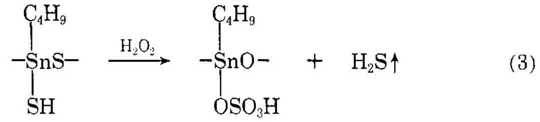

$$-\underset{\mathrm{SH}}{\overset{C_4H_9}{\mathrm{Sn}}}\mathrm{S}- \xrightarrow{H_2O_2} -\underset{\mathrm{OSO_3H}}{\overset{C_4H_9}{\mathrm{Sn}}}\mathrm{O}- + H_2S\uparrow \tag{3}$$

Potassium hydroxide easily hydrolyzes the sulfate into *n*-butylstannoic acid which, in turn, can be treated with sulfuric acid to revert to the *n*-butylstannoxy acid sulfate.

In summary, we can see that the reaction of hydrogen peroxide with alkyltin sulfides leads to the oxidation of tributyltin sulfide into the corresponding sulfate and to partial cleavage of dibutyltin sulfide and butylthiostannoic acid to form stannoxy sulfates with elimination of sulfur and hydrogen sulfide, respectively. Similar oxidation reactions were attempted with phenyl-substituted stannyl sulfides but extensive decomposition was observed in all cases.

The infrared spectra of most *n*-butyl-substituted stannyl sulfates show common vibrations at about 1100, 880, and 685 cm$^{-1}$ which have been assigned to the stretching and deformation bands of the sulfate ion.[9,10] However, we feel that these spectra are insufficient to determine the exact structure of organotin sulfates. This question is the object of a separate investigation[11] showing that the tin atom in bis(tri-*n*-butyltin) sulfate is most likely to be pentacoordinate.

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(10) D. H. Lohmann, *J. Organometal. Chem.* (Amsterdam), **4**, 382 (1965).
(11) C. H. Stapfer, K. L. Leung, and R. H. Herber, *Inorg. Chem.*, in press.

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# Triphenylphosphine and Triphenylarsine Complexes of Mercury(II) Thiocyanate, Nitrate, and Perchlorate[1,2]

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A variety of tertiary phosphine and arsine derivatives of mercury(II) halides have been known for some time.[4] Recently the infrared spectra of the series of compounds $[(C_6H_5)_3P]_2HgX_2$ and $[(C_6H_5)_3P\cdot HgX_2]_2$ (X = Cl, Br, or I) have been studied by Deacon and Green.[5,6] The replacement of halides by such potentially multidentate ligands as thiocyanate, nitrate, and perchlorate offer a number of interesting bonding possibilities.

This paper reports a study of the complexes formed between triphenylphosphine (TPP) or triphenylarsine (TPA) and mercury(II) thiocyanate, nitrate, or perchlorate. The structures of the solid complexes have been deduced from their stoichiometry, infrared spectra, and a comparison with previous investigations of the similar mercury(II) halide complexes.[4-6]

## Experimental Section

**Materials.**—All inorganic compounds were of reagent grade and were used as received. Triphenylphosphine was obtained from Matheson Coleman and Bell and was used without further purification. Triphenylarsine was purchased from Alfa Inorganics and was recrystallized from ethanol before use. All solvents were reagent grade.

**Analytical Procedures.**—Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

**Infrared Spectra.**—The infrared spectra were obtained with a Perkin-Elmer 521 spectrophotometer. The samples were prepared as Nujol mulls pressed between either KBr or AgCl plates.

**Preparation of Compounds.**—All the compounds reported in this paper were prepared by the same general method. TPP or TPA and the appropriate mercury(II) salt were allowed to react in either a 2:1 or a 1:1 molar ratio in the boiling solvent indicated in Table I. The only exception is the preparation of $(TPA)_2Hg(SCN)_2$, which required a 10% excess of TPA to give the required product. After boiling for several minutes, the reaction mixtures were cooled. The colorless crystals which appeared were filtered off and washed thoroughly with absolute ether to remove any unreacted ligand. The thiocyanate and nitrate complexes were air dried and used without further treatment. The $(TPP)_2Hg(ClO_4)_2$ and $(TPA)_2Hg(ClO_4)_2$ complexes were recrystallized from nitromethane. The $[(TPP)Hg(ClO_4)_2]_2$ and $[(TPA)Hg(ClO_4)_2]_2$ complexes were thoroughly washed with nitromethane to remove any contaminating 2:1 complex present. The melting points and analytical data for the various compounds prepared are summarized in Table I. Preparation of $[(TPP)Hg(SCN)_2]_2$ was repeated three times and the surprisingly low melting point was obtained each time. All of the compounds are stable in air.

*Caution!* On several occasions the TPP complexes of mercury(II) perchlorate exploded when heated above their melting points. The analogous TPA complexes merely decomposed slowly under the same conditions. All should be treated with caution, however.

## Results and Discussion

Class 1 compounds, prepared by the reaction of either triphenylphosphine or triphenylarsine with mercury(II) thiocyanate, nitrate, or perchlorate, in a 2:1 molar ratio, gave analyses consistent with the formulation

$$[(C_6H_5)_3E]_2HgX_2$$

1

where E = P or As and X$^-$ = SCN$^-$, NO$_3^-$, or ClO$_4^-$. Class 2 compounds were prepared by using a 1:1 molar ratio of $(C_6H_5)_3E$ to mercury(II) salt. Analyses of the products are consistent with the formulation

$$[(C_6H_5)_3E\cdot HgX_2]_2$$

2

The major infrared peaks of the compounds are recorded in Table II. Absorptions characteristic of triphenylphosphine or -arsine are not tabulated. Evans, *et al.*,[4] and Deacon and Green[5,6] have prepared analogous series of halide complexes. X-Ray crystallographic studies[4] and infrared studies[5,6] of these halide complexes have been interpreted in terms of class 1 com-

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[2] Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[3] Visiting Professor on leave from Ithaca College, 1967–1968. Now at East Stroudsburg State College, East Stroudsburg, Pa. 18301.

[4] R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940).

[5] G. B. Deacon and J. H. S. Green, *Spectrochim. Acta.*, **24A**, 845 (1968).

[6] G. B. Deacon, J. H. S. Green, and D. J. Harrison, *ibid.*, **24A**, 1921 (1968).

TABLE I

PREPARATION SOLVENTS AND ANALYTICAL DATA

| Compound | Prepn solvent | Mp, °C | Analyses % C Calcd | % C Found | % H Calcd | % H Found | % N Calcd | % N Found |
|---|---|---|---|---|---|---|---|---|
| $(TPP)_2Hg(SCN)_2$ | Acetone | 202–203 | 54.25 | 54.40 | 3.59 | 3.64 | 3.33 | 3.28 |
| $[(TPP)Hg(SCN)_2]_2$ | Acetone | 70 | 41.53 | 41.23 | 2.61 | 2.71 | 4.82 | 4.72 |
| $(TPA)_2Hg(SCN)_2$ | Ethanol | 122–124 | 49.15 | 49.13 | 3.24 | 3.20 | 2.98 | 2.98 |
| $[(TPA)Hg(SCN)_2]_2$ | Acetone | 129–131 | 37.95 | 38.20 | 2.38 | 2.44 | 4.92 | 4.31 |
| $(TPP)_2Hg(NO_3)_2$ | Methanol | 197–198 | 50.91 | 50.60 | 3.56 | 3.54 | 3.50 | 3.27 |
| $[(TPP)Hg(NO_3)_2]_2$ | Acetone | 175–177d | 36.83 | 36.59 | 2.58 | 2.66 | 4.76 | 4.57 |
| $(TPA)_2Hg(NO_3)_2$ | Methanol | 200–201 | 46.14 | 46.25 | 3.20 | 3.26 | 2.99 | 2.92 |
| $[(TPA)Hg(NO_3)_2]_2$ | Acetone | 172–174 | 34.27 | 34.88 | 2.38 | 2.43 | 4.45 | 4.35 |
| $(TPP)_2Hg(ClO_4)_2$ | Methanol | 190 explode | 46.90 | 46.10 | 3.27 | 3.77 | | |
| $[(TPP)Hg(ClO_4)_2]_2$ | Methanol | 189–190d | 32.67 | 32.96 | 2.28 | 2.79 | | |
| $(TPA)_2Hg(ClO_4)_2$ | Methanol | 208–210 dec | 43.18 | 42.90 | 2.98 | 3.01 | | |
| $[(TPA)Hg(ClO_4)_2]_2$ | Methanol | 186–188 | 30.63 | 31.49 | 2.14 | 2.51 | | |

TABLE II

INFRARED VIBRATIONAL FREQUENCIES (CM$^{-1}$) OF THIOCYANATES, NITRATES, AND PERCHLORATES OF CLASSES 1 AND 2

Thiocyanate

| | | |
|---|---|---|
| Class 1 | 2120 | 680 |
| Class 2 | 2130, 2100, 2080 | 760, 680 |

Perchlorate

| | | | |
|---|---|---|---|
| Class 1 | 1190 b, 1022 b | 912 | 618, 612 |
| Class 2 | 1120b, 1080 b, 1020 b | 906, 896 | 620, 616, 580 |

Nitrate

| | | | | |
|---|---|---|---|---|
| Class 1 | 1438, 1430, 1275, 1260 | 1017 | 810 | 750, 717 |
| Class 2 | 1495, 1477, 1415, 1400, 1275, 1252 | 1017 | 807, 800 | 750, 716, 702 |

pounds having structure A of Figure 1 and those of class 2 having structure B of Figure 1.

**Thiocyanate Complexes.**—The thiocyanate complexes of class 1 stoichiometry show a sharp absorption in the $\nu_{CN}$ region at 2120 cm$^{-1}$ and an absorption at 680 cm$^{-1}$ in the $\nu_{CS}$ region (Table II). These results may be interpreted in terms of Hg–SCN bonding.[7]

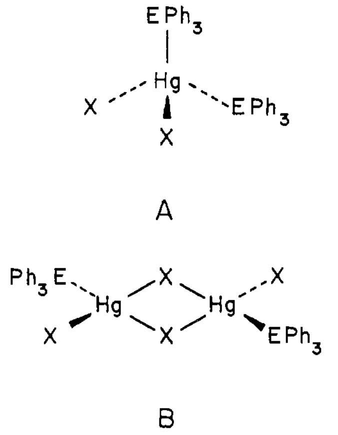

Figure 1.

The infrared spectral results and the stoichiometry of the class 1 thiocyanate complexes are consistent with structure A.

The infrared spectra of the class 2 thiocyanates show a considerable broadening and shifting to somewhat higher frequencies for the principal $\nu_{CN}$ band and the appearance of shoulders at 2100 and 2080 cm$^{-1}$. A new band also appears at about 760 cm$^{-1}$, in addition to the band at 680 cm$^{-1}$, in the CS stretching region. Although the $\nu_{CN}$ absorption of a bridging thiocyanate is usually found at frequencies higher than those displayed for monodentate thiocyanates,[7–10] a number of examples are known where the $\nu_{CN}$ absorption of a bridging thiocyanate appears at a relatively low frequency.[11,12] Other effects, such as coordination number, stereochemistry of the complex, and the character of the bonds may also affect the frequency of the $\nu_{CN}$ absorption.[11] The absence of high-frequency $\nu_{CN}$ absorptions, therefore, does not rule out the presence of bridging thiocyanates. The appearance of two absorptions in the $\nu_{CS}$ region further suggests the presence of two different kinds of thiocyanates in the class 2 complexes. We therefore conclude that the structure most compatible with both the stoichiometry and the infrared spectra of the class 2 thiocyanate complexes is structure B, with two Hg–SCN–Hg bridges and a thiocyanate bonded through sulfur on each mercury. Because of insolubility, neither the molecular weight in solution nor the conductivity could be determined.

**Perchlorate Complexes.**—The uncomplexed perchlorate ion of $T_d$ symmetry has two infrared-active modes: a very strong broad band at 1050–1170 cm$^{-1}$ and a weaker band at 630 cm$^{-1}$. Hathaway and Underhill[13] have shown that when the local symmetry of the perchlorate ion is lowered to $C_{3v}$, as in monodentate coordination, the two infrared-active bands each split into two components. When the perchlorate is bonded in a bidentate manner, its local symmetry is reduced to $C_{2v}$, and each of the infrared-active bands under $T_d$ symmetry is split into three components. Ross[14] has suggested that the splittings observed in the infrared spectra of some perchlorate compounds are attributable to lattice effects. We believe that the large splittings of the degenerate modes (Table II) and the intensity of the normally forbidden modes, under $T_d$ symmetry, cannot be simply explained by lattice effects and that the splittings are best interpreted in

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(7) (a) J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); (b) *ibid.*, **3**, 225 (1968), and references cited therein.

(8) J. Chatt and L. A. Duncanson, *Nature*, **178**, 997 (1956).

(9) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1416 (1961).

(10) P. G. Owston and J. M. Rowe, *Acta Cryst.*, **13**, 253 (1960).

(11) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(12) M. Nardell, G. F. Gasparri, A. Musatti, and A. Manfredotti, *Acta Cryst.*, **21**, 910 (1966).

(13) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(14) S. D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).

terms of coordination of the perchlorate to the metal.

The occurrence of two bands in the ~1100-cm$^{-1}$ region (1190 and 1022 cm$^{-1}$) and in the ~620-cm$^{-1}$ region (618 and 612 cm$^{-1}$) of the class 1 perchlorate complexes is thus consistent with the presence of monodentate perchlorate groups. The moderately intense band at 912 cm$^{-1}$ also indicates the presence of coordinated perchlorate. The class 1 perchlorate complexes may therefore be assigned structure A, consistent with their stoichiometry and infrared spectra.

The assignment of infrared bands for the class 2 perchlorate complexes is somewhat more difficult. If these compounds contain both monodentate and bridging perchlorates as in structure B, there will be two types of perchlorate local symmetry, $C_{3v}$ and $C_{2v}$. The observation of three bands in the ~1100-cm$^{-1}$ region (Table II) may be interpreted in terms of the presence of bridging bidentate perchlorate groups. The two bands originating from the monodentate perchlorates are probably overlapped by the bridging bidentate perchlorate bands. The totally symmetric stretch of the perchlorate ion, of $T_d$ symmetry, at about 935 cm$^{-1}$ is nondegenerate and normally infrared inactive. Therefore, even if the symmetry of the perchlorate groups was lowered to $C_{2v}$, only a single band should appear in the infrared spectrum in the 935-cm$^{-1}$ region. The occurrence of two bands at 896 and 906 cm$^{-1}$ indicates the presence of two different types of coordinated perchlorates in the class 2 complexes. The assignment of structure B to the class 2 perchlorates is thus consistent with their stoichiometry and infrared spectra. It should be noted, however, that a structure containing a monodentate and a bidentate perchlorate coordinated to a single mercury cannot be ruled out.

**Nitrate Compounds.**—The ionic nitrate group has four fundamental vibrations, three of which are infrared active at about 1400, 830, and 700 cm$^{-1}$. Coordination lowers the local symmetry of the nitrate with splitting of the 1400- and 700-cm$^{-1}$ bands into two components each. In addition, the normally infrared-inactive symmetric stretch (~1050 cm$^{-1}$) becomes active. Differentiation of mono- and bidentate nitrate bonding is usually possible only through Raman depolarization studies.[15]

The observation of four bands in the 1400-cm$^{-1}$ region, two bands in the 700-cm$^{-1}$ region, and a moderately intense band at 1017 cm$^{-1}$ in the infrared spectra of the class 1 nitrate compounds implies the presence of coordinated nitrate. Lattice effects can be ruled out on the bases of the large splittings in the 1400-cm$^{-1}$ region and the presence of the band at 1017 cm$^{-1}$. The presence of four bands in the 1400-cm$^{-1}$ region, instead of the two expected, may be attributed to vibration coupling between the two nitrate groups attached to mercury. The four bands may be divided into two groups. The bands at 1438 and 1430 cm$^{-1}$ may be assigned to the out-of-phase and in-phase $-NO_2$ asymmetric stretch vibrations, respectively. Those at 1275 and 1260 cm$^{-1}$ may be assigned, respectively, to out-of-phase and in-phase symmetric stretch vibrations. A similar effect was observed in a recent vibrational spectroscopic study of mercury(II) nitrate solutions.[16] The class 1 nitrate complexes are therefore assigned structure A consistent with their infrared spectra and stoichiometry. The same conclusion has been reached for the similar compound bis(pyridine)mercury(II) nitrate.[17]

The presence of two bands at 807 and 800 cm$^{-1}$, in the region where only a single nondegenerate band resulting from a nitrate out-of-phase deformation is expected, implies the presence of two kinds of nitrate in the molecule. In the compound $Ni(dien)(NO_3)_2$ a band at 816 cm$^{-1}$ has been assigned to monodentate nitrate, while a band at 807 cm$^{-1}$ has been assigned to bidentate nitrate.[18] The two bands in the class 2 nitrates are similarly assigned.

The presence of two types of nitrate is consistent with structure B if two of the nitrates act as bidentate bridges between mercury atoms and two others are bonded in a monodentate manner. This structure should result in the observation of six bands in the 1400-cm$^{-1}$ region, two due to monodentate nitrate and four due to bridging nitrate groups. The experimental results (Table II) are in agreement with this expectation. Unfortunately, the insolubility of the class 2 nitrates prevented a Raman depolarization study and a molecular weight determination. Therefore, an unbridged monomeric structure containing a monodentate and a bidentate nitrate cannot be ruled out.

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[15] R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, **5**, 1308 (1966).

[16] A. R. Davis and D. E. Irish, *ibid.*, **7**, 1699 (1968).

[17] J. I. Bullock and D. G. Tuck, *J. Chem. Soc.*, 1897 (1965).

[18] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

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# Correspondence

## Concerning Cation–Nitrate Ion Contact in Aqueous Solutions

*Sir:*

Recently Matwiyoff, *et al.*,[1] have obtained a hydration number of 6 for $Al^{3+}$ in $Al(NO_3)_3$ solutions by proton magnetic resonance spectroscopy. They therefore concluded that nitrate ion does not occupy the primary hydration sphere of $Al^{3+}$. They then suggested that this result is in disagreement with previous conclusions from Raman and infrared data. We wish to point out that our present understanding of the vibrational spectrum of aqueous nitrate solutions leads to a similar conclusion—*viz.*, that nitrate ion does not contact $Al^{3+}$ in aqueous solution.

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[1] N. A. Matwiyoff, P. E. Darley, and W. G. Movius, *Inorg. Chem.*, **7**, 2173 (1968).