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An Unexpected Stoichiometric Effect in both Solution and Solid State in Mercury-Rich Dithiocarbamate Cation Chemistry: Crystal and Molecular Structure of Polymeric Tris(piperidinecarbodithioato)dimercury(II) Perchlorate

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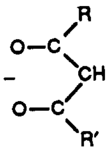
An unusual stoichiometric effect has been observed both in solution and in the solid state for mercury-rich cations derived from $Hg(RR'dtc)_2$ complexes (RR'dtc = dithiocarbamate) when the remote organic substituent is changed from two alkyl groups to one heterocyclic group. Polarographic and voltammetric studies have been carried out on dichloromethane (0.1 M Bu_4NClO_4) solutions of $Hg(pipdtc)_2$ (pip = piperidyl) at mercury electrodes. The product formed during the first oxidation process is shown to be $[Hg_4(pipdtc)_6]^{2+}$ or some multiple of this, and evaporation of the solution leads to the isolation of polymeric $[Hg_2(pipdtc)_3]ClO_4$. These are stoichiometries different from those of the products ($[Hg_3(Et_2dtc)_4]^{2+}$ and $[Hg_5(Et_2dtc)_8]^{2+}$) obtained under similar conditions from $Hg(Et_2dtc)_2$, so that merely varying the substituent on the dithiocarbamate ligand has the dramatic and highly unusual effect of changing the stoichiometry of the resulting mercury complexes in both phases. Crystal data for $[Hg_2(pipdtc)_3]ClO_4$: $M_r = 981.5$, monoclinic space group $P2_1/c$, $a = 9.743$ (2) Å, $b = 12.289$ (3) Å, $c = 24.618$ (4) Å, $\beta = 90.51$ (2)°, $Z = 4$, $\rho_{measd} = 2.21$ g cm^{-3}, Mo Kα radiation, $R = 0.070$, $R_w = 0.063$ for 2264 independent reflections. The crystal structure is composed of two parallel polymeric chains in the [0, 1, 0] direction, and the repeating unit of each chain is a pair of asymmetric $[Hg_2(pipdtc)_3]ClO_4$ units related by a center of symmetry at $(^1/_2, ^1/_2, 0)$. The environments of the unique mercury atoms Hg1 and Hg2 are very similar, apart from the weak coordination of the perchlorate ion to Hg2. Both are coordinated to four sulfur atoms at distances ranging from 2.36 to 2.92 Å, resulting in a grossly distorted tetrahedral configuration for both Hg1 and Hg2. Two dithiocarbamates of one type are chelated to one mercury atom with one of the sulfur atoms also bridging to another mercury atom, while the other type of dithiocarbamate ligand bridges between two mercury atoms.

Introduction

Substituent effects are an important feature of the chemistry of organic and inorganic compounds. In solution there are usually well-defined and predictable trends with varying substituents which can be correlated with Hammett, Taft, mesomeric, inductive, etc. parameters. For example, standard redox potentials in solution for a series of $M(RR'acac)_3$ complexes (RR'acac = substituted acetylacetonates, structure I) vary over a range of several volts on changing R and R' which can be correlated in a linear fashion with the Taft substituent parameter.[4] Similar observations have been made for organic molecules.[5] Dithiocarbamate complexes $M(RR'dtc)_x$ (x = 2 or 3; RR'dtc is shown in structure II) are particularly rich in examples of linear free energy relationships and other effects of substitution changes such as magnetic properties, NMR parameters, etc.[6] In all these cases in solution the compounds in a particular series have the same stoichiometry, and the free energy type relationships are due to electronic and steric effects within the homologous series.



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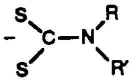
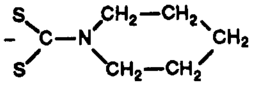


II

In contrast, in the solid state it is not unusual to observe different structures for complexes of the same stoichiometry, and indeed it is not uncommon for a particular compound to adopt more than one structure. Thus, it well-known that the structures of mercury dithiocarbamates, all of which have the stoichiometry $Hg(RR'dtc)_2$, display a rich variety of structures in which monomers, dimers, and various mercury stereochemistries are all apparent.[7] Indeed, the simple compound $Hg(Et_2dtc)_2$ is known to exist in at least three different structural forms.[7] These variations are usually ascribed to solid-state packing effects, and it is these factors that lead to the differences between the predictability of structures in solution and the unpredicability of structures in the solid state for a homologous series.

In a recent communication[8] we described the oxidation processes at a mercury electrode for $Hg(Et_2dtc)_2$ to give solutions containing $[Hg_3(Et_2dtc)_4]^{2+}$. The solid isolated from solutions was shown by X-ray crystallography to be $[Hg_5(Et_2dtc)_8](ClO_4)_2$ containing a polymeric cationic chain structure. In this paper we describe studies on $Hg(pipdtc)_2$ (pipdtc = piperidinecarbodithioate, structure III) whose electrochemical behavior in dichloromethane solution shows that a different-stoichiometry mercury-rich cation is produced and the solid product isolated from the solution is $[Hg_2(pipdtc)_3]ClO_4$. Thus the mere alteration of the remote organic substitutent of the ligand controls the *stoichiometry* of the complex in both solution and the solid state. This kind of substituent effect is unprecedented in metal dithiocarbmate chemistry.[6]



III

Experimental Section

Materials. All solvents and reagents used were of AR grade or better. The electrochemical supporting electrolyte tetrabutylammonium perchlorate, Bu_4NClO_4, was obtained wet with water from Southwestern Analytical and was dried under vacuum at 70 °C. Microanalyses were by AMDEL, Melbourne.

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Table I. Crystallographic Data for $[Hg_2(pipdtc)_3]ClO_4$

$C_{18}H_{30}O_4N_3S_6ClHg$	fw 981.5
$a = 9.743$ (2) Å	$P2_1/c$ (No. 14)
$b = 12.289$ (3) Å	$T = 22$ °C
$c = 24.618$ (4) Å	$\lambda = 0.71069$ Å
$\beta = 90.51$ (2)°	$\rho_{rho} = 2.21$, $\rho_{calcd} = 2.21$ g cm^{-3}
$V = 2947.4$ Å^3	$\mu = 108.9$ cm^{-1}
$Z = 4$	transm factors 0.2620–0.5204
$R\ (=\sum\Delta F/\sum F_o) = 0.070$	$R_w\ (=\sum w^{1/2}\Delta F/\sum w^{1/2}2F_o) = 0.063$

Preparations. (a) $Hg(pipdtc)_2$. This was prepared by a slight modification of the literature method[6a,b] by stirring 1:2 molar proportions of $Hg(NO_3)_2$ and Na[pipdtc] salt in water. The resulting precipitate was filtered, dried, and then purified by Soxhlet extraction into dichloromethane. The compound was characterized by its known mercury-199 NMR spectrum.[9-11]

Caution! Although we have experienced no difficulties with the compound prepared by the following methods, it should nevertheless be treated as a potentially explosive material and not be subjected to direct heat or sudden shock.

(b) $[Hg_2(pipdtc)_3]ClO_4$. Addition of solid $Hg_2(ClO_4)_2 \cdot 4H_2O$ (0.3 mmol) to a dichloromethane solution (30 cm^3) of $Hg(pipdtc)_2$ (0.9 mmol) with stirring for approximately 12 h resulted in a color change (yellow to pale yellow/green) and the deposition of elemental mercury. The solution was filtered and slow evaporation resulted in yellow/green crystals. Anal. Calcd for $[Hg_2(pipdtc)_3]ClO_4$: C, 22.0; H, 3.1; N, 4.3; S, 19.6. Found: C, 22.5; H, 3.9; N, 4.3; S, 20.4. This compound was also synthesized by oxidative controlled-potential electrolysis of a mercury electrode in the presence of $Hg(pipdtc)_2$ (see text).

Instrumentation. Polarographic measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyzer with a dropping-mercury electrode. For voltammetric experiments with a platinum rotating disk electrode either a Beckman or a Metrohm assembly was used. A platinum wire served as the auxiliary electrode, while the reference electrode was Ag/AgCl (CH_2Cl_2–saturated LiCl) separated from the test solution by a salt bridge. The $[(C_5H_5)_2Fe]^+/(C_5H_5)_2Fe$ (Fc^+/Fc) redox couple was measured frequently to report the potentials and to provide an internal check on the stability of the reference electrode. Unless otherwise stated, all measurements were made at 20 °C in dichloromethane (0.1 M Bu_4NClO_4).

Controlled-potential electrolysis experiments were performed at either a mercury-pool or a platinum-gauze working electrode with a PAR Model 173 potentiostat/galvanostat in conjunction with a Model 179 digital coulometer. The platinum-gauze auxiliary electrode was isolated from the test solution via a salt bridge, and the reference electrode was that used for voltammetry.

Crystal Structure Determination of $[Hg_2(pipdtc)_3]ClO_4$. Yellow platelike crystals of $[Hg_2(pipdtc)_3]ClO_4$, suitable for X-ray analysis, were grown by the slow evaporation of a solution produced by oxidative controlled-potential electrolysis of a dichloromethane solution (0.1 M NBu_4ClO_4) of $Hg(pipdtc)_2$ at 0.03 V vs Fc^+/Fc at a mercury-pool electrode. Oscillation and Weissenberg photographs showed that the crystals were monoclinic with systematic absences consistent with the space group $P2_1/c$. The details of the data collection and structure refinement are given in Table I. Accurate cell dimensions and crystal orientation matrix were obtained from the setting angles of 25 carefully centered reflections by using a least-squares procedure.[12] The intensity data were corrected for Lorentz, polarization, and absorption effects; absorption corrections[13,14] were numerically evaluated by Gaussian integration to a precision of 0.5%. No allowance was made for extinction. The mercury atoms were located by using the Patterson interpretation routine of the SHELXS-86 system,[15] and the positions of the remaining non-hydrogen atoms were found from subsequent difference maps. There was evidence of disorder for the perchlorate ion and the two piperidine rings, but difference electron density distributions calculated in the regions of the constituent atoms could not be resolved into their different components. The refinement was continued with the C–C and C–N bond distances initially constrianed to values of 1.54 and 1.47 Å, respectively, but the constraints were relaxed in the latter stages of the refinement. Anisotropic thermal parameters were employed for the Hg and S atoms whereas individual isotropic thermal parameters were used for the remaining non-hydrogen atoms. Evidence of all the hydrogen atoms was found in the difference map, and these were included at their geometrically calculated positions on the basis of a C–H bond distance of 1.08 Å. A common isotropic temperature factor was applied to all the methylene hydrogen atoms, which was included as a variable in the least-squares refinement. The values of R and R_w at convergence are given in Table I. The analysis of the variance showed no special features. Calculations were performed by using the SHELX-76 system[13] on a VAX 11/780 computer at the University of Melbourne, and crystallographic diagrams were obtained by using the ORTEP program.[16] Parameters for the atomic scattering curve of Hg were taken from ref 14 whereas for the remaining atoms those incorporated in SHELX-76[13] was used; anomalous dispersion corrections[14] were applied to the scattering factors for all non-hydrogen atoms.

Table II. Electrochemical Data for 5×10^{-4} M $Hg(pipdtc)_2$ Solutions in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C[a]

process	technique	measd param, V
1	CV at Hg	$E_p^{ox} = -1.05$ $E_p^{red} = -1.16$
2	CV at Pt	$E_p^{red} = -1.71$
	Pt RDE	$E_{1/2} = -1.45$
3	polarogram	$E_{1/2} = -0.05$
4	polarogram	$E_{1.2} = 0.08$

[a] Potential as volts vs Fc^+/Fc. CV = cyclic voltammetry; RDE = rotating disk electrode; E_p^{ox} = potential of the oxidation peak; E_p^{red} = potential of the reduction peak; $E_{1/2}$ = half-wave potential.

Results and Discussion

A. Solution Studies. The electrochemical techniques used to identify the species in solution following the oxidation process are identical with those previously described for the $Hg(Et_2dtc)_2$ system,[8] and reference may be made to that work for additional details. In that system the process of interest involves oxidation of the mercury electrode in the presence of $Hg(Et_2dtc)_2$

$$2Hg(Et_2dtc)_2 + Hg \rightleftharpoons [Hg_3(Et_2dtc)_4]^{2+} + 2e^- \qquad (1)$$

giving a one-electron process/mol of $Hg(Et_2dtc)_2$. The one-electron oxidation is time scale (polarography and bulk electrolysis) independent.

(a) Reduction of $Hg(pipdtc)_2$ at Mercury and Platinum Electrodes. Although oxidation processes involving $Hg(pipdtc)_2$ are the main concerns of this study, a knowledge of its electrochemical reduction contributes to the understanding of the procedures used to identify the products of the oxidation processes. The reduction behavior of $Hg(pipdtc)_2$ is very similar to that of $Hg(Et_2dtc)_2$ and all other mercury dithiocarbamates, which have been described in considerable detail,[8] so only a very brief description is given here. At mercury, an overall two-electron reversible process

$$Hg(RR'dtc)_2 + 2e^- \rightleftharpoons Hg + 2[RR'dtc]^- \qquad (2)$$

(process 1) is observed. At platinum, an irreversible two-electron reduction per molecule of $Hg(pipdtc)_2$ (process 2) is observed at a more negative potential than for process 1 for all concentrations. This reduction process is used as an internal standard in voltammetry to define the number of electrons involved in the oxidation processes. All electrochemical data for the $Hg(pipdtc)_2$ system are given in Table II.

(b) Electrochemical Oxidation at Mercury Electrodes in the Presence of $Hg(pipdtc)_2$. Dc polarograms (Figure 1a), differential-pulse polarograms, and cyclic voltammograms for the oxidation processes at a mercury electrode in the presence of a 5

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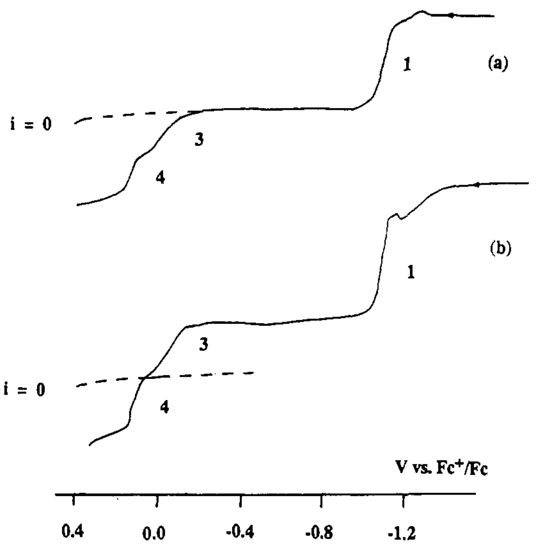

Figure 1. Current-sampled dc polarograms (drop time 0.5 s) at 20 °C for 5 × 10^{-4} M solutions of (a) $Hg(pipdtc)_2$ (b) $Hg(pipdtc)_2$ after oxidative electrolysis at a mercury-pool electrode.

× 10^{-4} M solution of $Hg(pipdtc)_2$ in dichloromethane (0.1 M NBu_4ClO_4) at 20 °C show two oxidation steps (processes 3 and 4), and cyclic voltammograms (not shown) indicate that both processes have considerable reversibility. The overall oxidation current is less than the limiting current of the known (standard) two-electron reduction process 1 and proceeds by two apparently 0.8-electron steps at this concentration. The overall oxidation limiting current is dependent upon concentration and tends toward a total of two electrons per molecule for extremely dilute solutions, indicating that the nature of the oxidation product varies with concentration under polarographic conditions. This is in contrast to the behavior of the $Hg(Et_2dtc)_2$ system,[8] in which both oxidation steps involve exactly one electron per molecule at all concentrations. This is the first indication of differences between the $Hg(Et_2dtc)_2$ and $Hg(pipdtc)_2$ systems in solution.

(c) Characterization of the Product of Oxidation. Oxidative controlled-potential electrolysis at 0.03 V vs Fc^+/Fc (between the two oxidation processes) at a mercury electrode in the presence of a 5 × 10^{-4} M dichloromethane solution (0.1 M NBu_4ClO_4) of $Hg(pipdtc)_2$ produces a pale yellow/green solution and results in the transfer of between 0.7 and 0.8 electron per molecule of $Hg(pipdtc)_2$, but the coulometry is difficult to quantify because the two oxidation steps are very close together. However, the number of electrons transferred per molecule in the first process is significantly less than 1. A polarogram for such an oxidized solution (Figure 1b) shows processes 1, 3, and 4, and the position of zero current bisects processes 3 and 4, confirming that the species produced by the oxidation process can be reduced to the starting material and that all processes are still chemically reversible. These observations are qualitatively the same as for the $Hg(Et_2dtc)_2$ system, but the quantitative aspects are different, since for $Hg(Et_2dtc)_2$ the oxidation step is a one-electron process on both voltammetric and bulk electrolysis experiments.

Figure 2 shows the reduction response at a platinum rotating disk electrode (RDE) for a solution of the oxidized product generated as above, and two reduction steps are observed. The processes result in the deposition of elemental mercury (identified from the stripping peak observed under conditions of cyclic voltammetry, not shown) from the mercury-rich species (process 5) and the reduction of $Hg(pipdtc)_2$ (process 1—reduction at a *mercury* electrode generated in situ by process 5), which is also released as a product of the first reduction (process 5) (see ref 8). The ratio of the wave heights is exactly 1:3, indicating that the deposition of 1 mol of mercury releases 3 mol of $Hg(pipdtc)_2$ and in addition no free $[pipdtc]^-$ is detected in solution. Thus, process 5 must correspond to eq 3, or some multiple of this

$$[Hg_4(pipdtc)_6]^{2+} + 2e^- \rightleftharpoons Hg + 3Hg(pipdtc)_2 \qquad (3)$$

equation. This result is in contrast to that for the $Hg(Et_2dtc)_2$ system in which *2* mol of $Hg(Et_2dtc)_2$ is released/mol of Hg in analogous experiments showing that in the diethyl system the mercury-rich cation is $[Hg_3(Etdtc)_4]^{2+}$ (reverse of eq 1).

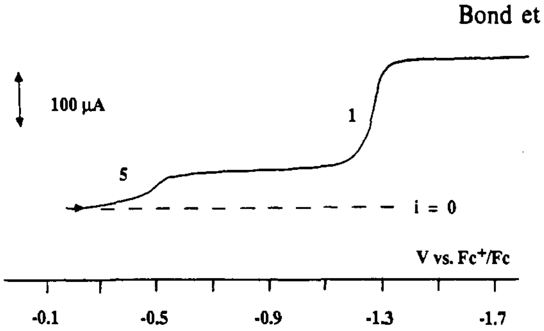

Figure 2. Voltammogram at a platinum rotating disk electrode (2000 rpm, scan rate 10 mV s^{-1}) at 20 °C for a dichloromethane solution (0.1 M Bu_4NClO_4) of $Hg(pipdtc)_2$ previously subjected to oxidative electrolysis at a mercury-pool electrode.

The stoichiometry of $[Hg_4(pipdtc)_6]^{2+}$ was confirmed by addition of dithiocarbamate anion to a solution of the mercury-rich species. Unfortunately, a pure, soluble salt of $[pipdtc]^-$ could not by synthesized with a cation that is electroinactive over the potential range of interest. Instead $[NBu_4][Et_2dtc]$ was used in the addition experiments, as previous studies have shown that mixtures of different mercury(II) dithiocarbamates are very labile and exchange rapidly, giving rise to a single reductive electrochemical response. For example, a 5 × 10^{-4} M solution of $Hg(Et_2dtc)_2$ gives a limiting current identical with that of an overall 5 × 10^{-4} M solution of a mixture of $Hg(Et_2dtc)_2$ and $Hg(pipdtc)_2$, although the potential is slightly different. After 2 molar equiv of $[Et_2dtc]^-$ is added to $[Hg_4(pipdtc)_6]^{2+}$, voltammograms show only a single response but with a wave height corresponding to a concentration four-thirds that of the original solution before oxidation. From these results, the first oxidation step at a mercury-pool electrode in the presence of $Hg(pipdtc)_2$ can be described by

$$3Hg(pipdtc)_2 + Hg \rightleftharpoons [Hg_4(pipdtc)_6]^{2+} + 2e^- \qquad (4)$$

That is, the oxidative reaction, which is actually oxidation of the mercury electrode in the presence of $Hg(pipdtc)_2$, involves a $^2/_3$-electron oxidation with respect to $Hg(pipdtc)_2$ and yields the mercury-rich cation $[Hg_4(pipdtc)_6]^{2+}$. The mercury-rich cation reacts with 2 mol of $[RR'dtc]^-$ to regenerate neutral mercury dithiocarbamate species of the type $Hg(RR'dtc)_2$ at a concentration four-thirds that of the original solution. That is, if $[RR'dtc]^-$ were pipdtc$^-$, then eq 5 would apply whereas if

$$[Hg_4(pipdtc)_6]^{2+} + 2[pipdtc]^- \rightleftharpoons 4Hg(pipdtc)_2 \qquad (5)$$

$[RR'dtc]^-$ were the $[Et_2dtc]^-$, then an equilibrium of neutral $Hg(pipdtc)_2$ (3 mol) and $Hg(Et_2dtc)_2$ (1 mol) would be formed. In this reaction no elemental mercury is released, thus ruling out the possibility of species containing proportionately more mercury than $[Hg(pipdtc)_6]^{2+}$. Therefore, the electrochemical evidence indicates that the oxidation process at a mercury-pool electrode in the presence of $Hg(pipdtc)_2$ produces a species with the empirical formula $[Hg_4(pipdtc)_6](ClO_4)_2$, which although still a mercury-rich polymeric species, is different from $[Hg_3(Et_2dtc)_4](ClO_4)_2$ produced in the $Hg(Et_2dtc)_2$ system. Nevertheless, despite the different stoichiometries of the polymeric cations, they show similar electrochemical responses in solution and similar reactivities with free $[RR'dtc]^-$, which is a reflection of the labile nature of the species in solution.

Hence, the remarkable result of this work is that, by merely changing the organic substituent on the dithiocarbamate ligand, one can alter the actual stoichiometry of the oxidized mercury-rich complex in solution. As a result of this observation, it seemed of interest to investigate whether the differences between the two systems persisted in the solid state.

B. Solid-State Studies. Evaporation of the electrochemically oxidized solution led to the isolation of small quantities of yel-

Table III. Fractional Atomic Coordinates for $[Hg_2(pipdtc)_3]ClO_4$[a]

	x	*y*	*z*
Hg1	0.45051 (12)	0.14634 (10)	0.02336 (4)
Hg2	0.55917 (13)	0.42335 (11)	0.06474 (4)
S1	0.3623 (9)	0.3756 (7)	0.1144 (4)
S2	0.5349 (8)	0.1733 (7)	0.1138 (3)
S3	0.3109 (7)	−0.0639 (6)	0.0204 (3)
S4	0.2982 (8)	0.1276 (6)	−0.0538 (3)
S5	0.7724 (7)	0.4371 (7)	0.0203 (3)
S6	0.5387 (7)	0.3584 (6)	−0.0486 (3)
N1	0.3573 (23)	0.2282 (18)	0.1904 (9)
N2	0.1699 (24)	−0.0588 (19)	−0.0726 (9)
N3	0.7966 (29)	0.3737 (23)	−0.0804 (11)
C1	0.4176 (25)	0.2516 (21)	0.1441 (10)
C2	0.3877 (31)	0.1224 (20)	0.2170 (11)
C3	0.4676 (31)	0.1446 (28)	0.2700 (11)
C4	0.3871 (37)	0.2243 (26)	0.3057 (13)
C5	0.3512 (35)	0.3298 (27)	0.2753 (12)
C6	0.2692 (28)	0.3012 (25)	0.2233 (11)
C7	0.2484 (26)	−0.0012 (22)	−0.0388 (10)
C8	0.1282 (26)	−0.0120 (26)	−0.1256 (10)
C9	−0.0292 (26)	−0.0119 (25)	−0.1272 (14)
C10	−0.0828 (33)	−0.1276 (25)	−0.1154 (11)
C11	−0.0308 (24)	−0.1722 (26)	−0.0607 (11)
C12	0.1266 (24)	−0.1720 (20)	−0.0620 (12)
C13	0.7112 (28)	0.3883 (23)	−0.0396 (11)
C14	0.0652 (32)	0.5755 (32)	0.0776 (19)
C15	−0.0366 (39)	0.6564 (32)	0.1020 (14)
C16	0.0070 (41)	0.6782 (36)	0.1611 (14)
C17	0.1513 (39)	0.7298 (36)	0.1609 (21)
C18	0.2533 (39)	0.6493 (34)	0.1364 (12)
Cl	0.1828 (13)	−0.3822 (11)	−0.2000 (5)
O1	0.2440 (39)	−0.4418 (33)	−0.1574 (16)
O2	0.1232 (47)	0.4459 (40)	−0.2359 (19)
O3	0.1467 (55)	−0.2759 (49)	−0.1997 (20)
O4	0.3007 (55)	−0.3538 (43)	−0.2235 (19)

[a] See note in the text regarding the C and N atoms of the piperidine rings.

low/green crystals. It was subsequently discovered that the same material could be synthesized in better yields by the interaction of $Hg(pipdtc)_2$ and mercurous perchlorate as described in the Experimental Section.

Description of the Structure of $[Hg_2(pipdtc)_3]ClO_4$. The crystal structure of $[Hg_2(pipdtc)_3]ClO_4$ is composed of two parallel polymeric chains, each of which extend infinitely in the [0, 1, 0] direction. Atoms of one chain are related to those of the other by a 2-fold screw axis. There are two mercury(II) atoms, three dithiocarbamate ligands, and one perchlorate group per asymmetric unit. The perchlorate anion is weakly associated with one mercury atom, Hg2, in contrast to the case of pentamercury species $[Hg_5(Et_2dtc)_8](ClO_4)_2$, in which the perchlorate anions are wholly ionic. The repeating unit of each chain is a pair of asymmetric $[Hg_2(pipdtc)_3]ClO_4$ units, related by a center of symmetry.

Figure 3a is an ORTEP[16] diagram showing the important features of $[Hg_2(pipdtc)_3]ClO_4$, together with the atomic numbering scheme. For clarity, the piperidine rings of the dithiocarbamate ligands and the perchlorate anions have been omitted. Figure 3b shows a similar view but includes all atoms. Only two carbon atoms of each unique piperidine ring are numbered in Figure 3b, such that the labels 2 and 6 identify the piperidine ring containing C2, C3, C4, C5, and C6. Positional parameters and important bond distances and bond angles are given in Tables III–V respectively.

The asymmetric units are linked together by an interesting arrangement of dithiocarbamate ligands, based around the two centers of symmetry at ($^1/_2$, $^1/_2$, 0) and ($^1/_2$, 0, 0) in the example shown in Figure 3a. As in the case of $[Hg_5(Et_2dtc)_8](ClO_4)_2$, simple bidentate chelation is not a feature of this structure.

The environments of the unique mercury atoms Hg1 and Hg2 are very similar, apart from the weak coordination of the perchlorate ion to Hg2. Both are coordinated to four sulfur atoms at distances ranging from 2.36 to 2.92 Å, resulting in a grossly distorted tetrahedral configuration for both Hg1 and Hg2. The distortions arise partly from the bite angle imposed by the chelated ligands (67.2 and 68.2° for Hg1 and Hg2, respectively) and partly from to a fifth mercury–sulfur contact at ~3.3 Å. If the fifth contact is taken into account, both mercury atoms could be regarded as having a distorted trigonal-bipyramidal geometry. The weak interaction of the perchlorate ion with Hg2 (Hg2′–O1 = 2.98 Å) causes only very slight distortion. A similar pentacoordinate environment has been observed for mercury in the

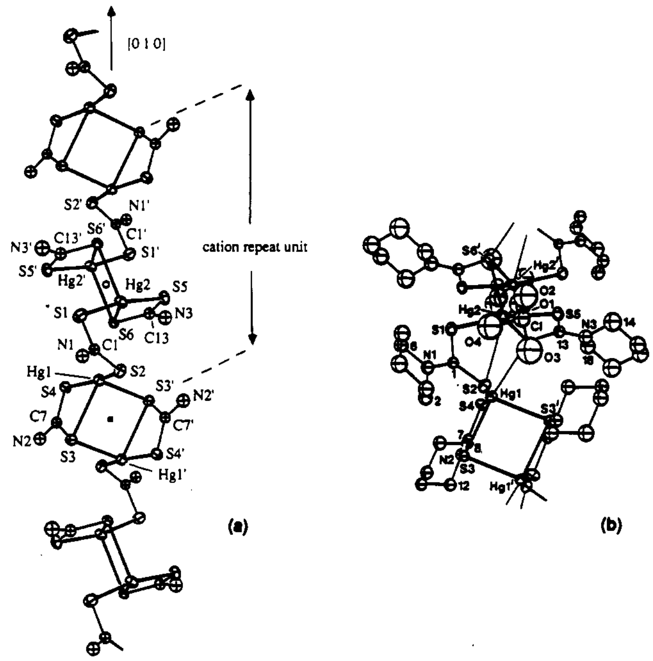

Figure 3. (a) View of the crystal structure of $[Hg_2(pipdtc)_3]ClO_4$ in the [0, 1, 0] direction, with the piperidine and perchlorate groups omitted for clarity. The centers of symmetry at ($^1/_2$, $^1/_2$, 0) and ($^1/_2$, 0, 0) are represented by ■ and ○, respectively. (b) Portion of the same view with all atoms included.

Table IV. Interatomic Distances (Å) for $[Hg_2(pipdtc)_3]ClO_4$

	(A) Hg–X Distances		
Hg1–S2	2.389 (7)	Hg2–S1	2.358 (8)
Hg1–S3	2.921 (7)	Hg2–S2	3.311 (8)
Hg1–S3′	2.763 (7)	Hg2–S5	2.362 (7)
Hg1–S4	2.411 (7)	Hg2–S6′	2.873 (8)
Hg1–S6	3.271 (8)	Hg2–S6	2.907 (8)
		Hg2–O1	2.98 (2)
	(B) Dithiocarbamate Bond Lengths		
	(i) Dithiocarbamate 1		
S1–C1	1.772 (26)	C3–C4	1.537 (10)
S2–C1	1.675 (25)	C4–C5	1.536 (10)
C1–N1	1.319 (27)	C5–C6	1.543 (10)
C2–N1	1.484 (10)	C6–N1	1.487 (10)
C2–C3	1.538 (10)		
	(ii) Dithiocarbamate 2		
S3–C7	1.753 (26)	C9–C10	1.543 (10)
S4–C7	1.697 (27)	C10–C11	1.537 (10)
C7–N2	1.329 (29)	C11–C12	1.534 (10)
C8–N2	1.481 (10)	C12–N2	1.478 (10)
C8–C9	1.534 (10)		
	(iii) Dithiocarbamate 3		
S5–C13	1.697 (28)	C15–C16	1.537 (10)
S6–C13	1.732 (28)	C16–C17	1.542 (10)
C13–N3	1.322 (31)	C17–C18	1.531 (10)
N3–C14	1.485 (10)	C18–N3	1.484 (10)
C14–C15	1.531 (10)		
	(C) Cl–O Bond Lengths		
Cl–O1	1.407 (39)	Cl–O3	1.353 (57)
Cl–O2	1.313 (48)	Cl–O4	1.337 (50)
	(D) Important Nonbonded Contacts		
Hg1···Hg1′	3.902 (2)	Hg2···Hg2′	3.709 (2)
Hg1···Hg2	3.872 (2)		

Table V. Interatomic Bond Angles (deg) for $[Hg_2(pipdtc)_3]ClO_4$

(A) S–Hg1–S Angles			
S2–Hg1–S6	107.7 (2)	S2–Hg1–S4	162.1 (2)
S2–Hg1–S3	107.6 (2)	S2–Hg1–S3′	97.5 (2)
S3–Hg1–S4	67.2 (2)	S3–Hg1–S3′	93.4 (2)
S3–Hg1–S6	144.6 (2)	S3′–Hg1–S4	99.9 (2)
S3′–Hg1–S6	81.8 (2)	S4–Hg1–S6	79.1 (2)
(B) S–Hg–S Angles			
S1–Hg2–S2	61.2 (3)	S1–Hg2–S5	168.7 (3)
S1–Hg2–S6	112.3 (3)	S1–Hg2–S6′	92.0 (3)
S2–Hg2–S5	107.5 (3)	S2–Hg2–S6	95.2 (2)
S2–Hg2–S6′	153.2 (2)	S5–Hg2–S6	68.2 (3)
S5–Hg2–S6′	99.3 (3)	S6–Hg2–S6′	95.9 (2)
(C) Hg1–S–X Angles			
Hg1–S2–C1	105.3 (9)	Hg1–S2–Hg2	79.3 (2)
Hg1–S3–C7	77.9 (9)	Hg1–S3–Hg1′	86.7 (2)
Hg1–S3′–C7′	97.1 (8)	Hg1–S3′–Hg1′	86.7 (2)
Hg1–S4–C7	95.3 (9)	Hg1–S6–Hg2	73.5 (2)
Hg1–S6–C13	110.9 (9)	Hg1–S6–Hg2′	137.0 (2)
(D) Hg2–S–X Angles			
Hg2–S1–C1	100.6 (9)	Hg2–S2–C1	71.3 (9)
Hg2–S5–C13	94.2 (9)	Hg2–S6–C13	76.0 (9)
Hg2–S6–Hg2′	84.0 (2)	Hg2–S6′–C13′	98.0 (9)
Hg2–S6′–Hg2′	84.0 (2)		
(E) Angles within the Ligand			
(i) Dithiocarbamate 1			
S1–C1–S2	121.1 (15)	N1–C2–C3	108.4 (24)
S1–C1–N1	114.1 (19)	C2–C3–C4	110.0 (26)
S2–C1–N1	124.8 (21)	C3–C4–C5	111.9 (28)
C1–N1–C2	118.9 (23)	C4–C5–C6	109.0 (27)
C1–N1–C6	127.1 (24)	C5–C6–N1	107.0 (23)
C2–N1–C6	113.8 (23)		
(ii) Dithiocarbamate 2			
S3–C7–S4	119.6 (2)	C8–C9–C10	109.6 (26)
S3–C7–N2	118.7 (2)	C9–C10–C11	112.6 (27)
S4–C7–N2	121.6 (2)	C10–C11–C12	107.6 (24)
C7–N2–C8	119.8 (2)	C11–C12–C13	107.0 (22)
C7–N2–C12	123.7 (24)	C12–N2–C8	116.4 (25)
N2–C8–C9	106.8 (24)		
(iii) Dithiocarbamate 3			
S5–C13–S6	121.4 (16)	C14–C15–C16	108.0 (34)
S5–C13–N3	117.4 (17)	C15–C16–C17	108.2 (35)
S6–C13–N3	119.4 (23)	C16–C17–C18	109.3 (35)
C13–N3–C14	118.9 (29)	C17–C18–N3	106.3 (32)
C13–N3–C18	121.9 (29)	C18–N3–C14	114.3 (32)
N3–C14–C15	107.4 (30)		
(F) ClO_4^- Angles			
O1–Cl–O2	112.0 (27)	O2–Cl–O3	117.8 (32)
O1–Cl–O3	127.3 (30)	O2–Cl–O4	104.0 (28)
O1–Cl–O4	95.7 (26)	O3–Cl–O4	88.6 (29)

polymeric chain structure of mercury methyl xanthate.[17] Long interactions are also a feature of the mercury coordination sphere in this structure.

For both unique mercury atoms, there are two short mercury–sulfur bond distances (2.36–2.41 Å) which are almost in a linear arrangement forming bond angles of 162.1 (2) and 168.7 (3)° for Hg1 and Hg2, respectively. In addition, there are two longer contacts (2.76–2.92 Å) which have been elongated due to sharing of the relevant sulfur atoms with the symmetrically related mercury atoms Hg1′ and Hg2′. Overall, both mercury environments show five S–Hg–S bond angles which deviate significantly from tetrahedral geometry, ranging from 67.2 to 168.7°, and one which approaches the ideal tetrahedral angle.

According to Lawton's classification,[18] Hg1 and Hg2 both clearly belong to the HgS_2 category of mercury atoms. The geometries of Hg1 and Hg2 are very similar to that found for Hg2 in $[Hg_5(Et_2dtc)_8](ClO_4)_2$ and indeed a range of mercury dithiolates.[18–22]

Hg1 is linked to Hg2 via a μ-bridging dithiocarbamate and by two long mercury–sulfur contacts involving the atoms S2 and S6. The asymmetric units are linked via two single sulfur bridges involving the centrosymmetrically related sulfur atoms S6 and S6′ and S3 and S3′. The S6 atom in fact bridges three mercury atoms, Hg1, Hg2, and Hg2′, and a similar feature is also observed in the structure of $[Hg_5(Et_2dtc)_8](ClO_4)_2$. Each pair of symmetry-related mercury atoms in $[Hg_2(pipdtc)_3]ClO_4$ forms part of an eight-membered ring-like structure consisting of two mercury, four sulfur, and two carbon atoms, which assumes a "chair" conformation. This linkage is very similar to the arrangement of mercury and sulfur atoms found in α-$Hg(Et_2dtc)_2$, which consists of isolated centrosymmetric $Hg_2(Et_2dtc)_4$ units.[19] The separation between the symmetry-related mercury atoms of $[Hg_2(pipdtc)_3]ClO_4$ is of the order of 3.9 Å, which is markedly greater than for similar atoms in $[Hg_5(Et_2dtc)_8](ClO_4)_2$ (3.26 Å). A slightly smaller separation is observed between the unique mercury atoms of $[Hg_2(pipdtc)_3]ClO_4$ (~3.7 Å).

The displacements of Hg1 and Hg2 from the planes of the chelated dithiocarbamate ligands are 0.19 and 0.15 Å, respectively. The dihedral angles between the planes of the chelated dithiocarbamate group and the plane passing through the mercury and two sulfur atoms belonging to each group are 1.4° (Hg2) and 2.3° (Hg1). A planar arrangement of S_2CN groups is observed, and the piperidine rings adopt a chair conformation. The C–N and C–S bond distances are very similar to those observed in $[Hg_5(Et_2dtc)_8](ClO_4)_2$ and are typical for coordinated dithiocarbamates.

Conclusions

While this work demonstrates that the formation of mercury-rich species is a general phenomenon when mercury undergoes oxidation processes in the presence of mercury(II) dithiocarbamates or by reaction of the mercury(II) dithiocarbamates with mercury(I), it shows that the stoichiometry of the species generated in solution depends upon the nature of the remote organic substituent of the dithiocarbamate ligand. This is a remarkable result, and as far as we are aware, it is unprecedented for variation of the R group to change the stoichiometry of a complex in dithiocarbamate chemistry.

We have found that the dibenzyldithiocarbamate and dicyclohexyldithiocarbamate systems exhibit behaviors that almost exactly parallel that of the diethyldithiocarbamate, even to the extent that crystallizations from $[Hg_3(Bz_2dtc)_4]^{2+}$ solutions give $[Hg_5(Bz_2dtc)_8]^{2+}$ in the solid state.[23] We have also found[23] that $Hg(morpholinecarbodithioate)_2$ behaves exactly the same as $Hg(pipdtc)_2$, so it appears to be the heterocyclic nature of the organic group on the dithiocarbamate that is responsible for the unusual differences in behavior. Changes in electronic and steric factors are likely to be important when a change is made from a dialkyl acyclic to a heterocyclic ligand system. For example, restriction of the C–N–C angle in the ring may occur in the cyclic system to limit the hybridization of the nitrogen and induce an electronic effect. However, a comparison of the bond distances and angles around the nitrogens in $[Hg_2(pipdtc)_3]^+$ and $[Hg_5(Et_2dtc)_5]^{2+}$ fails to reveal any significant differences although the disorder in the piperidyl complex may disguise this feature. Additionally, replacement of an acyclic ligand with a cyclic ligand considerably reduces the steric demand. However, the reasons for the different behaviors are clearly not simple steric factors when substituents as diverse as ethyl and cyclohexyl behave identically, so the factors that determine the exact nature of the oxidation products are not yet clear.

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Registry No. Hg(pipdtc)$_2$, 21439-62-3; CH_2Cl_2, 75-09-2; Bu_4NClO_4, 1923-70-2; Hg, 7439-97-6; Hg_2(pipdtc)$_3$]ClO_4, 130882-78-9; $Hg(NO_3)_2$, 10045-94-0; Na(pipdtc), 873-57-4; $Hg_2(ClO_4)_2$, 7616-83-3.

Supplementary Material Available: Tables S-I–S-V, listing experimental crystallographic details, hydrogen coordinates, anisotropic themal parameters for Hg and S, isotropic thermal parameters for C, N, O, and Cl, and equations of least-squares planes (7 pages); a listing of structure factor data (11 pages). Ordering information is given on any current masthead page.

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Association of a Methylplatinum Fluoroalkoxide Complex with a Fluoro Alcohol through O–H···O Hydrogen Bonding in the Solid State and in Solution

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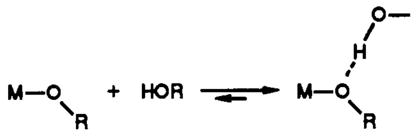
X-ray crystallography of *cis*-PtMe($OCH(CF_3)_2$)(PMe_3)$_2$($HOCH(CF_3)_2$) (**1**), which has been prepared by reaction of *cis*-PtMe($OCH(CF_3)_2$)(PMe_3)$_2$ (**2**) with 1,1,1,3,3,3-hexafluoro-2-propanol, reveals its molecular structure with square-planar coordination and association of the alkoxide ligand with the fluoro alcohol through O–H···O hydrogen bonding. Crystals of **1** are trigonal, space group $P3_1$, with $a = 9.347$ (6) Å, $c = 23.317$ (3) Å, and $Z = 3$. Structure calculation converged to $R = 0.089$ and $R_w = 0.111$ for 2397 reflections with $I \geq 3\sigma(I)$. The short distance between two oxygen atoms in the molecule (2.63 (5) Å) indicates the presence of O–H···O hydrogen bonding between the alkoxide ligand and the associated alcohol. Results of calorimetric titration of complex **2** with 1,1,1,3,3,3-hexafluoro-2-propanol in toluene solutions show formation of **1** as the exclusive adduct of **2** with the alcohol in the solution. Thermodynamic parameters for association, **2** + $HOCH(CF_3)_2 \rightleftarrows$ **1**, are obtained as $\Delta H° = -24.7$ kJ mol^{-1}, $\Delta S° = -46.0$ J mol^{-1} K^{-1}, and $\Delta G° = -10.9$ kJ mol^{-1} at 25 °C in toluene.

Introduction

Recent studies on alkoxide, aryloxide and hydroxide complexes of group 8–10 metals (Rh, Ru, Ni, Pd, and Pt) revealed their association with alcohols or water through O–H···O hydrogen bonding.[2–6]



(1)

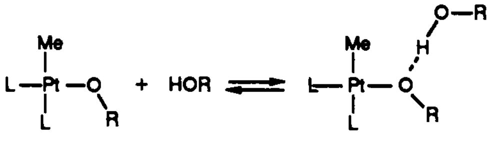
The above equilibrium in the solution is shifted to the right when R is an electron-withdrawing group such as aryl and fluorinated alkyl groups. Several complexes having the alcohol associated through O–H···O hydrogen bonding were isolated as crystals. Studies on chemical properties of these transition-metal alkoxides having hydrogen-bonded alcohol revealed that these compounds were involved as intermediates in associative exchange of the alkoxide group ligated to a late transition metal with alcohol in solution.[5b,7] Comparison of detailed features of the association through O–H···O hydrogen bonding is deemed worthwhile to understand the chemistry of the late-transition-metal alkoxides.

Table I. Crystal Data and Details of Refinement

formula	$C_{13}H_{24}F_{12}O_2P_2Pt_1$	*T*, °C	25
mw	697.35	λ, Å	0.71069
cryst size, mm	0.3 × 0.4 × 0.4	d_{calcd}, g cm^{-1}	1.967
cryst syst	trigonal	μ, cm^{-1}	62.49
space group	$P3_1$[a]	R	0.089
a, Å	9.347 (6)	R_w[b]	0.111
c, Å	23.317 (3)	no. of variables	220
V, Å^3	1767 (2)	no. of observns ($I > 3\sigma(I)$)	2397
Z	3		

[a] See Experimental Section for the determination of the space group. [b] $\omega = [\sigma(F_o)]^{-2}$.

Previously we reported that *cis*-PtMe($OCH(CF_3)_2$)(PMe_3)$_2$ (**2**) reacted with 1,1,1,3,3,3-hexafluoro-2-propanol to give a complex formulated as *cis*-PtMe($OCH(CF_3)_2$)(PMe_3)$_2$($HOCH(CF_3)_2$) (**1**).[5a] The IR spectrum of complex **1** (KBr disk) shows a broad peak due to ν(OH) at ca. 2800 cm^{-1}, suggesting formation of hydrogen bonding of the OH group in the associated alcohol with the ligated oxygen atom in the alkoxide ligand. The ^{1}H NMR spectrum of **1** at −40 °C in CD_2Cl_2 shows a signal at 8.2 ppm due to the OH hydrogen in the alcohol moiety. The exceptionally high chemical shift of the OH proton is also observed in the ^{1}H NMR spectra of the other transition-metal fluoroalkoxides having a hydrogen-bonded fluoro alcohol[3–5] and suggests that the equilibrium shown below is shifted toward the right in the solution.



(2)

2

L = PMe_3; R = $CH(CF_3)_2$

^{1}H NMR spectra of toluene-d_8 solutions of mixtures of **2** and 1,1,1,3,3,3-hexafluoro-2-propanol in various ratios were measured

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