury(II) Perchlorate.**—A solution of mercury(II) perchlorate hexahydrate (1.6 g, 3.15 mmoles) in absolute ethanol (40 ml) was added to a solution of triphenylarsine oxide (2.4 g, 7.45 mmoles) in absolute ethanol (40 ml). Immediately, a white precipitate formed which was filtered, washed with ethanol, and dried under vacuum (mp 175–178° dec). *Anal.* Calcd for $C_{72}H_{60}As_4Cl_2HgO_{12}$: C, 50.15; H, 3.59. Found: C, 50.69; H, 3.92.

**P. Reaction of Mercury(I) Perchlorate Tetrahydrate with Triphenyl Phosphate.**—Alcoholic solutions of the two compounds were mixed, but no new compound precipitated upon evaporation of the solvent.

**Q. Reaction of Mercury(I) Perchlorate Tetrahydrate with Triphenylphosphine Sulfide.**—The addition of a solution of mercury(I) perchlorate tetrahydrate to a solution of triphenylphosphine sulfide, both in 1,2-dimethoxyethane, resulted in disproportionation.

**R. Preparation of Tetrakis(triphenylphosphate sulfide)mercury(II) Perchlorate.**—A solution of mercury(II) perchlorate hexahydrate (1.0 g, 1.99 mmoles) in 1,2-dimethoxyethane (30 ml) was added to a solution of triphenylphosphine sulfide (3.0 g, 10.2 mmoles) in 1,2-dimethoxyethane (50 ml). A colorless oil formed and soon turned to a white solid which was collected and dried under vacuum (mp 206–210° dec). *Anal.* Calcd for $C_{72}H_{60}Cl_2HgO_8P_4S_4$: C, 54.83; H, 3.84. Found: C, 53.01; H, 3.98.

**S. Reaction of Mercury(I) with Carbon Monoxide.**—Carbon monoxide was bubbled through a solution of mercury(I) perchlorate tetrahydrate (2.4 g) in absolute methanol (75 ml) at several temperatures. Mercury appeared after a few minutes at 25°, only after 10 hr at −22.9°, only after 12 hr at −45.2°, and not at all at −78.5°. No absorption of gas or deposition of mercury was observed during an attempted tensiometric titration at −78.5°. Also, no detectable quantity of carbon monoxide was absorbed at −45.2°.

**T. Reaction of Mercury(I) Nitrate Dihydrate with Hydrazine.**—Hydrazine was added both to an acidic aqueous solution and to crystals of mercury(I) nitrate dihydrate. Highly exothermic disproportionation occurred immediately.

**U. Reactions of Mercury(I) Compounds with Other Compounds Which Produce Disproportionation.**—Mercury(I) perchlorate tetrahydrate or mercury(I) nitrate dihydrate in alcoholic or aqueous solutions disproportionated when a solution containing any of the following compounds was added: sodium dimethyldithiocarbamate dihydrate, diethyldithiophosphate, urea, thiourea, sodium tetraphenylborate, acetone, triphenylphosphine, triphenyl phosphite, triphenylstibine, 3-hexyne, cyclohexene, 2,5-norbornadiene.

**V. Reactions of Mercury(I) Perchlorate Tetrahydrate with Amines and Substituted Hydrazines.**—The reaction of mercury(I) perchlorate tetrahydrate with 2,2′,4,4′,6,6′-hexanitrodiphenylamine, diphenylamine, *as*-diphenylhydrazine hydrochloride, and 2,4,6-trinitrohydrazobenzene was carried out by a method similar to that used by Brodersen and Kunkel[10] in the preparation of mercury(I) diacetylhydrazide. No products containing mercury(I)–nitrogen bonds were recovered. The reactions were also run with methanol as the solvent.

**Analysis.**—Analyses were performed either by Micro-Tech Laboratories, Inc., Skokie, Ill., or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**Infrared Spectra.**—Infrared spectra were obtained on a Beckman IR9 spectrometer over the region 400–4000 cm$^{-1}$. The compounds were run in Nujol mulls between sheets of polyethylene film. Where it was necessary to observe bands under the Nujol–polyethylene absorptions, hexachlorobutadiene was used as the mulling agent.

## Results and Discussion

**New Complexes of Uncharged Oxygen-Donor Ligands.**—Two complexes of mercury(I) with triphenylphosphine oxide have been prepared, the perchlorate and hexafluorosilicate, as well as tetrakis(triphenylphosphine oxide)mercury(II) perchlorate. The corresponding P–O stretching frequencies are listed in Table I. An attempt to prepare a complex of mercury(I) nitrate with this ligand or with dimethyl sulfoxide was unsuccessful. The occurrence of four ligands in one compound and five in the other presents an interesting point. On a simple analogy with the mercury(I) halides, two ligands would be expected to coordinate to $Hg_2^{2+}$. A structure of mercury(I) with four groups attached to it has not been reported although fourfold coordination has been suggested for the complex ions in solution.[9] From the results of this research, four is believed to be a common coordination number for $Hg_2^{2+}$. The occurrence of more than one P–O stretching frequency in complexes of the above type is not unusual[18,19] but the absorption at 1193 cm$^{-1}$ in the perchlorate complex is very close to that for the free ligand. This result may indicate that all four ligands are not equivalent. The frequencies due to the perchlorate ($\nu_3$ 1100 s, 1065 s; $\nu_4$ 626 m, 623 m, 621 m, 618 m cm$^{-1}$) and hexafluorosilicate ($\nu_1$ 881 s, 785 s cm$^{-1}$) anions in these two mercury(I) complexes are split, probably a result of distortion. The conductivity study of tetrakis(triphenylphosphine oxide)mercury(I) perchlorate indicates that the complex is a 2:1 electrolyte.[20] Molecular weight measurements were unsuccessful owing to the lack of a proper solvent.

The mercury(I) complexes of pyridine N-oxide, Table I, are comparable to those mentioned above. Again the perchlorate complex contains four ligands and the

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hexafluorosilicate complex, five. The latter complex is hygroscopic, as is the free ligand, and this fact may indicate that the fifth ligand in the compound is more loosely bound. The preparation of these complexes is not clean-cut since a large amount of impure material, possibly containing basic mercury(I) compounds, is precipitated first. The infrared frequencies for these two complexes are similar to those of other pyridine N-oxide complexes.[21,22] The frequency at 1218 $cm^{-1}$ in the hexafluorosilicate complex may be due to a nonequivalent ligand.

Complexes, listed in Table I, containing a constant nonintegral number of ligands were generally obtained when the sulfoxides were used as ligands even though reaction conditions and concentrations were varied. Of the perchlorate complexes, only the compound with di-*n*-propyl sulfoxide analyzed for a simple tetrakis complex. No complex could be prepared with di-*n*-butyl sulfoxide. The lack of simple stoichiometry may result either from the fact that the sulfoxides can bond through the sulfur or oxygen atoms[23] or from the formation of mixed crystals. The only sulfoxide complex with mercury(I) hexafluorosilicate is with dimethyl sulfoxide which perhaps merely substitutes for one of the water molecules in the dihydrate compound.

Similar problems of ill-defined compounds between the sulfoxides and mercury(II) salts have been reported,[23] but several complexes of simple stoichiometry have been prepared.[24,25] Some controversy has occurred over the assignment of the S–O stretching frequency in sulfoxide complexes. Several research groups have assigned this vibration to the strong band appearing at about 1000 $cm^{-1}$,[19,25,26] while another is in favor of the strong band at about 940 $cm^{-1}$.[27] The spectra observed here fit the latter assignment best since the diphenyl and di-*n*-propyl sulfoxide complexes give no bands in the 1000-$cm^{-1}$ region. The lowering of the S–O frequency indicates that the complexes are O-bonded rather than S-bonded.[27] The frequencies of the anions show them to be the simple, undistorted anion except for the diphenyl sulfoxide complex. The $\nu_3$ frequency of the perchlorate anion in this compound is split (1135–1140 s, 1070–1090 s, 1035–1040 s) probably for reasons given above.

The reaction of mercury(I) with a ligand analogous to triphenylphosphine oxide, triphenylarsine oxide, resulted only in disproportionation. At low temperatures the complex is stable, but it could not be isolated for identification. The mercury(II) complex, tetrakis(triphenylarsine oxide)mercury(II) perchlorate, has not been previously reported although other mercury(II) salts form complexes with this ligand.[20]

Triphenyl phosphate was not a suitable ligand. Apparently, the groups attached to the phosphorus atom withdraw electrons to such an extent that the oxygen atom is only a weak donor since only starting materials were recovered.

Acetone can act as an oxygen donor ligand[19] but causes disproportionation of mercury(I).

**Reactions of Ligands Having Donor Atoms Other Than Oxygen.**—Triphenylphosphine is a ligand in a number of metal–metal bonded compounds, but it causes disproportionation of mercury(I). The observation has been made that in certain metal–metal bonded compounds, triphenylphosphine tends to destabilize the metal–metal bond and favors the formation of monomers, while triphenyl phosphite stabilizes the metal–metal bond and favors dimerization.[28] However, triphenyl phosphite also produces disproportionation with mercury(I). Triphenylstibine also causes disproportionation of mercury(I).

Although triphenylphosphine sulfide is structurally similar to triphenylphosphine oxide, the reaction of this compound with mercury(I) is disproportionation. The preparation of tetrakis(triphenylphosphine sulfide) mercury(II) perchlorate was achieved. The P–S stretching frequency of this complex, Table I, is nearly the same as that in (triphenylphosphine sulfide)gold(I) chloride (590 $cm^{-1}$).[29]

Carbon monoxide caused disproportionation of mercury(I). Since no carbonyl compounds of mercury(I) or -(II) have been isolated, the fact that a reaction occurred is of interest. No absorption of the gas over a mercury(I) solution was noted, even after mercury appeared. The temperature dependence of the reaction must be due to a decrease in the reaction rate rather than the formation of a complex stable at lower temperatures.

Mercury(I) and unsaturated carbon compounds were combined in a search for complexes. The reactions of mercury(I) with 3-hexyne, cyclohexene, and 2,5-norbornadiene yield disproportionation which probably involves mercuration. Mercury(I) acetylide is known, but its structure is not.

The reactions of mercury(I) with *as*-diphenylhydrazine hydrochloride, 2,4,6-trinitrohydrazobenzene, diphenylamine, and 2,2′,4,4′,6,6′-hexanitrodiphenylamine did not lead to monomeric or polymeric mercury(I) compounds comparable to the polymeric mercury(I) diacetylhydrazide prepared by a similar procedure.[10]

A reaction of hydrazine with mercury(I) was carried out to check the report[2] of the formation of an addition compound. The existence of this complex is doubtful since a violent reaction with disproportionation was observed in this research.

**Survey of Other Mercury(I) Systems and the Spectrochemical Series.**—The previously known mercury(I) systems, including compounds not generally classified as complexes, as well as the currently reported mercury(I) complexes, can be examined in terms of

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coordination chemistry. Ligands which form compounds (currently known) with mercury(I) are in the lower half of the spectrochemical series. No compounds of mercury(I) are known with ligands above water in the recently compiled[30] spectrochemical series: $CN^- > \mathit{N}O_2^- > NH_3 > \mathit{N}CS^- > H_2O \sim (COO)_2^{2-} > OH^- > (NH_2)_2C\mathit{O} > (C_2H_5)_2NCS_2^- > F^- > (C_2H_5O)_2PS_2^- > N_3^- \sim \mathit{S}CN^- \sim Cl^- > Br^- > I^-$.

The crystal structures[31] of the mercury(I) halides involve linear molecules which may be taken as linear complexes, X–Hg–Hg–X. Yamane and Davidson[9] advanced the hypothesis that the stronger the Hg–L bond, the longer and weaker the Hg–Hg bond. The mercury–mercury bond distances[5,6,10,31] increase from the fluoride to the iodide as expected from consideration of soft acid–base criteria.[32] The softest base, iodide, forms the strongest bond with the soft acid, mercury(I), and gives the longest mercury–mercury bond distance.

Although the thiocyanate ion is low in the spectrochemical series when it is S-bonded, mercury(I) thiocyanate is unstable toward disproportionation.[33] Throughout this research and in other reports,[34] the general observation has been made that mercury(I) is unstable when the donor atom is the readily polarizable sulfur.

The next ligand, azide, in the series forms a compound stable toward disproportionation.

The reactions of mercury(I) with diethyldithiophosphate and dimethyldithiocarbamate led to disproportionation as has been observed for other sulfur donors.

Mercury(I) disproportionates in the presence of urea and thiourea. Urea is low in the spectrochemical series when bonded through the oxygen. However, since mercury(II) bonds to nitrogen very strongly, nitrogen may coordinate initially in these compounds and then cause disproportionation.

Mercury(I) hydroxide has not been isolated although it is suggested to be present in the reddish yellow precipitate which forms when base is added to a mercury(I) solution.[35,36] Complexes containing one hydroxide ion per $Hg_2^{2+}$ have been detected.[9,37]

Mercury(I) oxalate exhibits an infrared spectrum similar to those for oxalate complexes given by Nakamoto:[38] 1615 s, 1580 sh, 1385 w, 1285 s, 1268 s, 893 vw, 780 s, 541 m, 511 w, 498 w, 485 sh, 409 w. Organic acid ions, acetate,[39] and substituted halogen acetates[40] also form stable complexes.

As previously mentioned, the aquo complex $[H_2O–Hg–Hg–OH_2]^{2+}$ exists in mercury(I) nitrate dihydrate and has been suggested to exist in aqueous solution.[5,6] The other hydrated mercury(I) compounds such as mercury(I) perchlorate dihydrate and tetrahydrate and hexafluorosilicate dihydrate are also probably aquo complexes. Mercury(I) perchlorate tetrahydrate may contain the diaquo complex with the other two waters hydrogen-bonded to the perchlorate anion. Two of the four water molecules can be removed while the last two cannot without destroying the compound.

The nitrite anion is the only other ligand in the above spectrochemical series for which a mercury(I) compound has been reported.[17,41] All attempts to prepare mercury(I) nitrite in this research were unsuccessful. If this compound does exist, the nitrite anion would be expected to be bonded to the mercury(I) through the oxygen, nitrito-, rather than the nitrogen, nitro-.

Although a correlation involving mercury(I) compounds and the spectrochemical series exists, no comparable correspondence is apparent with the nephelauxetic series.

In view of the above complexes, a survey was made of mercury(I) systems containing sulfate, nitrate, perchlorate, hexafluorosilicate, and tetraphenylborate anions, which are generally weakly coordinating or noncoordinating.

An infrared study of mercury(I) sulfate was carried out, and the frequencies due to the sulfate group have been assigned in Table II. The assignments are based on $C_{2v}$ symmetry and the spectra of the sulfate group in other environments.[42]

TABLE II

ASSIGNMENTS OF INFRARED FREQUENCIES FOR MERCURY(I) SULFATE ($cm^{-1}$)

| $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ |
|---|---|---|---|
| ... | 517 w | 950 s, b | 580 m |
| | | 1093 s, b | 604 m |
| | | 1200 s, b | 654 m |

The $\nu_1$ frequency is believed to be under the strong and broad $\nu_3$ frequencies. The spectrum of this compound has been reported in the cesium bromide region and corresponds well with what was found here: 508 w, 568 m, 593 w, 643 m.[43] As for the structure of mercury(I) sulfate, little can be said from this infrared study except that the sulfate group is restrained in some manner. This fact does however establish that the sulfate group is not acting as a simple anion but is perhaps coordinated to mercury(I) in some way to give it $C_{2v}$ symmetry.

Mercury(I) nitrate dihydrate, a diaquo complex, upon dehydration gives anhydrous mercury(I) nitrate. A recent review of anhydrous metal nitrates stated that this compound was unknown,[44] but a previous

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report of its preparation has been found.[17] The unusual property of some anhydrous metal nitrates, relatively high volatility,[45,46] was not observed in this research with this compound. The absence of volatility may be due simply to thermal instability. The infrared spectrum of mercury(I) nitrate indicates that the nitrate group is coordinated. The frequencies and assignments are reported in Table III. The assignments are made on the basis of the nitrate group having $C_{2v}$ symmetry which has been found for other nitrato complexes.[47,48]

TABLE III

ASSIGNMENTS OF INFRARED FREQUENCIES OF MERCURY(I) NITRATE ($\text{cm}^{-1}$)

| $\nu_2$ | $\nu_6$ | $\nu_1$ | $\nu_4$ | $\nu_5$ | $\nu_3$ |
|---|---|---|---|---|---|
| 1010 s | 794 m | 1308 sh | 1515 w | 707 m | 748 m |
| 995 s | 790 s | 1285 vs | 1490 vs | 700 m | 740 s |
| 960 s | | 1250 vs | 1436 vs | | 732 m |

The occurrence of more than one frequency under an assignment may be due to more than one type of nitrate group in the crystal structure[49] or a further lowering of the symmetry of the molecule as a whole.

The compounds of mercury(I) with the perchlorate and hexafluorosilicate anions have been discussed and are believed to be diaquo complexes. Weak complexes between mercury(I) and the nitrate and perchlorate anions in aqueous solution have been described.[7]

The reaction of mercury(I) with the tetraphenylborate anion led to disproportionation. If this mercury(I) compound did exist, it would probably be the diaquo complex and be soluble. Undoubtedly, the mercury(II) compound with this anion is insoluble since this anion is used to precipitate large cations, and hence disproportionation of mercury(I) results.

**Conclusions.**—The fact has been noted here and by other workers that the chemistry of mercury(I) is governed by the disproportionation reaction which greatly depends on the groups L attached to the ions.[9]

$$\text{Hg} + \text{Hg}^{\text{II}}\text{L}_m = \text{Hg}^{\text{I}}{}_2\text{L}_n + (m - n)\text{L}$$
$$K = 88 \pm 4\ (\text{L} = \text{H}_2\text{O})^{7}$$

Mercury(I) compounds or complexes exist because the mercury(II) species is soluble, the mercury(I) species has a greater stability than the mercury(II) species, and the mercury(I) species is itself stable toward the heterolytic cleavage of the Hg–Hg bond resulting from the extreme lengthening and weakening of that bond by a strong $\text{Hg}^{\text{I}}$–L bond.

In view of the stability of the new mercury(I) complexes of triphenylphosphine oxide, di-*n*-propyl sulfoxide, diphenyl sulfoxide, dimethyl sulfoxide, and pyridine N-oxide, the interaction of such ions as nitrate and sulfate with mercury(I), and the existence of a moderate number of compounds containing mercury(I) and ligands from the lower part of the spectrochemical series, the tendency of mercury(I) to form complex ions is surprisingly favorable.

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# The Photochemical Synthesis of Pentacarbonyliron(0) Derivatives

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Complexes of the type $\text{Fe(CO)}_4\text{L}$ (L = pyridine, α- and γ-picoline, piperidine) have been synthesized photochemically and characterized. CO-stretching frequencies of several other unstable complexes with nitrogen-containing ligands are reported and briefly discussed. Substitution always occurs in the axial position. Acetonitrile and acrylonitrile coordinate with the metal through the nitrogen rather than by π bonding through the CN group or double bond. A new complex di-μ-acrylonitrile-bis(tricarbonyliron(0)) with the formula $[(\text{CO})_3\text{FeCH}_2{=}\text{CH}{-}\text{CN}]_2$ is described.

## Introduction

As Hieber and co-workers have already reported,[1] iron pentacarbonyl reacts with various nitrogen-containing bases in a "basic reaction" with disproportionation of the zero-valent metal atom, forming ionic compounds. These ionic species are generally hexacoordinated bivalent cations and polynuclear anions of the general formula $[\text{Fe(B)}_6][(\text{A})]$, where A is $[\text{Fe(CO)}_4]^{2-}$, $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, or $[\text{Fe}_4(\text{CO})_{13}]^{2-}$, and B is an amine or other nitrogen-containing base. The reaction mixture is heated while the ligand, B, is employed as solvent. Recently, it has been shown that

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