Lewis-base Adducts of Lead(II) Complexes. Part 6.[1] X-Ray Structural Characterisation of Adducts of Lead(II) Bis(perchlorate) with Dimethyl Sulfoxide*

Jack M. Harrowfield, Brian W. Skelton and Allan H. White
Department of Chemistry, University of Western Australia, Nedlands, WA 6009, Australia

Crystallisation of lead(II) perchlorate from aqueous ethanolic solution containing various amounts of dimethyl sulfoxide (dmso) has resulted in the isolation of three distinct solvates of Pb^{II}:dmso stoichiometry 1:3, 1:5 and (probably) 1:6. Varying degrees of structural authentication have been provided for these materials. The 1:3 compound forms monoclinic crystals, space group $P2_1/c$, a = 15.722(7), b = 17.18(1), c = 15.032(5) Å, β = 101.78(3)°, Z = 4 dimers; the structure was refined to a residual of 0.055 for 3526 independent, 'observed' reflections. The compound is novel, comprising two distinctly different isomeric, centrosymmetric dimers, one half of each comprising the asymmetric unit. In dimer 1, the two lead atoms are bridged by a pair of *O,O'*-perchlorate groups [Pb–O 2.78(2) and 2.79(2) Å]; the remainder of the lead co-ordination sphere is made up of three dmso and one perchlorate ligand, all unidentate [Pb–O(dmso) 2.30(2)–2.37(1) Å, Pb–O(ClO_4) 3.04(3) Å]. In dimer 2, a compact PbO_2Pb central ring is found with bridging *O*-dmso ligands [Pb–O 2.42(1) and 2.79(1) Å]; the remainder of the lead co-ordination sphere consists of a pair of unidentate dmso ligands [Pb–O 2.31(1) and 2.25(1) Å] and a pair of bidentate perchlorate ligands [Pb–O 2.81(1)–3.12(2) Å]. A similar single crystal X-ray structural characterisation of the 1:5 compound shows the cell to be triclinic, space group $P\bar{1}$, a = 11.572(2), b = 11.344(3), c = 11.276(6) Å, α = 91.74(3), β = 102.71(3), γ = 90.48(2)°, Z = 2. The structure was refined to a residual of 0.050 for 4217 independent 'observed' reflections. The lead(II) environment comprises five unidentate *O*-dimethyl sulfoxide ligands and a symmetrically-co-ordinated bidentate perchlorate ligand, the latter equatorial in a quasi-pentagonal-bipyramidal array: Pb–O(dmso, axial) 2.531(7) and 2.433(7); Pb–O(dmso, equatorial) 2.348(7), 2.406(7) and 2.516(7); and Pb–O(ClO_4) 3.08(2) and 3.21(2) Å. For crystals of the material analysing as a 1:6 adduct, the symmetry is trigonal-hexagonal, with a = 20.479(3) and c = 6.777(8) Å. From cell-volume comparisons with the 1:3 and 1:5 phases, it would seem reasonable that this (at present) unresolved phase is a 1:6 complex.

In pursuing our joint objectives of a systematic study of important co-ordination complexes of lead(II),[1] and the structural characterisation of simple homoleptic co-ordination complexes, in particular, those of the ligand dimethyl sulfoxide (dmso),[2] our attention was drawn to a literature report of the tris(dimethyl sulfoxide) adduct of lead(II) perchlorate.[3] This compound is unusual in that co-ordinative saturation (or close to it) of a metal ion by dimethyl sulfoxide is the common observation when perchlorate is the counter anion.[4,5] Although it is possible that $Pb(ClO_4)_2$·3dmso might, as suggested,[3] contain three-co-ordinate lead(II) this would be uncommon[6] and unexpected for a donor of only moderate strength such as dmso. On the other hand, the binding of perchlorate ion as a ligand in the presence of dmso (or other *O*-donor solvents as present in the preparative medium[3]) would seem unlikely, nonetheless only leaving the equally 'unlikely' possibility of bridging dmso and/or perchlorate ligands as providing a co-ordination number above three for the lead(II) Thus, it was anticipated that determination of the structure of $Pb(ClO_4)_2$·3dmso might reveal several new features of dmso and/or lead(II) co-ordination chemistry. Unfortunately, we have been unable to reproduce exactly the original preparation of this compound, though we have been able to isolate tris-, pentakis- and hexakis(dimethyl sulfoxide) adducts of lead(II) perchlorate under similar preparative conditions, and report herein crystallographic studies of all three complexes, revealing interesting aspects of the co-ordination chemistry of both perchlorate anion and dimethyl sulfoxide when bound to lead(II).

Experimental

Syntheses.—$Pb(ClO_4)_2$·(6 + x)dmso. Lead(II) carbonate (0.54 g) was dissolved in the minimum volume of concentrated perchloric acid (70%, *ca.* 0.4 cm^3), gentle warming being used to drive off the last of the CO_2 and form a slightly cloudy, colourless syrup. The syrup was cooled on ice, then dissolved in ethanol (20 cm^3) and filtered (542 paper) to remove a trace of insoluble matter. The filtrate was mixed with dimethyl sulfoxide (10 cm^3), followed by diethyl ether to the point of permanent turbidity. Refrigeration (*ca.* 4 °C) of this mixture led to the slow deposition of extremely long, fine, white, needle-like crystals. After 24 h these were collected, washed quickly with 10% ethanol in diethyl ether, then diethyl ether, briefly sucked dry, and then rapidly transferred to a desiccator containing silica gel. As immediately isolated, the crystals appeared to be strongly deliquescent, although this may have been partly a consequence of water-vapour condensation due to evaporation of the diethyl ether, as, after 24 h of desiccation, they could be handled in the ordinary atmosphere without noticeable change for 5–10 min. The initial yield of solid was *ca.* 0.7 g, although addition of more diethyl ether to its filtrate could be used to provide further material. The stored crystals did appear slowly to exude some involatile liquid (presumed to be dmso) and metal analysis (ethylenediaminetetraacetate titration) after 24 h desiccation indicated a lead content of 22.8%, consistent with a value *ca.* 0.4 for x in the above formula, whereas a repeat analysis after another 72 h of desiccation gave a lead content of 24.0%, consistent with $x \approx -0.2$ (^1H NMR spectroscopy showed no solvent other than dmso to be present at either stage). After several months of desiccation, the lead content was 26.1%, closely consistent with the formulation $Pb(ClO_4)_2$·5dmso (*i.e.*, $x = -1$).

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Non-hydrogen positional parameters for the $Pb(ClO_4)_2 \cdot 5dmso$ adduct

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb	0.125 47(3)	0.223 53(3)	0.194 90(3)	C(42)	0.177(1)	0.405(1)	0.577(1)
O(1)	0.305 2(5)	0.250 0(6)	0.134 2(6)	O(5)	0.245 5(9)	0.049 2(8)	0.279 3(8)
S(1)	0.429 2(3)	0.241 6(3)	0.217 5(3)	S(5A)	0.326 4(9)	0.013 1(7)	0.400 6(7)
C(11)	0.498(1)	0.124(1)	0.150(1)	S(5B)	0.219 8(9)	−0.033 0(8)	0.372 9(8)
C(12)	0.508(1)	0.359(1)	0.175(1)	C(51)	0.317(3)	−0.120(2)	0.409(3)
O(2)	0.051 5(7)	0.139 4(7)	−0.019 0(7)	C(52)	0.231(3)	0.052(2)	0.503(2)
S(2)	0.080 0(3)	0.055 8(3)	−0.114 9(3)	Cl(1)	−0.124 3(3)	0.241 8(3)	0.356 4(3)
C(21)	0.205(1)	−0.018(2)	−0.047(2)	O(11)	−0.082(1)	0.328(1)	0.291(1)
C(22)	0.141(3)	0.145(2)	−0.200(3)	O(12)	−0.055(1)	0.142(1)	0.357(1)
O(3)	0.102 1(6)	0.417 6(6)	0.113 4(7)	O(13)	−0.239(1)	0.216(2)	0.323(1)
S(3)	0.201 7(3)	0.505 1(3)	0.117 9(3)	O(14)	−0.107(1)	0.283(1)	0.479(1)
C(31)	0.135(1)	0.646(1)	0.134(2)	Cl(2)	0.491 7(3)	0.266 5(3)	−0.202 2(3)
C(32)	0.218(1)	0.514(2)	−0.028(2)	O(21)	0.416(1)	0.335(1)	−0.151(1)
O(4)	0.231 9(7)	0.326 4(7)	0.379 7(7)	O(22)	0.526(2)	0.327(1)	−0.286(1)
S(4)	0.200 5(3)	0.440 5(3)	0.436 8(3)	O(23)	0.583(1)	0.226(2)	−0.122(2)
C(41)	0.340(1)	0.514(1)	0.489(1)	O(24)	0.432(2)	0.174(1)	−0.247(2)

Table 2 Non-hydrogen positional parameters for the $Pb(ClO_4)_2 \cdot 3dmso$ adduct

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pb(1)	0.508 02(5)	0.398 73(6)	−0.088 52(5)	Pb(2)	0.986 53(5)	0.595 67(5)	0.415 55(5)
Cl(11)	0.348 8(5)	0.563 6(4)	−0.162 5(5)	Cl(21)	1.176 0(5)	0.623 3(5)	0.322 5(5)
O(111)	0.363(1)	0.487(1)	−0.163(1)	O(211)	1.130(2)	0.670(2)	0.360(2)
O(112)	0.401(1)	0.603(1)	−0.091(1)	O(212)	1.121(2)	0.564(1)	0.315(2)
O(113)	0.367(3)	0.585(2)	−0.239(2)	O(213)	1.250(1)	0.606(2)	0.369(2)
O(114)	0.267(2)	0.574(2)	−0.163(3)	O(214)	1.189(2)	0.648(2)	0.244(2)
Cl(12)	0.403 3(6)	0.207 4(5)	−0.100 2(6)	Cl(22)	0.935 2(4)	0.796 1(4)	0.412 2(4)
O(121)	0.393(2)	0.261(1)	−0.160(2)	O(221)	0.977(1)	0.762 2(9)	0.495(1)
O(122)	0.475(3)	0.179(4)	−0.095(4)	O(222)	0.926(1)	0.740 0(8)	0.341(1)
O(123)	0.364(5)	0.153(3)	−0.125(4)	O(223)	0.977(2)	0.861(1)	0.392(1)
O(124)	0.397(4)	0.229(2)	−0.023(2)	O(224)	0.854(1)	0.814(1)	0.422(2)
O(11)	0.500 8(8)	0.396 6(9)	−0.248(1)	O(21)	0.990 9(9)	0.455 0(7)	0.404 9(8)
S(11)	0.579 1(4)	0.387 8(4)	−0.289 0(4)	S(21)	1.003 5(4)	0.415 8(3)	0.318 2(3)
C(111)	0.549(2)	0.436(2)	−0.393(1)	C(211)	0.931(2)	0.337(1)	0.301(2)
C(112)	0.571(2)	0.293(2)	−0.328(2)	C(212)	1.100(2)	0.360(1)	0.348(1)
O(12)	0.638(1)	0.340(1)	−0.095(1)	O(22)	0.911 6(9)	0.575 8(8)	0.268 4(8)
S(12)	0.695 8(4)	0.284 3(4)	−0.028 4(4)	S(22)	0.922 3(4)	0.619 5(3)	0.181 0(4)
C(121)	0.794(2)	0.330(2)	−0.012(2)	C(221)	0.939(2)	0.544(1)	0.106(2)
C(122)	0.723(3)	0.211(2)	−0.097(2)	C(222)	0.818(2)	0.643(2)	0.129(2)
O(13)	0.590(1)	0.511 0(9)	−0.080(1)	O(23)	0.851 6(8)	0.579 7(8)	0.442 0(8)
S(13)	0.615 5(6)	0.551 6(5)	−0.161 5(6)	S(23)	0.767 0(4)	0.555 8(4)	0.373 1(4)
S(13′)	0.661(3)	0.565(2)	−0.083(3)	C(231)	0.699(2)	0.515(1)	0.438(2)
C(131)	0.722(2)	0.534(2)	−0.152(3)	C(232)	0.711(2)	0.647(2)	0.347(2)
C(132)	0.624(3)	0.649(2)	−0.130(2)				

Table 3 Lead co-ordination environments in $[Pb(dmso)_5(O_2ClO_2)]ClO_4$ *

Atom	*r*	O(2)	O(3)	O(4)	O(5)	O(11)	O(12)
O(1)	2.348(7)	84.3(2)	78.5(3)	83.0(3)	76.3(3)	149.7(3)	159.0(3)
O(2)	2.531(7)		88.3(3)	166.4(3)	97.3(3)	110.0(3)	108.4(3)
O(3)	2.406(7)			84.5(3)	153.5(3)	75.5(3)	117.5(3)
O(4)	2.433(7)				84.4(3)	79.2(3)	85.1(3)
O(5)	2.516(7)					125.4(4)	85.2(3)
O(11)	3.08(2)						42.0(3)
O(12)	3.21(2)						

* *r* is the metal–oxygen distance (Å); the other entries are the angles (°) subtended at the lead atom by the relevant atoms at the head of the row and column. For the dmso ligands [1,2,3,4,5(A,B)]: S–O 1.537(6), 1.510(9), 1.505(8), 1.511(8), 1.55(1) and 1.51(1) Å; Pb–O–S 125.3(4), 144.2(4), 124.8(4), 128.4(4), 138.4(6) and 126.9(7)°.

$Pb(ClO_4)_2 \cdot 5dmso$. Lead(II) carbonate (2.67 g) was dissolved in the minimum volume of concentrated perchloric acid (70%, *ca.* 2 cm^3), gentle warming being used to drive off the last of the CO_2 and form a slightly cloudy, colourless syrup. The syrup was cooled on ice, then dissolved in ethanol (40 cm^3) and filtered (542 paper) to remove a trace of insoluble matter. The filtrate was mixed with dimethyl sulfoxide (3.9 g), followed by diethyl ether (10 cm^3), and the resultant clear solution was placed in a deep-freezer to cool at *ca.* −30 °C. A white crystalline precipitate usually formed rapidly under these conditions, though frequently an oil deposited first and had to be induced to solidify by vigorous stirring with a glass rod. Once crystallisation had occurred, the mixture was warmed in a refrigerator (*ca.* 4 °C) for *ca.* 60 min, before the solid (5.7 g) was collected by filtration, washed with diethyl ether and immediately placed in a desiccator over silica gel. Though deliquescent, this solid was far less so than the hexakis(dmso) adduct, and could be safely handled in the ordinary atmosphere for quite extended periods

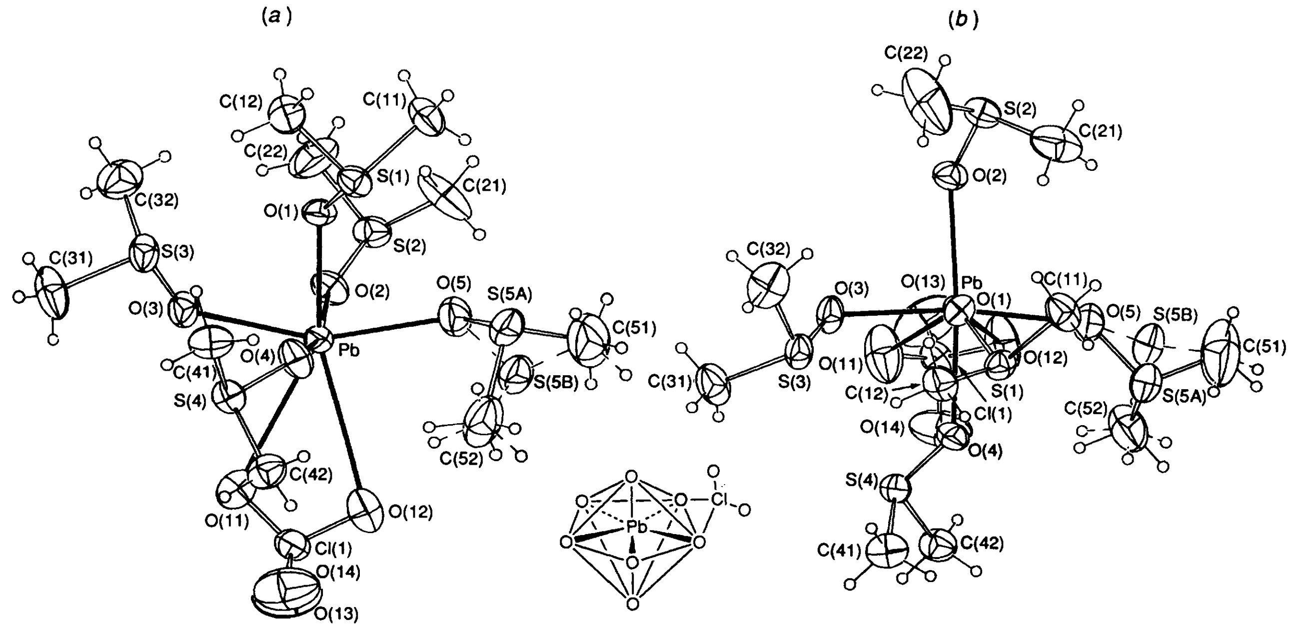


Fig. 1 Approximate projections of the cation of the 1 : 5 adduct (*a*) down and (*b*) normal to the axis of the co-ordination sphere showing 20% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. A simplified representation of the co-ordination environment of the lead atom is shown in the inset (O = oxygen of dmso)

Table 4 Lead co-ordination environments in $[Pb_2(dmso)_6(ClO_4)_4]$[a]

Pb(1)[b]

Atom	*r*	O(12)	O(13)	O(111)	O(121)	*O(112)*
O(11)	2.37(1)	79.2(5)	88.7(6)	74.7(6)	74.3(7)	152.5(5)
O(12)	2.30(2)		83.2(6)	152.6(6)	96.5(7)	75.6(5)
O(13)	2.31(2)			88.1(6)	162.6(7)	77.8(5)
O(111)	2.78(2)				84.2(5)	127.8(6)
O(121)	3.04(3)					119.1(6)
O(112)	2.79(2)					

Pb(2)[c]

Atom	*r*	O(22)	O(23)	O(211)	O(212)	O(221)	O(222)	*O(21)*
O(21)	2.42(1)	78.8(4)	86.0(5)	113.1(8)	75.3(6)	160.9(4)	150.1(4)	75.7(4)
O(22)	2.31(1)		80.6(5)	93.7(8)	75.9(6)	116.6(4)	71.5(4)	145.1(4)
O(23)	2.25(1)			158.7(7)	152.3(6)	85.5(5)	85.5(3)	74.3(4)
O(211)	2.86(4)				39.3(9)	78.7(8)	73.3(8)	118.0(7)
O(212)	2.89(3)					118.0(6)	100.5(6)	119.1(6)
O(221)	3.12(2)						45.8(4)	85.5(4)
O(222)	2.81(1)							128.8(4)
O(21)	2.79(1)							

[a] Entries as in Table 3; italicised atoms are generated by the intra-dimer inversion centre. [b] For the dmso ligands (11, 12, 13, 13′): S–O 1.50(2), 1.54(2), 1.53(2) and 1.46(4) Å; Pb–O–S 123.2(7), 131.3(9), 125(1) and 162(2)°; Pb(1) ··· *Pb(1)* 4.419(2) Å; Pb(1)–O(111)–Cl(11) 131(1), *Pb(1)*–*O(112)*–Cl(11) 148(1) and Pb(1)–O(121)–Cl(12) 109(1)°. [c] For the dmso ligands (21, 22, 23): S–O 1.52(1), 1.55(1) and 1.56(1) Å; Pb–O–S 120.8(7), 128.1(8) and 128.2(7)°, *Pb*–O–S 132.8(7)°; Pb ··· Pb 4.122(2) Å; Pb–O(21)–Pb 104.3(4), Pb(2)–O(211)–Cl(21) 113(2), Pb(2)–O(212)–Cl(21) 111(1), Pb(2)–O(221)–Cl(22) 95.1(7) and Pb(2)–O(222)–Cl(22) 109.0(7)°.

of time (hours) after mild desiccation had removed any volatile crystallisation solvents. Recrystallisation from acetone (15 cm^3), containing a small amount (0.2 cm^3) of dimethyl sulfoxide, by the addition of diethyl ether (*ca.* 2 cm^3) to the point of permanent turbidity and storage at −30 °C, provided thin, colourless rhombs (though again, in repeat preparations, formation of an oil sometimes preceded crystallisation). Analysis after 24 h desiccation over silica gel gave a lead content of 26.2% (Calc. for $C_{10}H_{30}Cl_2O_{13}PbS_5$: Pb, 26.0%).

$Pb(ClO_4)_2$·3dmso. Lead(II) carbonate (2.67 g) was dissolved in the minimum volume of concentrated perchloric acid (70%, *ca.* 2 cm^3), gentle warming being used to drive off the last of the CO_2 and form a slightly cloudy, colourless syrup. The syrup was cooled on ice, then dissolved in ethanol (25 cm^3) and filtered (542 paper) to remove a trace of insoluble matter. The filtrate was mixed with dimethyl sulfoxide (2.3 g), followed by diethyl ether (10 cm^3), and the resultant clear solution was placed in the deep-freezer to cool at *ca.* −30 °C. Almost invariably, a colourless oil rapidly deposited, but this soon transformed into a solid without the necessity for agitation with a glass rod, though this certainly accelerated the process. Once crystallisation had occurred, the mixture was warmed in the refrigerator (*ca.* 4 °C) for *ca.* 60 min, before the solid (1.6 g) was collected by filtration, washed with diethyl ether and immediately placed in a desiccator over silica gel (though deliquescent, it was not markedly more so than the pentakis

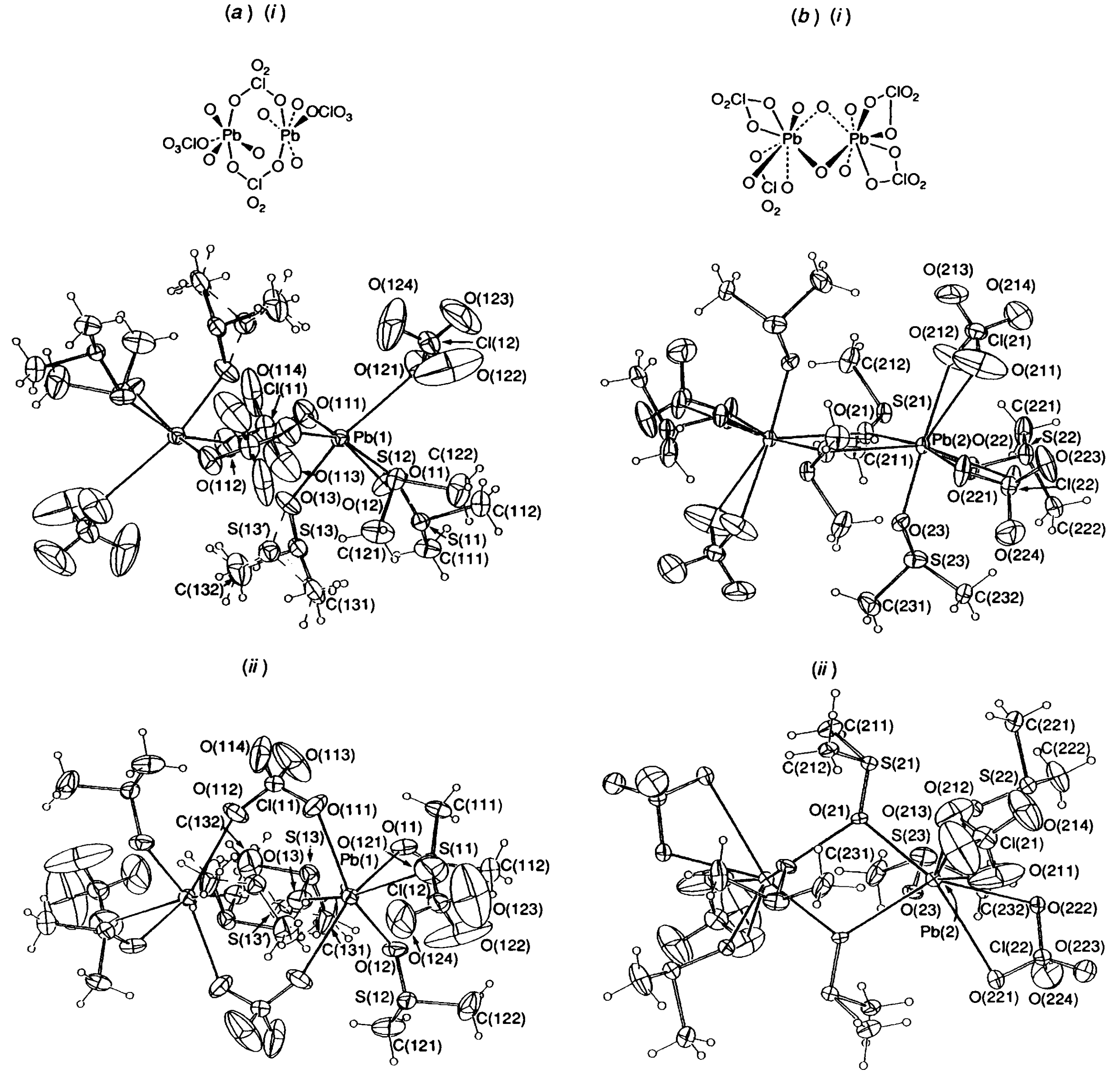


Fig. 2 Projections of (*a*) the perchlorate-bridged and (*b*) the dmso-bridged binuclear cation of the 1 : 3 adduct, (*i*) 'through' and (*ii*) approximately normal to the 'plane' of the two lead and their bridging ligand atoms. Simplified representations of the co-ordination environments of the lead atoms are shown in the insets

adduct). Mixture of the filtrate and wash produced more oil, which could again be transformed into a white solid by cooling to −30 °C, though occasionally spontaneous crystallisation occurred at 4 °C, and when it did, rather large colourless plates could be obtained. Attempts to recrystallise the complex from acetone[3] were unsuccessful (all of the complexes presently isolated being, in fact, extremely soluble in this solvent), though an oil could be obtained and solidified after the addition of diethyl ether. Recrystallisation from ethanol (*ca.* 10 cm^3 g^{-1}) by adding diethyl ether to the point of turbidity, cooling at −30 °C until the precipitate was solid, and then tempering this solid for several hours at *ca.* 4 °C until uniform crystal growth had occurred, was the only method presently developed to give crystals reproducibly. Analysis of recrystallised material after one week of desiccation over silica gel gave a lead content of 31.7% (Calc. for $C_6H_{18}Cl_2O_{11}PbS_3$: Pb, 32.4%).

Structure Determinations.—Crystallographic work was initially focused on the solvate now considered to be the hexakis(dmso) species, but at that stage taken to be the tris solvate described in the literature.[3] Data acquisition on this compound proved unusually difficult; the rather soft, needle-like crystals decomposed in the X-ray beam after a relatively small number of hours. Using a rapid scan and a limited 2θ range, a unique data set was eventually obtained, but difficulties arising from ambiguous space-group assignment and the presence of a very weak superlattice, presumably arising from the occupancy of a special position in the cell by the lead atom, resulted in an unsatisfactory structure solution. In the course of the tribulations involved in the many attempts to obtain useful data, many crystals were capillary mounted and examined under a variety of conditions. Most crystals were mounted appreciably damp with mother-liquor in consequence of speculation that loss of solvent might have been responsible for the decomposition observed, but excessive amounts of liquid caused problems with crystal movement, and a number were set aside for a period of months while the dilemma was further contemplated. On returning, it was found that the specimen of most robust aspect when mounted on the diffractometer diffracted with unexpected intensity, proving to have a quite different unit cell and yielding good data without appreciable decomposition. Solution of its structure, described below, showed it quite unambiguously to be the pentakis(dmso) compound. Recognition of this result led to a more systematic examination of the syntheses of the dimethyl sulfoxide solvates of lead(II) perchlorate, and ultimately to the procedures detailed above.

Unique data sets were measured at 295 K within the limit $2\theta_{max} = 50°$ using an Enraf-Nonius CAD-4 diffractometer (conventional 2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å). N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms (x, y, z, U_{iso}) were constrained at estimated values. Conventional residuals R, R' on $|F|$ at convergence are quoted [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral-atom complex scattering factors were employed;[7] computation used the XTAL 3.0 program system.[8] Pertinent results are given in Figs. 1 and 2 and Tables 1–4.

Abnormal features. The dmso solvent molecule 5 in the pentakis solvate displays the sulfur disorder frequently observed with this ligand. Site-occupancy refinement suggested the two dispositions to be equally prevalent, and a model with equal constrained populations of 0.5 [S(5A) and S(5B)] was adopted. Perchlorate thermal motion is very high, but with no resolvable disorder. The dmso solvent molecule 13 in the 'tris' solvate also displays sulfur disorder. Site-occupancy refinement resulted in values of 0.81(2) and 1 – 0.81(2) for S(13) and S(13') respectively.

Crystal data. $Pb(ClO_4)_2 \cdot 5dmso$. $C_{10}H_{30}Cl_2O_{13}PbS_5$, $M = 796.8$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 11.572(2)$, $b = 11.344(3)$, $c = 11.276(6)$ Å, $\alpha = 91.74(3)$, $\beta = 102.71(3)$, $\gamma = 90.48(2)°$, $U = 1443$ Å^3, D_c $(Z = 2) = 1.83$ g cm^{-3}, $F(000) = 780$, $\mu_{Mo} = 62$ cm^{-1}, specimen 0.27 × 0.17 × 0.48 mm, $A^*_{min,max} = 2.70, 4.68$, $N = 5075$, $N_o = 4217$, $R = 0.050$, $R' = 0.056$.

'$Pb(ClO_4)_2 \cdot 3dmso$'. $C_{12}H_{36}Cl_4O_{22}Pb_2S_6$, $M = 1281.0$, monoclinic, space group $P2_1/c$, (C_{2h}^5, no. 14), $a = 15.722(7)$, $b = 17.18(1)$, $c = 15.032(5)$ Å, $\beta = 101.78(3)°$, $U = 3975(4)$ Å^3, D_c $(Z = 4) = 2.14$ g cm^{-3}, $F(000) = 2448$, $\mu_{Mo} = 85$ cm^{-1}, specimen 0.28 × 0.36 × 0.28 mm, $A^*_{min,max} = 5.2, 7.9$, $N = 6843$, $N_o = 3526$, $R = 0.055$, $R' = 0.054$.

For the unsolved 1:6 phase, the symmetry is trigonal–hexagonal, with $a = 20.479(3)$, $c = 6.777(8)$ Å and $U = 2460.5(7)$ Å^3. For this phase, $U/3 = 820$ Å^3, while for the 1:3 and 1:5 adducts the volume of one $Pb(ClO_4)_2 \cdot n$dmso entity is 498 and 722 Å^3, respectively. Given the origin of the 1:5 specimen for the X-ray work and these volumes, it would seem reasonable that this (at present) unsolved phase is a 1:6 complex.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Discussion

In any system where a solid depositing from a solution has a stoichiometry or form very different from that of any species present in that solution, it is obviously possible that crystallisation of the solid may be slow, may be very dependent upon solution concentrations, and may perhaps be subject to capricious catalysis. Given the exceptionally poor co-ordinating ability of perchlorate ion,[9] it is to be expected that this ligand should provide many examples in its complexes of systems where special procedures and conditions may be necessary to assist in their isolation—the synthesis of $[Co(NH_3)_5(OClO_3)][ClO_4]_3$[10] is a case in point. The formation of solids containing co-ordinated perchlorate from solutions containing other good ligands such as dimethyl sulfoxide, water and ethanol is expected therefore to be retarded by the presence of these ligands, and we consider that some of the complications we have experienced in attempting fully to characterise the dimethyl sulfoxide adducts of lead(II) perchlorate, even though they are very labile systems, arise from this factor.

The most readily crystallised adduct of a dimethyl sulfoxide with lead(II) perchlorate is that obtained in the presence of a large (*ca.* 50-fold) excess of the ligand. Although the nature of the isolated material is such that accurate analysis is difficult, the determined lead content, along with the indication from X-ray diffraction of the cell volume and the fact that the complex ion present must be of relatively high symmetry, is taken as consistent with the presence of the hexakis(dimethyl sulfoxide) species, $[Pb(dmso)_6]^{2+}$. Its ready crystallisation can then be seen as indicative of the presence of a simple solvento complex (possibly, though not necessarily, $[Pb(dmso)_6]^{2+}$) as the dominant species in solution, just as is known to be the case with other divalent metal-ion perchlorates which give various solid-state species.* The apparent transformation of this solid $[Pb(dmso)_6][ClO_4]_2$ into a perchlorato–pentakis(dimethyl sulfoxide) complex is consistent with the need for a very high effective concentration of the anion to be achieved before its entry into the primary co-ordination sphere of the lead(II) can be achieved, though other factors, such as lattice energies and the ability of lead(II) to adopt co-ordination numbers higher than six,[6] must be of some importance in the formation of the particular product.

Crystallisation of the materials which we have defined analytically and crystallographically as tris- and pentakis-(dmso) solvates of lead(II) perchlorate is characterised under most circumstances by the initial deposition of an oil which then undergoes a transformation to the crystalline solid containing co-ordinated perchlorate. The exclusive deposition of crystals directly from preparative media was observed only rarely. We presume that the oils may well be mixtures of various dimethyl sulfoxide–ethanol–diethyl ether (and, given that the lead perchlorate is provided as an aqueous syrup, water) complexes, and that perchlorate co-ordination only occurs rapidly in the highly concentrated oil, though epitaxial growth on some initial solid may well be important, as the oils are very persistent if the temperature is not reduced to *ca.* –30 °C, at which temperature the first sign of solid results in rapid crystallisation of the whole mass. Some problems in our work may have been associated with the presence of a minor impurity in the lead carbonate used as a reactant (and observed as an insoluble powder on addition of the carbonate to perchloric acid) causing the stoichiometric ratio of lead(II) to dmso to be imprecise. This may have been the reason that initial precipitates of the pentakis(dmso) complex commonly analysed for a dmso:Pb ratio nearer 4.8–4.9 than 5.0, a factor which was allowed for in recrystallisation by adding a small amount of dmso to the recrystallisation solvent. On most occasions, this compound behaved well on recrystallisation and deposited directly as colourless plates from acetone–diethyl ether on cooling to *ca.* –30 °C. The reasons for our inability to reproduce the reported[3] synthesis of $Pb(ClO_4)_2 \cdot 3dmso$ are obscure, since the original work contains minimal information on the isolation and recrystallisation procedures, but the methods we have found to be successful seem sufficiently close to the original to justify the belief that the same product material must have been isolated. Although the nature of any isolated product is certainly quite sensitive to the preparative stoichiometry,[3] we have found in attempting to investigate the 1:4 $Pb(ClO_4)_2$:dmso system, for example, that the crystalline phase of the precipitate sometimes contains the 1:3 adduct, but on other occasions contains a different phase which we assume may be the true 1:4 adduct. Except with the putative 1:6 adduct, the products of all preparations presently described appeared to be heterogeneous initially, often containing gel-like material, and it may well be that we have simply been fortunate in isolating as crystalline species those which are dominant in a given solution.

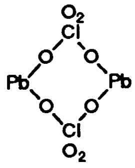
---

* Sandström *et al.*[5] have discussed in some detail the interactions of, in particular, the perchlorates of the divalent metal ions Zn^{II}, Cd^{II} and Hg^{II} with dmso in both the solid and solution state.

A single crystal X-ray structure determination has provided a definitive authentication and a detailed description of the bonding and stereochemistry of the pentakis(dmso) adduct. The structure is comprised of complex cations of stoichiometry $[Pb(dmso)_5(ClO_4)]^+$, with a perchlorate counter ion free in the lattice, one of each moiety making up the asymmetric unit of the structure. Both dmso and perchlorate moieties have high thermal-motion amplitudes. The dmso molecules are bound as unidentate ligands of the central lead atom of the cation by way of their oxygen atoms; the ligated perchlorate is bidentate. The stereochemistry about the lead atom is interesting; a pair of dmso oxygen atoms from ligands 2 and 4 at distances 2.531(7) and 2.433(7) Å are nearly linearly bound as a quasi-axial pair in the co-ordination environment [O(2)–Pb–O(4) 166.4(3)°]; angles between O(2) and the 'equatorial' oxygen atoms O(1,3,5,11,12) range between 84.3(2) and 110.0(3)°, while those from O(4) and O(1,3,5,11,12) lie between 79.2(3) and 85.1(3)°. The angle sum in the equatorial array is 357.6°; the perchlorate oxygen atoms subtend an angle of 42.0(3)°, while the other angles are clustered between 75.5(3) and 85.3(3)°, *i.e.*, the geometry may be regarded alternatively as octahedral or pentagonal bipyramidal, perturbed by the perchlorate. χ^2 for a plane defined by O(1,3,5,11,12) is 230; defining atom deviations are 0.04(1), −0.07(1), −0.04(1), 0.20(2) and −0.09(2) Å, with the lead atom lying −0.300(2) Å out of the plane towards O(2). Within the equatorial plane, Pb–O(11,12) are longer than the other Pb–O distances by an appreciable margin, being 3.08(2) and 3.21(2) Å, a result in keeping with the aspect of the perchlorate as a bidentate of small bite. The Pb–O bond *trans* to the bound perchlorate is the shortest [at 2.348(7) Å] by a considerable margin. Some inverse correlation exists, among the ordered dmso ligands, between Pb–O lengths on the one hand, and O–S distances and Pb–O–S angles on the other, but the trend is not a rigorous one. There appears to be no substantial evidence for the presence of a stereochemically active lone pair, unless it be directed toward the bidentate perchlorate.

Assignment of the stoichiometry of the 1:3 adduct is assisted by its single crystal X-ray structure determination, the result of which is remarkable. The asymmetric unit of the structure is twice the empirical formula unit of $Pb(ClO_4)_2\cdot 3dmso$, thus containing a pair of independent lead atoms. Each of these lies close to a crystallographic inversion centre in close association with both ligands and cations, giving rise to a pair of binuclear $[Pb_2(ClO_4)_4(dmso)_6]$ units which differ radically from each other in their connectivity so as to constitute the novel situation of two isomeric types in equal amounts within the same crystal.

In the dimer arising from Pb(1), the two lead atoms, separated from each other by 4.419(2) Å, are linked by a pair of *O,O'*-perchlorate bridging groups forming an eight-membered ring. The two independent Pb–O distances are indistinguishable in length [Pb–O(111) 2.78(2) and Pb–O(112) 2.79(2) Å]. The ring is not planar; O(111) and O(112) deviate by approximately equal amounts [−0.45(2) and 0.38(2) Å] to either side of the plane defined by $Pb(1)_2Cl(11)_2$ and the torsion angles Pb(1)–O(111)–Cl(11)–O(112) and O(111)–Cl(11)–O(112)–*Pb(1)* are approximately equal [24(2) and 31(3)°] so that the aspect of the Pb_2O_4 ring viewed side on is that of a 'chair' (Fig. 2). The lead atom is six-co-ordinate, distorted considerably from octahedral or trigonal-prismatic stereochemistry (Table 2); in terms of the former, the bridging perchlorate oxygen atoms lie *trans* to a pair of *O*-dmso ligands, with the other pair of opposed sites occupied by unidentate perchlorate and dmso species. The Pb–O(dmso) distances are similar [2.30(2)–2.37(1) Å], much more so than in the 1:5 compound, and generally shorter, a rather surprising result, given that in the present situation they are *cis* and crowded to give O–Pb–O angles all less than 90°, while the face of the octahedron defined by the three perchlorate oxygen atoms [the unidentate one of which is very weakly co-ordinated at 3.04(3) Å] is splayed [Fig. 2(*a*)(*ii*)] (accommodating a sterically active lone pair?).



In the dimer arising from Pb(2), the two lead atoms separated from each other by 4.122(2) Å are linked into a four-membered ring by a pair of centrosymmetrically related μ,μ'-*O*-dmso ligands; the Pb–O distances are unsymmetrical [2.42(1) and 2.79(1) Å]. The co-ordination number of this lead atom is higher, 8, further comprising a pair of chelating perchlorate moieties [Pb–O 2.81(1)–3.12(2) Å, the two extreme distances arising from somewhat unsymmetrical co-ordination by anion 22] and two unidentate dmso ligands, these again having the shortest distances and with the short bridging distance lying *fac* in the co-ordination sphere. Again, room for the accommodation of a sterically active lone pair may be postulated in the region opposite these three atoms.

Despite the general difficulties in obtaining perchlorate complexes, various co-ordination modes have been characterised structurally.[11] In the present systems, three are exemplified: unidentate, chelate and *O,O'*-bridging, with Pb–O distances 3.04(3); 2.81(1)–3.12(2) or 2.86(4) and 2.89(3) in the symmetrical example; and 2.78(2) and 2.79(2) Å, respectively.

Acknowledgements

Support of this work by the Australian Research Council is gratefully acknowledged.

References

1 L. M. Engelhardt, B. M. Furphy, J. M. Harrowfield, J. M. Patrick and A. H. White, *Inorg. Chem.*, 1989, **28**, 1410 and refs. therein.
2 J. M. Harrowfield, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1990, **43**, 759 and refs. therein.
3 J. Selbin, W. E. Bull and L. H. Holmes, jun., *J. Inorg. Nucl. Chem.*, 1961, **16**, 219.
4 J. A. Davies, *Adv. Inorg. Chem. Radiochem.*, 1981, **24**, 116; W. L. Reynolds, *Prog. Inorg. Chem.*, 1970, **12**, 1.
5 M. Sandström, I. Persson and S. Ahrland, *Acta Chem. Scand., Ser. A*, 1978, **32**, 607 and refs. therein.
6 P. G. Harrison, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 3, ch. 26, p. 183.
7 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
8 S. R. Hall and J. M. Stewart (Editors), *The XTAL Reference Manual, Version 3.0*, Universities of Western Australia and Maryland, 1990.
9 G. A. Lawrance, *Adv. Inorg. Chem.*, 1989, **34**, 145.
10 J. M. Harrowfield, A. M. Sargeson, B. Singh and J. C. Sullivan, *Inorg. Chem.*, 1975, **14**, 2864.
11 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, ch. 15.5, p. 413.

Received 21*st January* 1993; *Paper* 3/00379E