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NMR studies of mercury 1,1-dithiolate tricyclohexylphosphine complexes. The crystal and molecular structure of $[Hg(S_2CNEt_2)(P(C_6H_{11})_3)(ClO_4)]_2 \cdot \sim 0.6CH_2Cl_2$

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Abstract

The crystal structure of $Hg(S_2CNEt_2)(P(C_6H_{11})_3)(ClO_4)$ shows a dimeric complex resulting from two bridging sulfur atoms linking two mercury atoms together. Each mercury atom is coordinated by three sulfur atoms, a phosphorus atom and an oxygen atom from a weakly coordinating perchlorate anion. The resulting coordination environment may be described as an irregular five-coordinate geometry. The crystals of $[Hg(S_2CNEt_2)(P(C_6H_{11})_3)(ClO_4)]_2$ are monoclinic, $P2_1/c$ (C^5_{2h}, No. 14), $a=13.726(4)$, $b=23.623(6)$, $c=20.256(6)$ Å, $\beta=108.36(3)°$, $Z=4$. ^{35}Cl NMR data show that in the complexes $Hg(S\text{-}S)(P(C_6H_{11})_3)(ClO_4)$ (S-S = S_2CNEt_2, S_2CO^iPr, $S_2P(O^iPr)_2$) the perchlorate anion is coordinated in dichloromethane solution at low temperature.

Introduction

We recently reported a study of tricyclohexylphosphine adducts of mercury 1,1-dithiolate cations [1] which indicated that the anion, A, is not involved in the coordination spheres of the 1:2 adducts, $Hg(S\text{-}S)(Pcyc_3)_2A$ (S-S = isopropylxanthate (ipxa), diisopropyldithiophosphate (ipdtp), diethyldithiocarbamate (edtc); $Pcyc_3$ = tricyclohexylphosphine; A = ClO_4^-, $CF_3SO_3^-$) in either solution or the solid state. In each case the mercury atom is only coordinated by the two tricyclohexylphosphine ligands and a chelating dithiolate which results in a monomeric four-coordinate complex. The ^{199}Hg and ^{31}P solution NMR data reported for the 1:1 adducts, $Hg(S\text{-}S)(Pcyc_3)A$, did not indicate whether the counter anion, A, was involved in the coordination sphere of the mercury atom.

This study has now been extended in order to provide further information on the nature of the 1:1 adducts. The crystal structure of $Hg(edtc)(Pcyc_3)(ClO_4)$ is reported in addition to further solution studies of the 1:1 adducts.

Experimental

$Hg(edtc)_2$ [2], $Hg(ipxa)_2$ [3], $Hg(ipdtp)_2$ [4] and $Hg(Pcyc_3)_2(ClO_4)_2$ [5] were prepared according to literature methods. $Hg(edtc)(Pcyc_3)(ClO_4)$ was prepared by mixing equimolar quantities of $Hg(edtc)_2$ and $Hg(Pcyc_3)_2(ClO_4)_2$ in dichloromethane. Crystals were obtained by slow evaporation of the solution.

NMR spectra were recorded on a JEOL FX100 spectrometer, ^{31}P at 40.26 MHz, ^{35}Cl at 9.70 MHz and ^{199}Hg at 17.76 MHz with external ^7Li lock. All spectra were proton decoupled. ^{31}P spectra were referenced against external 85% H_3PO_4; ^{35}Cl against external aqueous 0.25 M NaCl and ^{199}Hg against external 1.0 M phenylmercuric acetate in dmso. Temperatures were maintained by means of a JEOL NM 5471 temperature controller.

Crystallography

Data collection

Intensity data were collected with an Enraf-Nonius CAD-4F four circle, single crystal automatic diffractometer using Mo Kα (graphite monochromatized) radiation. Accurate cell dimensions were obtained by a least-squares procedure from the setting angles of 25

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reflections. The ω:2θ scan technique was employed to measure 12 802 reflections up to a maximum Bragg angle of 25°. Of these, 10 771 reflections were unique and 5239 satisfied the $I \geqslant 3\sigma(I)$ criterion of observability. Four reflections, which were measured every 3600 s of X-ray exposure time, showed a decrease in intensity of 12% during the data collection. The data were corrected in accordance with this variation in intensity and also for Lorentz, polarization and absorption [6] effects, however no corrections were made for extinction. Amalgamation of equivalent reflections led to an agreement factor, R_{amal}, of 0.039.

Crystal data

Formula $C_{46}H_{86}Cl_{12}Hg_2N_2O_8P_2S_4 \cdot 0.61CH_2Cl_2$, $M_r = 1509.3$, monoclinic, $P2_1/c$ (C_{2h}^5, *No.* 14), $a = 13.726(4)$, $b = 23.623(6)$, $c = 20.256(6)$ Å, $\beta = 108.36(3)°$, $U = 6234$ Å^3, $D_m = 1.62$ g cm^{-3}, $Z = 4$, $D_c = 1.608$ g cm^{-3} (based on an average of 2.42 molecules of dichloromethane per unit cell), $F(000) = 3010.8$, $\mu = 5.24$ mm^{-1}, absorption corrections applied, maximum and minimum transmission factors 0.4069 and 0.1356, crystal dimensions $\pm(0\,0\,1)$ 0.27, $\pm(0\,2\,1)$ 0.22, $\pm(1\,0\,0)$ 0.09, $\pm(0\,2\,-1)$ 0.21 mm.

Structure determination

The structure was solved by normal heavy atom methods and refined by a blocked-matrix least-squares procedure in which the function $\Sigma w\Delta^2$ was minimized where $\Delta = \|F_o| - |F_c\|$ and w was the weight applied to each reflection. Anisotropic thermal parameters were assigned to all non-hydrogen atoms of the complex. The difference maps indicated the presence of chlorine atoms from two unique dichloromethane molecules which were both disordered across centres of symmetry. Only the chlorine atoms could be located and each of these was assigned an isotropic temperature factor and a site occupation factor both of which were allowed to vary in the refinement procedure. This resulted in an average of 2.42 molecules of dichloromethane per unit cell. No hydrogen atoms could be located unambiguously in the final difference map and therefore hydrogen atoms were not included in the model. A weighting scheme of the type $w = k[\sigma^2(F) + gF^2]^{-1}$ was included in the final cycles of refinement. Both k and g were redetermined after each refinement process. At convergence k, g, R and R_w were 2.1197, 0.0003, 0.058 and 0.057, respectively. The maximum shift/e.s.d. was 0.04. The maximum residual electron density, which was close to the mercury atom, was 1.93 e Å^{-3}. An analysis of variance showed that a satisfactory weighting scheme had been employed. The SHELXS-86 [7] and SHELX-76 [6] programs were used on the University of Melbourne's VAX11/8650 and 11/780 computer systems. The scattering factors for atomic Hg (corrected for $\Delta f'$ and $\Delta f''$) were taken from ref. 8 and those for the remaining atoms were those incorporated in SHELX-76 [6].

The final fractional atomic coordinates and their estimated standard deviations are listed in Table 1. Significant bond lengths and angles are given in Table 2. The atomic numbering scheme is shown in Fig. 1. See also 'Supplementary material'.

Results

NMR studies

The ^{35}Cl nucleus is quadrupolar and as a result the resonance is generally too broad to observe unless the chlorine atom is in a highly symmetrical environment such as exists in the uncoordinated perchlorate anion. For example the ^{35}Cl NMR spectrum of a dichloromethane solution of tetrabutylammonium perchlorate shows a single resonance with a width at half height ($w_{1/2}$) < 10 Hz whilst there is no observable resonance for the chlorine atoms in the solvent. Coordination of the perchlorate anion in Hg(S-S)(Pcyc$_3$)(ClO$_4$) complexes would reduce the symmetry around the chlorine atom thereby causing broadening of the ^{35}Cl resonance. Thus the ^{35}Cl resonance may be employed as a probe which is sensitive to any coordination interactions of the perchlorate anion in solution [9].

The ^{35}Cl NMR spectrum of a dichloromethane solution of Hg(edtc)(Pcyc$_3$)(ClO$_4$) recorded at 20 °C shows a single resonance with a $w_{1/2}$ of 100 Hz. As the solution is cooled the resulting resonance broadens until at −95 °C the resonance is too broad to observe. The temperature dependence of this resonance may be interpreted in terms of the following exchange equilibrium

$$[\mathrm{Hg(edtc)(Pcyc_3)}]^+ + (\mathrm{ClO_4})^- \rightleftharpoons \mathrm{Hg(edtc)(Pcyc_3)(ClO_4)}$$

The observed ^{35}Cl resonance will represent a time average of the coordinated and uncoordinated perchlorate anions depending upon the position of the equilibrium. Lowering the temperature most likely moves the equilibrium to the right and this would cause coordinated perchlorate to make a greater contribution to the time average resonance resulting in broadening of the resonance. Alternatively the temperature dependent behaviour of the ^{35}Cl resonance may be a consequence of the rate of exchange of the perchlorate in the above equilibrium slowing on the NMR time scale with decreasing temperature. Both explanations require that a substantial amount of the coordinated perchlorate species is present in solution at low temperature. To ensure that the resonance width of the free perchlorate anion showed no temperature depen-

TABLE 1. Final fractional atomic coordinates for $[Hg(edtc)(Pcyc_3)(ClO_4)]_2 \cdot \sim 0.6CH_2Cl_2$ (e.s.d. values are in parentheses)

Atom	*x*	*y*	*z*
Hg(1)	0.03324(5)	0.08930(3)	0.22695(4)
Hg(2)	−0.23509(5)	0.17664(3)	0.18794(4)
S(1)	−0.0551(3)	0.1561(2)	0.3066(2)
S(2)	−0.2622(3)	0.1025(2)	0.2629(2)
C(1)	−0.141(1)	0.1077(6)	0.3214(8)
N(1)	−0.111(1)	0.0735(5)	0.3776(7)
C(2)	−0.007(1)	0.0737(7)	0.427(1)
C(3)	0.002(2)	0.1165(8)	0.4848(9)
C(4)	−0.189(1)	0.0344(7)	0.3914(9)
C(5)	−0.177(2)	−0.0239(8)	0.364(1)
S(3)	−0.1408(3)	0.1162(2)	0.1081(2)
S(4)	−0.0874(3)	0.0115(2)	0.1968(3)
C(6)	−0.172(1)	0.0461(6)	0.1236(9)
N(2)	−0.250(1)	0.0187(6)	0.0832(8)
C(7)	−0.275(2)	−0.0397(7)	0.088(1)
C(8)	−0.348(2)	−0.0413(8)	0.136(1)
C(9)	−0.322(1)	0.0487(8)	0.023(1)
C(10)	−0.285(2)	0.042(1)	−0.040(1)
P(1)	0.1958(3)	0.1324(2)	0.2388(2)
C(11)	0.218(1)	0.1825(7)	0.314(1)
C(12)	0.238(1)	0.1514(8)	0.3823(9)
C(13)	0.239(2)	0.1957(9)	0.438(1)
C(14)	0.326(2)	0.240(1)	0.448(1)
C(15)	0.316(2)	0.2696(9)	0.379(2)
C(16)	0.307(2)	0.2269(8)	0.314(1)
C(17)	0.298(1)	0.0765(7)	0.2605(8)
C(18)	0.263(1)	0.0244(7)	0.215(1)
C(19)	0.355(2)	−0.0210(9)	0.244(1)
C(20)	0.451(2)	−0.001(1)	0.235(1)
C(21)	0.485(1)	0.052(1)	0.282(2)
C(22)	0.400(1)	0.1020(8)	0.254(1)
C(23)	0.188(1)	0.1699(7)	0.1569(9)
C(24)	0.107(1)	0.2197(8)	0.150(1)
C(25)	0.094(2)	0.2510(9)	0.078(1)
C(26)	0.058(2)	0.209(1)	0.016(1)
C(27)	0.139(2)	0.1611(9)	0.025(1)
C(28)	0.157(1)	0.1273(8)	0.0957(9)
P(2)	−0.2811(3)	0.2693(2)	0.1383(3)
C(29)	−0.188(1)	0.3219(6)	0.1909(9)
C(30)	−0.184(1)	0.3201(8)	0.267(1)
C(31)	−0.106(2)	0.361(1)	0.309(1)
C(32)	0.001(2)	0.345(1)	0.309(1)
C(33)	0.004(1)	0.3479(8)	0.234(1)
C(34)	−0.078(1)	0.3051(7)	0.186(1)
C(35)	−0.411(1)	0.2868(6)	0.139(1)
C(36)	−0.435(1)	0.3508(7)	0.129(1)
C(37)	−0.547(2)	0.363(1)	0.128(2)
C(38)	−0.561(2)	0.342(1)	0.195(2)
C(39)	−0.546(2)	0.2769(9)	0.197(2)
C(40)	−0.433(1)	0.2622(8)	0.203(1)
C(41)	−0.268(2)	0.2705(8)	0.0486(8)
C(42)	−0.350(2)	0.2259(9)	0.003(1)
C(43)	−0.334(2)	0.224(1)	−0.073(1)
C(44)	−0.342(2)	0.282(1)	−0.104(1)
C(45)	−0.250(3)	0.313(1)	−0.049(2)
C(46)	−0.282(3)	0.326(1)	0.018(1)
Cl(1)	0.1917(5)	−0.0195(2)	0.4002(4)
O(1)	0.132(2)	0.0093(7)	0.3400(8)
O(2)	0.221(1)	0.0220(6)	0.4564(9)
O(3)	0.276(1)	−0.0466(7)	0.388(1)
O(4)	0.131(1)	−0.0585(7)	0.4192(9)
Cl(2)	−0.5346(4)	0.1245(2)	0.0709(3)
O(5)	−0.534(1)	0.1319(7)	−0.0007(9)
O(6)	−0.437(1)	0.1294(7)	0.1176(9)
O(7)	−0.596(2)	0.1647(8)	0.088(1)
O(8)	−0.577(2)	0.0711(7)	0.076(1)
Cl(3)	0.492(1)	0.0523(7)	0.4714(9)
Cl(4)	0.986(2)	0.468(1)	0.449(1)

TABLE 2. Significant bond lengths (Å) and angles (°) for $[Hg(edtc)(Pcyc_3)(ClO_4)]_2 \cdot \sim 0.6CH_2Cl_2$ (e.s.d. values are in parentheses)

Hg(1)–S(1)	2.792(5)	Hg(1)–S(3)	2.878(4)
Hg(1)–S(4)	2.420(4)	Hg(1)–P(1)	2.395(4)
Hg(1)–O(1)	2.95(2)	Hg(2)–S(1)	2.894(4)
Hg(2)–S(2)	2.422(5)	Hg(2)–S(3)	2.765(5)
Hg(2)–P(2)	2.409(4)	Hg(2)–O(6)	2.91(1)
S(1)–C(1)	1.74(2)	S(2)–C(1)	1.72(1)
C(1)–N(1)	1.35(2)	N(1)–C(2)	1.46(2)
N(1)–C(4)	1.51(2)	C(2)–C(3)	1.52(3)
C(4)–C(5)	1.51(3)	S(3)–C(6)	1.76(2)
S(4)–C(6)	1.77(2)	C(6)–N(2)	1.30(2)
N(2)–C(7)	1.43(2)	N(2)–C(9)	1.49(2)
P(1)–C(11)	1.88(2)	P(1)–C(17)	1.88(2)
P(1)–C(23)	1.85(2)	P(2)–C(29)	1.86(2)
P(2)–C(35)	1.84(2)	P(2)–C(41)	1.88(2)
Cl(1)–O(1)	1.41(2)	Cl(1)–O(2)	1.46(2)
Cl(1)–O(3)	1.41(2)	Cl(1)–O(4)	1.38(2)
Cl(2)–O(5)	1.46(2)	Cl(2)–O(6)	1.38(1)
Cl(2)–O(7)	1.38(2)	Cl(2)–O(8)	1.41(2)
S(1)–Hg(1)–S(3)	87.8(1)	S(1)–Hg(1)–S(4)	100.8(2)
S(1)–Hg(1)–P(1)	105.2(1)	S(1)–Hg(1)–O(1)	95.2(3)
S(3)–Hg(1)–S(4)	68.6(1)	S(3)–Hg(1)–P(1)	119.4(1)
S(3)–Hg(1)–O(1)	148.0(4)	S(4)–Hg(1)–P(1)	152.9(2)
S(4)–Hg(1)–O(1)	79.6(4)	P(1)–Hg(1)–O(1)	90.5(4)
S(1)–Hg(2)–S(2)	67.5(1)	S(1)–Hg(2)–S(3)	88.0(1)
S(1)–Hg(2)–P(2)	122.8(1)	S(1)–Hg(2)–O(6)	140.8(4)
S(2)–Hg(2)–S(3)	100.7(1)	S(2)–Hg(2)–P(2)	147.9(2)
S(2)–Hg(2)–O(6)	73.7(4)	S(3)–Hg(2)–P(2)	109.5(2)
S(3)–Hg(2)–O(6)	93.7(4)	P(2)–Hg(2)–O(6)	93.4(3)
Hg(1)–S(1)–Hg(2)	91.6(1)	Hg(1)–S(3)–Hg(2)	92.5(1)
Hg(1)–S(1)–C(1)	99.8(6)	Hg(2)–S(1)–C(1)	78.8(5)
Hg(2)–S(2)–C(1)	94.3(6)	S(1)–C(1)–S(2)	119.4(9)
S(1)–C(1)–N(1)	120(1)	S(2)–C(1)–N(1)	121(1)
Hg(1)–S(3)–C(6)	80.1(5)	Hg(2)–S(3)–C(6)	101.3(6)
S(3)–C(6)–S(4)	116.8(8)	S(3)–C(6)–N(2)	124(1)
S(4)–C(6)–N(2)	119(1)	Hg(1)–P(1)–C(11)	104.9(6)
Hg(1)–P(1)–C(17)	109.2(5)	Hg(1)–P(1)–C(23)	108.9(5)
C(11)–P(1)–C(17)	109.6(7)	C(11)–P(1)–C(23)	112.0(8)
C(17)–P(1)–C(23)	112.0(9)	Hg(2)–P(2)–C(29)	109.0(5)
Hg(2)–P(2)–C(35)	109.2(5)	Hg(2)–P(2)–C(41)	108.9(9)
C(29)–P(2)–C(35)	109.8(7)	C(29)–P(2)–C(41)	106.6(9)
C(35)–P(2)–C(41)	113.1(9)	Hg(1)–O(1)–Cl(1)	168(1)
Hg(2)–O(6)–Cl(2)	160(1)		

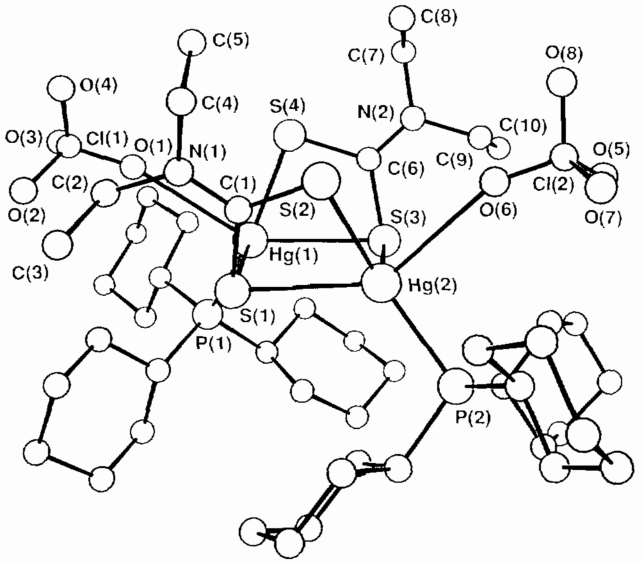

Fig. 1. The structure of [Hg(edtc)(Pcyc$_3$)(ClO$_4$)]$_2$ showing the numbering scheme.

dence, the ^{35}Cl NMR spectrum of tetrabutylammonium perchlorate was recorded at temperatures in the range 20 to −95 °C. The resulting resonance remained sharp over this temperature range.

Although the analogous isopropylxanthate and diisopropyldithiophosphate complexes could not be isolated, they were prepared *in situ* by mixing equimolar quantities of Hg(S-S)$_2$ and Hg(Pcyc$_3$)$_2$(ClO$_4$)$_2$. Variable temperature ^{35}Cl NMR spectra yielded similar results to those obtained for Hg(edtc)(Pcyc$_3$)(ClO$_4$) indicating that here also, the perchlorate anion is coordinated to the mercury atom at low temperatures.

In an effort to provide further confirmation of the perchlorate–cation interaction a mole equivalent of NEt$_4$Cl was added to the Hg(edtc)(Pcyc$_3$)(ClO$_4$) solution. The ^{35}Cl NMR spectrum recorded at room temperature shows a sharp resonance (δ ^{35}Cl 1006 ppm, $w_{1/2} \sim 5$ Hz) which broadened only marginally as the temperature was lowered to −90 °C (δ ^{35}Cl 1005 ppm, $w_{1/2} \sim 10$ Hz). No resonance for free chloride ion was observed. These results indicate that the weak perchlorate–cation interaction can be completely disrupted through the introduction of a more strongly coordinating anion.

Similarly, the perchlorate coordination can be reduced if dichloromethane is replaced by a solvent with a larger coordinating potential. When dimethylformamide is used as a solvent the ^{35}Cl resonance of the perchlorate remains sharp even when the temperature is lowered to −60 °C. Similar results were obtained when dimethyl sulfoxide was added to a dichloromethane solution of the complex. As indicated in Table 3 the addition of either chloride ion or a coordinating solvent to solutions of Hg(S-S)(Pcyc$_3$)A is accompanied by relatively large changes in the ^{199}Hg resonance and the ^{199}Hg–^{31}P coupling constants. These changes represent significant differences in the coordination sphere of the mercury atom, through the interaction of the chloride ion or solvent molecules.

Description of the structure

The complex is dimeric with two dithiocarbamate ligands bridging two mercury atoms as shown in Fig. 1. Each mercury atom is coordinated by three sulfur atoms from two dithiocarbamate ligands, a phosphorus atom from the tricyclohexylphosphine ligand and an oxygen atom from a weakly coordinating perchlorate anion.

A four-membered ring is formed by the two mercury atoms and the two bridging sulfur atoms. The formation of similar four-membered mercury–sulfur rings has been observed in the dimeric complex, Hg(edtc)$_2$ [2] and the polymeric complex Hg$_2$(pipdtc)$_3$(ClO$_4$) (pipdtc = S$_2$CN(CH$_2$)$_5$) [10]. The complex Hg$_5$(edtc)$_8$(ClO$_4$)$_2$ [11] also contains such rings but the sulfur bridges are quite weak. In contrast the mercury–sulfur bonds of the ring in [Hg(edtc)(Pcyc$_3$)(ClO$_4$)]$_2$ are of similar length. An interesting difference between [Hg(edtc)(Pcyc$_3$)(ClO$_4$)]$_2$ and the other complexes displaying the four-membered rings is that the dithiocarbamate ligands reside on the same side of the ring resulting in a ‘boat-like’ configuration being adopted by the two dithiocarbamate ligands and the Hg$_2$S$_2$ plane. The adoption of this configuration is believed to be a consequence of the bulky nature of the tricyclohexylphosphine ligand. In a ‘chair’ conformation large steric effects could be envisaged between the tricyclohexylphosphine ligand and the alkyl groups of the dithiocarbamate, whereas in a boat conformation the tricyclohexylphosphine ligands are diagonally opposite and orientated away from each other.

Each of the mercury atoms is bound to five donor atoms which form an irregular five-coordinate geometry. Hg(1) lies very close (0.1318(8) Å) to a plane defined by atoms P(1), S(1) and S(4). The donor atom set is completed by O(1) and S(3) which are situated on either side of the plane. Hg(2) is in a very similar environment and is displaced by 0.1792(7) Å from a plane passing through atoms P(2), S(2) and S(3). Atoms O(6) and S(1) are located on either side of the plane.The non-bridging sulfur atoms and the phosphorus atoms form bonds to the mercury centres (Hg(1)–S(4) 2.420(4) Å, Hg(1)–P(1) 2.395(4) Å, Hg(2)–S(2) 2.422 Å, Hg(2)–P(2) 2.409(4) Å) which are much shorter than the sum of the tetrahedral covalent radii for the respective atoms (Hg–P 1.48 + 1.10 = 2.58 Å, Hg–S 1.48 + 1.04 = 2.52 Å) [12]. As would be expected the Hg–S bond lengths of the bridging sulfur atoms are considerably longer (2.765(5)–2.894(4) Å.

TABLE 3. NMR data for the Hg(S-S)(Pcyc$_3$)(ClO$_4$) complexes

Solution	Solvent	Temperature (°C)	δ ^{31}P (ppm)	δ ^{199}Hg (ppm)	J(^{199}Hg–^{31}P) (Hz)	δ ^{35}Cl (ppm)	^{35}Cl $w_{1/2}$ (Hz)
Hg(edtc)(Pcyc$_3$)(ClO$_4$)	DCM	20	69.8[a]	593d[a]	5330[a]	1006	~100
	DCM	−90	64.7[a]	632d[a]	5435[a]		
	DMF	20	67.5	460d	5723	1007	<5
	DMF	−60	65.4	462d	5816	1005	<10
Hg(edtc)(Pcyc$_3$)(ClO$_4$)+2 DMSO	DCM	20	67.3	497d	5747	1006	<10
	DCM	−90	65.7	514d	5766	1005	<10
Hg(edtc)(Pcyc$_3$)(ClO$_4$)+NEt$_4$Cl	DCM	20	58.5	661d	5840	1006	<5
	DCM	−90	65.7	686d	5913	1005	<10
Hg(ipxa)(Pcyc$_3$)(ClO$_4$)	DCM	20	73.0[a]	355d[a]	5075[a]	1006	~100
	DCM	−80	69.6[a]	365d[a]	5300[a]		
Hg(ipdtp)(Pcyc$_3$)(ClO$_4$)	DCM	20	73.6, 96.0[a]	487d[a]	5410[a]	1003	~100
		−80	75.7, 96.7[a]	488d[a]	5550[a]		

DCM = dichloromethane; DMF = dimethylformamide; DMSO = dimethyl sulfoxide; d = doublet. [a]From ref. 1.

The two mercury–oxygen distances (2.91(1) and 2.95(2) Å) are only marginally shorter than Bondi's estimation of the sum of the van der Waals radii [13] (3.02 Å) and indicate weak coordination of the perchlorate anion. This interaction is further supported if the van der Waals radii of mercury is 1.73 Å as claimed by Canty and Deacon [14]. This yields a sum for the van der Waals radii of 3.25 Å. The persistence of this interaction in solution as demonstrated by the ^{35}Cl NMR data confirms that the cation–anion interaction, although weak, is significant and that the oxygen–mercury separation is not merely a consequence of fortuitous packing. The coordination of the perchlorate anions, despite their weak donor strength, suggests that the dithiocarbamate and tricyclohexylphosphine ligands are unable to satisfy the Lewis acidity of the mercury atom. Similar coordination of the perchlorate anions has been observed in other mercury complexes where there are sufficient strong donor atoms, e.g. Hg(Pcyc$_3$)$_2$(ClO$_4$)$_2$ [15] and Hg$_2$(pipdtc)$_3$(ClO$_4$) [10].

Despite the rather novel general structure, the geometries of the individual ligands including the perchlorate anions are normal.

Conclusions

Whereas the cationic complexes Hg$_2$(pipdtc)$_3$(ClO$_4$) [10] and Hg$_5$(edtc)$_8$(ClO$_4$)$_2$ [11] display extensive dithiocarbamate bridging, the presence of tricyclohexylphosphine reduces the extent of dithiocarbamate bridging resulting in the formation of a dimer for the 1:1 phosphine adduct and a monomer for the 1:2 phosphine adduct. The disruption of 1,1-dithiolate bridging is also observed when suitable Lewis bases are added to the Group IIb metal bisxanthates to form adducts [16–19].

Supplementary material

Full lists of bond lengths and angles, atomic thermal parameters, equations of mean planes and the observed and calculated structure factors are available from the authors on request.

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