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SYNTHESES AND PROPERTIES OF THE LEAD 1,3-DITHIOLE-2-THIONE-4,5-DITHIOLATE (DMIT) COMPOUNDS: Ph_2Pb(DMIT), [Q] [Ph_2Pb(DMIT) I] [Q = NEt_4 OR 1,4-Me_2-PYRIDINIUM], $(Ph_3Pb)_2$(DMIT) AND Pb(DMIT)

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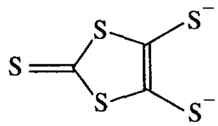
Abstract—Syntheses of Ph_2Pb(dmit) (**3**), [Q] [Ph_2Pb(dmit)I] (**5**, Q = NEt_4 or 1,4-Me_2-pyridinium), $(Ph_3Pb)_2$(dmit) (**4**) and Pb(dmit) (**6**) are reported [H_2-dmit = 4,5-dimercapto-1,3-dithiole-2-thione]. Compound **3** was produced from $Ph_2Pb(OAc)_2$ and $[NEt_4]_2[Zn(dmit)_2]$, while **4** was obtained from Ph_3PbOAc and either Na_2(dmit) or $[NEt_4]_2[Zn(dmit)_2]$. The ionic species, **5**, were obtained by addition of [Q] I to **3** (*eg*. for Q = 1,4-Me_2-pyridinium) or from reaction of Ph_2PbI_2 with $[NEt_4]_2[Zn(dmit)_2]$. Reaction of either $Pb(OAc)_2$ or $Pb(NO_3)_2$ with $[NEt_4]_2[Zn(dmit)_2]$ produced **6**. NMR spectra, including the solid state spectra for **3**, have been obtained. X-ray crystallography revealed **4** to be a monomeric compound with each Pb atom having a distorted tetrahedral geometry. The C—Pb—S bond angles are less and the C—Pb—C bond angles greater than ideal tetrahedral angles. The dmit ligand is effectively inserted between two phenyl rings of different Ph_3Pb groups in **4**, with short non-bonded C—C and C—S distances of 3.4–3.7 Å. Cyclic voltammetric studies of **3** and of **4** in DMF have also been carried out.

The dmit group (**1**) has been found to be an interesting delocalised dithiolato ligand,[1] able to form a variety of complexes, all coloured and some having good conducting properties. Various of its com-



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plexes have been found, by X-ray crystallography, to exhibit in the solid state sulfur···metal and sulfur···sulfur interanionic separations of less than the sum of the appropriate van der Waals' radii. These sulfur···metal and sulfur···sulfur associations provide ordered two- and three-dimensional polymeric structures. Transition metal–dmit complexes in particular have attracted considerable attention:[1] the reports of superconducting properties of some nickel and palladium compounds have clearly fueled the interest in their study.[2] Much less attention has been paid to main-group metal species. Although no useful conducting properties have as yet been found for main-group metal bis- and tris-dmit complexes, such as [Q] [RSn(dmit)$_2$] (**2**),[3] [Q]$_2$[Sn(dmit)$_2$I$_2$],[4] [Q]$_2$[Sn(dmit)$_3$][5] and [Q][Sb(dmit)$_2$] (Q = NR$_4$ or 1,4-Me$_2$-pyridinium),[6] their study has revealed some interesting solid-state structures. As well as **2**, other types of organotin dmit compounds obtained in our earlier studies have been the mono-dmit species, R$_2$Sn(dmit)[5] and [Q][R$_2$Sn(dmit)X].[7]

As indicated above, a variety of tin–dmit compounds, both inorganic and organometallic species, have been isolated in our earlier work. We have turned our attention to lead complexes and we now wish to report our findings.

EXPERIMENTAL

Solution NMR spectra were obtained on a Bruker 250 MHz instrument; solid state NMR spectra were obtained by the EPSRC NMR solid state service, based at the University of Durham. IR spectra were recorded on a Philips Analytical PU 9800 Fourier-transform spectrometer. The zinc dmit salts, [NEt$_4$]$_2$[Zn(dmit)$_2$] and [1,4-Me$_2$-pyridinium]$_2$[Zn(dmit)$_2$], were prepared by a general procedure.[8] The compound (PhCO)$_2$(dmit) was obtained[9] from [NEt$_4$]$_2$[Zn(dmit)$_2$] and PhCOCl. It had a m.p. of 141–143°C (lit. value[9] 145°C). Di- and tri-phenyllead compounds were obtained by the methods of Willemsens.[10]

Preparation of Ph$_2$Pb(dmit) (**3**). Diphenyllead diacetate[10] (0.357 g, 0.744 mmol) and [NEt$_4$]$_2$[Zn (dmit)$_2$] (0.268 g, 0.372 mmol) were added to methanol (25 cm^3). The reaction mixture was agitated in an ultrasonic bath for 20 min and then filtered. The precipitate was recrystallized from acetone–methanol to give **2** as a gold-coloured solid; m.p. 179–184°C (dec.). The temperature during recrystallization had to be controlled in order to avoid decomposition. (Found: C, 31.5; H, 1.9. C$_{15}$H$_{10}$PbS$_5$ requires: C, 32.2; H, 1.8%.)

ν_{max}(KBr) (cm^{-1}) 3050, 1655, 1468, 1426, 1400, 1017, 992, 727, 719.

^{1}H NMR (CD$_3$COCD$_3$, 250 MHz). δ: 7.45–7.81 (*m*, 6H, *m*-H+*p*-H), 8.07 (*m*, 4H, *J* (^{207}Pb—^{1}H) = 157.6 Hz, *o*-H).

^{13}C NMR (CD$_3$COCD$_3$, 62.9 MHz). δ: 128.99 (C=C), 130.86 (*p*-C), 131.16 (*J* (^{207}Pb—^{13}C) = 141.9 Hz, *m*-C), 135.90 (*J* (^{207}Pb—^{13}C) = 109.2, *o*-C), 163.34 (*i*-C), 212.14 (C=S).

^{13}C NMR (Solid state, 75.4 MHz). δ: 131.43–137.45 (C=C+aryl), 161.66, 166.52, 211.28 (C=S).

^{207}Pb NMR (solid state, 62.7 MHz). δ: 248.0.

Preparation of (Ph$_3$Pb)$_2$(dmit) (**4**). A solution of Na$_2$(dmit) (1.00 mol) in methanol (15 cm^3) was obtained by addition of a suspension of (PhCO)$_2$ (dmit) (0.41 g, 1.00 mmol) in MeOH (5 cm^3) to a solution of MeONa (5.00 mmol) in MeOH (20 cm^3). To this red solution was added, under nitrogen and with stirring, a slurry of Ph$_3$PbOAc (0.995 g, 2 mmol) in MeOH (20 cm^3). There was an immediate colour change and a yellow solid (**4**) precipitated. This was collected and recrystallized from MeOH/Me$_2$CO as yellow plates; m.p. 179–181°C. Found: C, 43.7; H, 2.9. C$_{39}$H$_{30}$Pb$_2$S$_5$ requires: C, 43.6; H, 2.8%.

ν_{max} (KBr) (cm^{-1}) 3061–3042, 2982, 1568, 1474, 1443, 1431, 1327, 1298, 1051, 1032, 1014, 993, 968, 729, 719, 690.

^{1}H NMR (CDCl$_3$, 250 MHz). δ: 7.23–7.66 (*m*, 18H, *m*-H+*p*-H), 7.79 (*m*, 12H, *J* (^{207}Pb—^{1}H) = 107.2 Hz, *o*-H).

^{13}C NMR (CDCl$_3$, 62.9 MHz). δ: 129.7 (*J* (^{207}Pb—^{13}C) = 21.6 Hz), 130.1 (*J* (^{207}Pb—^{13}C) = 94.7 Hz, *m*-C), 136.9 (*J* (^{207}Pb—^{13}C) = 82.0 Hz, *o*-C), 139.3 (C=C), 154.1 (*J* (^{207}Pb—^{13}C) = 477.7 Hz, *i*-C), 212.1 (C=S).

^{13}C NMR (solid state, 125.8 MHz). δ: 129.2, 130.4, 136.6, 141.3 (aryl+C=C), 155.1 (*i*-C), 210.9 (C=S).

Compound **4** was also prepared from: (i) Na$_2$ (dmit) (1.00 mmol), Ph$_3$PbOAc (0.498 g, 1.00 mmol), and 1,4-dimethylpyridinium iodide (0.470 g, 2.00 mmol) in MeOH; or (ii) [NEt$_4$]$_2$[Zn(dmit)$_2$] (0.381 g, 0.53 mmol) and Ph$_3$PbOAc (1.054 g, 2.12 mmol) in MeOH.

Preparation of [NEt$_4$] [Ph$_2$Pb(dmit)I]. (**5**,Q = NEt$_4$). Solutions of Ph$_2$PbI$_2$ (0.669 g, 1.086 mmol) in CH$_2$Cl$_2$ (25 cm^3) and [NEt$_4$]$_2$[Zn(dmit)$_2$] (0.390 g, 0.543 mmol) in CH$_2$Cl$_2$ (15 cm^3) were mixed to give a dark yellow solution and a precipitate. The reaction mixture was filtered and the filtrate was evaporated to leave a solid residue, which was fractionally recrystallized from MeOH to give initially a yellow–orange solid, m.p. 158–159°C (unknown A) and secondly orange–brown [NEt$_4$] [Ph$_2$Pb(dmit)I], m.p. 85–87°C.

Compound A. Found: C, 31.1; H, 2.4; N, 0.72%.

Atom ratios: C : H : N = 50.3 : 46.5 : 1.0.

ν_{max} (KBr) (cm^{-1}) 3038, 2982–2932, 1561, 1470, 1389, 1057, 1034, 1019, 992, 727, 720, 679.

^{1}H NMR (CD_3COCD_3), 250 MHz), δ: 1.39 (t of t, 12H, J (^{1}H—^{1}H) = 7.3 Hz, J (^{1}H—N) = 1.9 Hz, Me), 3.48 (q, 8H, J (^{1}H—^{1}H) = 7.3 Hz, NCH_2), 7.45 (*m*, 4H, *p*-H), 7.61 (*m*, 8H, J (^{207}Pb—^{1}H) = 60 Hz, *m*-H), 8.14 (*m*, 8H, J (^{207}Pb—^{1}H) = 153 Hz, *o*-H).

[NEt_4] [Ph_2Pb(dmit)I]. Found: C, 33.8; H, 3.9; N, 1.8. $C_{23}H_{30}INPbS_5$: C, 33.9; H, 3.7; N, 1.7%.

ν_{max} (KBr) (cm^{-1}) 3034, 2980–2932, 1561, 1482, 1472, 1429, 1389, 1373, 1364, 1169, 1059, 1038, 1019, 1011, 990, 735, 693.

^{1}H NMR (CD_3COCD_3, 250 MHz). δ: 1.35 (t of t, 12H, J (^{1}H—^{1}H) = 7.3 Hz, J (^{1}H—N) = 1.9 Hz, Me), 3.42 (*q*, 8H, J (^{1}H—^{1}H) = 7.3 Hz, NCH_2), 7.39 (*m*, 2H, *p*-H), 7.55 (*m*, 4H, J (^{207}Pb—^{1}H) = 58 Hz, *m*-H), 8.27 (*m*, 4H, J (^{207}Pb—^{1}H) = 155.4 Hz, *o*-H).

^{13}C NMR (CD_3COCD_3, 62.9 MHz). δ: 7.65 (Me), 52.92 (*t*, $J = 3$ Hz, NCH_2), 130.12 (*p*-C), 130.44 (J (^{207}Pb—^{13}C) = 141.2 Hz, *m*-C), 133.34 (C═C), 135.80 (J (^{207}Pb—^{13}C) = 109.8 Hz, *o*-C), 163.2 (*i*-C), 209.3 (C═S).

Preparation of [1,4-Me_2-pyridinium] [Ph_2Pb(dmit)I]. (5,Q = 1,4-Me_2-pyridinium). Solutions of Ph_2Pb(dmit) (0.352 g, 0.63 mmol) in MeOH (20 cm^3) and [1,4-Me_2-pyridinium]I (0.470 g, 2 mmol) in MeOH (20 cm^3) were mixed. After stirring for 1 h, the reaction mixture was filtered and the solid was recrystallized from MeOH–petroleum ether (b.p. 40–60°C) to give the title-compound as a dark-red solid, m.p. 117–119°C. Found: C, 33.4; H, 2.4; N, 1.8. $C_{22}H_{20}INPbs_5$ requires: C, 33.3; H, 2.5; N, 1.8%.

ν_{max} (KBr) (cm^{-1}) 3038, 2923–2853, 1638, 1561, 1468, 1429, 1053, 1032, 1008, 990, 808, 733.

^{1}H NMR (CD_3COCD_3, 250 MHz). δ: 2.72 (*s*, 3H, Me), 4.53 (*s*, 3H, MeN), 7.37 (*m*, 2H, *p*-H), 7.54 (*m*, 4H, J (^{207}Pb—^{1}H) = 55.4 Hz, *m*-H), 8.03 (*d*, 2H, H-3+H-5 of cation), 8.26 (*m*, 4H, J (^{207}Pb—^{1}H) = 155.2 Hz, *o*-H), 8.90 (*d*, 2H, H-2+H-6 of cation).

Preparation of lead(II)(dmit), (**6**). (a) The compound, $Pb(OAc)_2 \cdot 3H_2O$ (0.758 g, 2.00 mmol), was added to a stirred solution of $[NEt_4]_2[Zn(dmit)_2]$ (0.719 g, 1.00 mmol) in acetone (50 cm^3). The reaction mixture was stirred for 30 min and filtered to give **5** as a black solid. This was collected and washed with acetone, stirred in hot water for 20 min, washed again with acetone and dried at 100°C under vacuum, yield 0.54 g 67%; m.p. > 215°C. Found: C, 8.8; H, <0.3; S, 39.7. C_3PbS_5 requires C, 8.9; H, 0.0; S, 39.8%.

ν_{max} (KBr) (cm^{-1}) 1410, 1015.

^{13}C NMR (solid state, 75.4 MHz). δ: broad signal 50–170 ppm, with a relatively sharp signal at 142.77.

(b) Compound **6** was also prepared from a solution of $[NEt_4]_2[Zn(dmit)_2]$ (0.719 g, 1.00 mmol) in acetone and a solution of $Pb(NO_3)_2$ (0.662 g, 2.00 mmol) in water (40 cm^2).

X-ray crystallography. Crystal structure of **4**

X-ray diffraction data were obtained using a Philips-100 computer controlled four-circle diffractometer with graphite monochromator Mo-Kα radiation. Standard centering and auto-indexing procedures indicated the primitive monoclinic lattice $P2_1/a$. The orientation matrix and accurate cell dimensions were determined from a least-square fit of 25 symmetry-related reflections. Intensity data were collected at 25°C using the θ–2θ scan method. Two standard reflections, monitored every 150 reflection measurements, fluctuated within 2% of their mean value. The intensities were corrected for Lorentz and polarization effects and for absorption by empirical methods (ψ-scan).

The positions of Pb and S were determined from a three-dimensional Patterson synthesis. Most of the hydrogen atoms were located from the least difference synthesis yet they have been geometrically re-calculated, assigned isotropic thermal parameters and included in the final calculations, but not refined. Anisotropic thermal parameters were used for all the non-hydrogen atoms. Blocked-cascade least-square refinements were used: they converged to the conventional R index of 0.034. Data collection and structure refinement parameters are shown in Table 1.

Cyclic voltammetry

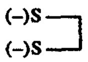
Electrochemical measurements were made using an Autostat Sycopel Scientific Voltameter. The electrochemical cell comprised a platinum disc working electrode, a platinum wire as the auxiliary electrode and a 0.1 M solution of Ag–$AgNO_3$ in acetonitrile, as the reference electrode, solutions of the lead-dmit species (10^{-3} M) and the supporting electrolyte, $[NMe_4]ClO_4$ (10^{-1} M), in dry spectroscopic grade DMF were used. The solutions were degassed with argon before measurement began, and an argon blanket was maintained over the solution during the experiment.

RESULTS AND DISCUSSION

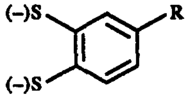
A variety of compounds of the types, R_3PbX and R_2PbX_2, are known, but of the $RPbX_3$ type the

Table 1. Data collection and structure refinement parameters for $(Ph_3Pb)_2(dmit)$ (4)

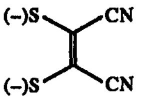
Formula	$C_{39}H_{30}Pb_2S_5$
F.Wt. (amu)	1073.36
Space group	$P2_1/a$
a (Å)	18.089 (8)
b (Å)	17.248 (8)
c (Å)	12.238 (8)
β (°)	95.6 (1)
V (Å^3)	3800.2
Z	4
D_c (g cm^{-3})	1.88
μ (cm^{-1})	85.54
crystal size (mm)	0.15 × 0.10 × 0.15
T (K)	298
radiation	graphite monochromated Mo-Kα ($\lambda = 0.7107$)
Take-off angle (°)	3
Scan speed (° min^{-1})	2.0 in 2θ scan mode
Scan width (°)	1.2
2θ range	$2.0 < 2\theta < 45$
Observed reflections ($F_0^2 > 2\,(F_0^2)$)	3607
R (on F_0)	0.034
R_w	0.041
Goodness of fit	1.07
Highest map residuals (e Å^3)	0.58



(7) edt



(8) R = Me, tdt
R = H, dmb



(9) mnt

only species having appreciable stability are the tricarboxylates and the areneplumbonic acids.[10–11] In this study, the only organolead–dmit complexes we were able to isolate were di- and tri-phenyllead species. Attempts to prepare [Q] [ArPb(dmit)$_2$] from $[Q]_2[Zn(dmit)_2]$ and $ArPb(OAc)_3$ (Ar = Ph or p-$MeOC_6H_4$), generated according to literature procedures,[12,13] only led to decomposition and the formation of black intractable products. No mono-organolead dithiolate of the form [Q] [RPb(dithiolate)$_2$] has indeed been reported previously, in contrast to the situation known for tin. This is also in contrast to the number of reported di- and tri-organolead–dithiolate complexes, *eg*. with ligands **7**–**9**. The di- and tri-phenyllead–dmit compounds obtained in this study were $Ph_2Pb(dmit)$ (**3**), [Q] [$Ph_2Pb(dmit)I$] (**5**) and $(Ph_3Pb)_2(dmit)$ (**4**). As indicated above, analogous tin–dmit complexes to **3** and **5**, but not **4**, have been isolated. Previously reported organolead–dithiolate compounds related to **3**–**5** are R_2PbL_2 (R = Me, Ph; L_2 = edt, tdt, dmb or mnt),[14–18] [Q] [$Ph_2Pb(mnt)Cl$][18] and [$(Ph_3Pb)_2(tdt)$];[14,16] in addition $[Q]_2[Ph_2Pb(mnt)_2]$ and [Q] [$Ph_3Pb(mnt)$][19] have also been reported.

Diphenyllead–dmit species

Compound **3** was obtained from $Ph_2Pb(OAc)_2$ and $[NEt_4]_2[Zn(dmit)_2]$ (2 : 1 mol ratio), Ph_2PbI_2 and [1,4-Me-pyridinium]$_2$ [$Zn(dmit)_2$] (2 : 1 mol ratio), and Ph_2PbI_2 and $Na_2(dmit)$ (1 : 1 mol ratio). Compound **3** is stable in the dark at room temperature for prolonged periods; solutions, in particular, are light sensitive. It is only sparingly soluble in organic solvents. Attempts to obtain satisfactory X-ray diffraction data from crystals of **3** failed. However it is expected to be associated in the solid state, as found[15] for $Ph_2Pb(edt)$. Solid state ^{13}C and ^{207}Pb NMR spectra of **3** were obtained. The most significant difference between the solid state and solution ^{13}C NMR spectra of **3** is found for the values for the aryl *ipso*-carbon atoms: in the solid state, two values (161.7 and 166.5 ppm) for these carbon atoms are observed in contrast to the single value found in solution (163.3 ppm). This suggests that in the solid state structure, the two phenyl groups in **3** are in different environments. The solid state ^{207}Pb value is 248 ppm, which indicates a higher coordination number than four.

Addition of iodide to **3** to give the complex anion, $[Ph_2Pb(dmit)I]^-$, occurred on reaction with excess [1,4-Me_2-pyridinium]I in MeOH; direct reaction between Ph_2PbI_2 and $[NEt_4]_2[Zn(dmit)_2]$ (2 : 1 mol ratio) similarly gave (**5**, Q = [NEt_4]). The latter reaction contrasts with that between [1,4-Me_2-pyridinium]$_2$[$Zn(dmit)_2$] and Ph_2PbI_2 from which **3** was isolated. The differences in the type of products obtained from these two reactions is probably only linked to differences in solubilities. The complex anion, $[Ph_2Pb(mnt)Cl]^-$, has previously been reported[18] to be formed directly from Ph_2PbCl_2 and $Na_2(mnt)$ (1 : 2 mol ratio), in the presence of Ph_4AsCl.

Cyclic voltammetry

The cyclic voltammogram for **3** is displayed in Fig. 2 and can be compared with that for [NMe_4] [$Ni(dmit)_2$]. Both the voltammograms involve one oxidation and one reduction peak. The compound [NMe_4] [$Ni(dmit)_2$] exhibits simple reversible behaviour. The voltammogram for **3**, in contrast, is highly irreversible: on scanning cathodically from 0.29 V_{Ag/Ag^+}, a sharp reduction peak was observed at -0.50 V and on the reverse scan a smooth oxidation peak was detected at 0.08 V. Scanning cathodically from -0.36 V, no reduction peak was seen;

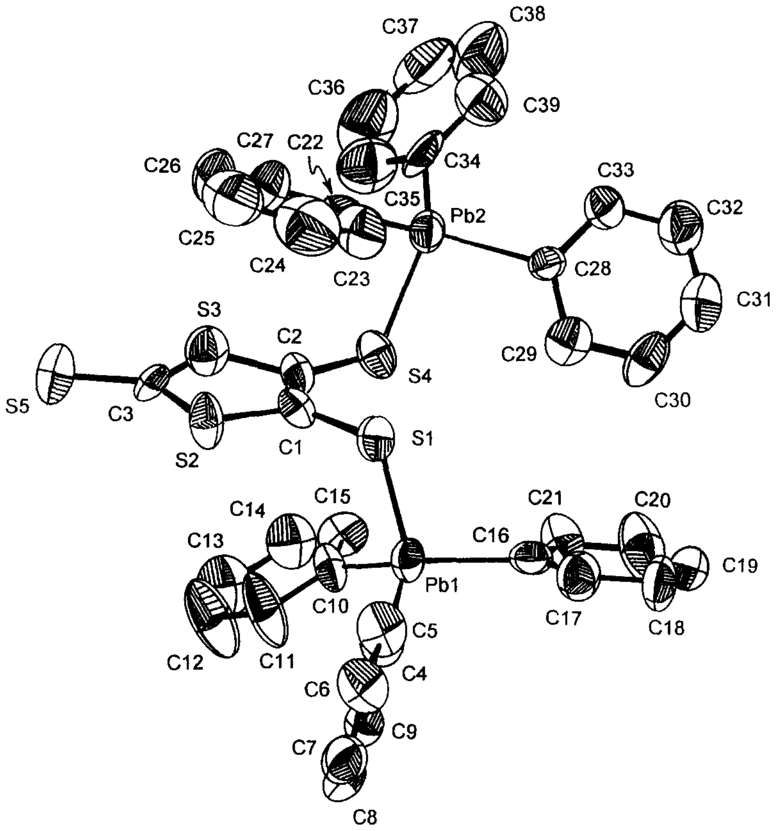


Fig. 1. Molecular structure (thermal ellipsoids at the 30% level) of $(Ph_3Pb)_2(dmit)$ with the atom numbering scheme.

however on scanning anodically from -0.36 V a similar oxidation peak was observed although its magnitude was less and it had shifted to slightly positive potential. This demonstrated that the peaks were related. The oxidation and reduction peak currents peaks showed similar dependences upon the square root of the scan rate $(v)^{0.5}$ (Fig. 3), suggesting that both events were due to an electron transfer rather than on adsorption process. The system was far from reversible with a peak separation of almost 10 times that of the theoretical Nernst value. The shape of the oxidation peak suggests it is simply an oxidative electron transfer. The slope of the graph of E_p against $\log v$ (Fig. 3) is 40 mV, which is intermediate between those expected for the transfer of one and two electrons (58 and 29 mV, respectively). A two electron transfer is indicated. The sharpness of the reduction peak and

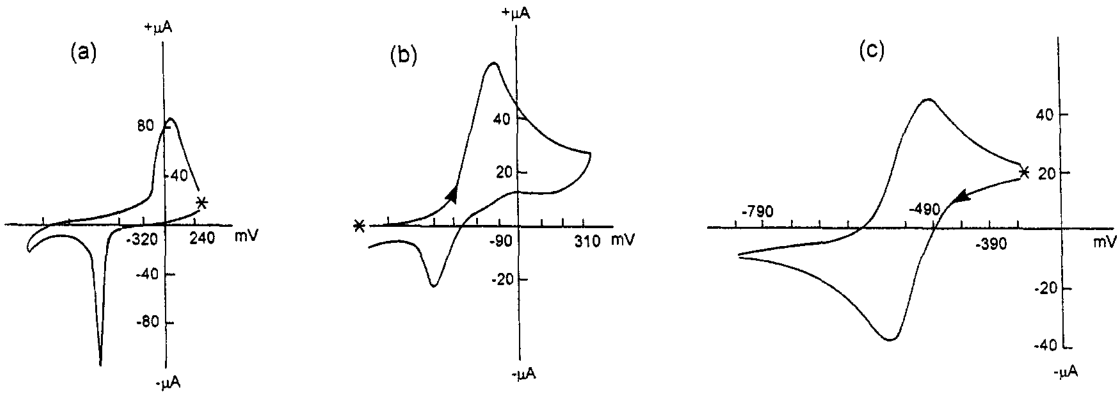
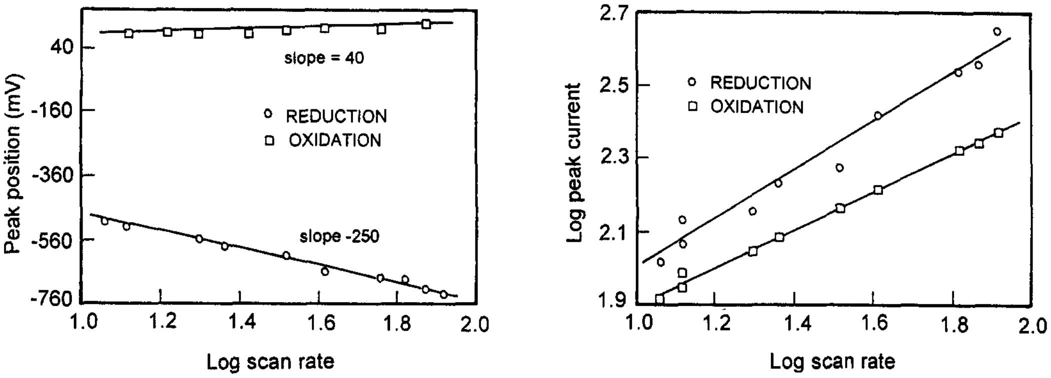


Fig. 2. Cyclic voltammagrams for (a) $Ph_2Pb(dmit)$ (3), (b) $(Ph_3Pb)_2(dmit)$ (4) and (c) $[NMe_4]$ $[Ni(dmit)_2]_2$ at 10^{-3}M in DMF, in 0.1M $[NMe_4]ClO_4$ vs Ag/0.1M $AgNO_3$ reference electrode.



Peak position vs scan rate (mVs^{-1})

Log peak current vs scan rate (mVs^{-1})

Fig. 3. Summary of cyclic voltammetry results for $Ph_2Pb(dmit)$.

the large slope $d(E_p)/d(\log v)$ for the reduction peak suggests that another reaction is occurring, such as a following one electron transfer with a redox potential positive of the first electron transfer. This sharp reduction peak is a common feature of dmit electrochemistry,[5,20] and may be related to a reorganization within the dmit ligand.

Triphenyllead-dmit species, 4

Light-sensitive **4** was isolated from the reaction of Ph_3PbOAc with either $[NEt_4]_2[Zn(dmit)_2]$ (4 : 1 mol ratio), $Na_2(dmit)$ (2 : 1 mol ratio) or $Na_2(dmit)$ (1 : 1 mol ratio) in the presence of excess $[NEt_4]Br$. The dithiolato-bridged compounds,[16] $(Ph_3Pb)_2(edt)$ and $(Ph_3Pb)_2(tdt)$[14] have been previously reported, as have ionic complexes,[19] $[NEt_4]$ $[R_3Pb(mnt)]$. No evidence was obtained in this study for the formation of $[Q]$ $[Ph_3Pb(dmit)]$.

In order to establish the arrangement of the bulky Ph_3Pb groups about the dmit group, the crystal structure of **4** was determined. Compound **4** is monomeric in the solid state, with no intermolecular $S \cdots S$ or $S \cdots Pb$ interactions. The molecular structure, and numbering system are shown in Fig. 1, with selected bond lengths and angles in Table 2. The geometry about each Pb atom is significantly distorted away from tetrahedral. The angles at the lead atoms range from *ca* 99 to 120°. The distortion is similar to that observed[21] in Ph_3PbSPh, in which the S—Pb—C angles are smaller and the C—Pb—C angles larger than ideal tetrahedral angles. The Pb—S bond lengths (2.523(5) and 2.580(4) Å) and Pb—C bond lengths (2.166(7)–2.229(9) Å) in **4** are within expected ranges.

Excluding the phenyl groups, ϕ_2 [C(16)–C(21)], ϕ'_2 [C(28)–C(33)], ϕ_3 [C(4)–C(9)], and ϕ'_3 [C(34)–C(39)], the molecule possesses a pseudo-binary C_2 symmetry. This is due to three aspects of the molecular confirmation: (a) the torsion angles, C(2)—C(1)—S(1)—Pb(1) and C(1)—C(2)—S(4)—Pb(2), are almost equal (*ca* 80°); (b) the torsion angles C(2)—S(4)—Pb(2)—C(22) and C(1)—S(1)—Pb(1)—C(10) are both almost 0° (Table 2); and (c) the planes of ϕ_1 [C(10)–C(15)] and ϕ'_1 [C(22)–C(27)] are nearly orthogonal to the planes of S(1)—Pb(1)—C(10) and S(4)—Pb(2)—C(22), respectively.

Features (b) results in the unfavourable eclipsed conformation of ϕ_1 and ϕ'_1 with respect to the bonds S(1)—C(1) and S(4)—C(2). The planes of ϕ_1 and ϕ'_1 are arranged as in (c) to reduce the non-bonded interactions between the phenyl rings and the dmit ligand. The dmit ligand is effectively inserted between two phenyl rings, with non-bonded C—C and C—S distances of 3.4–3.7 Å. This may be the feature that counterbalances the observed molecular constraints; it resembles a graphite-like system, which results where London dispersion forces may be operating. This would require that the electric vectors of the resonant systems of ϕ_1 and ϕ'_1 and the dmit group were orientated in the same direction.

The crystal structure of $(Ph_3Pb)_2(dmit)$ is dominated by the packing of the phenyl groups. Although there is alignment of alternating dmit ligands, they are too far apart for any interaction to occur.

Cyclic voltammetry of 4

At moderate scan rates (<20 mV s^{-1}), the voltammogram of **4** shows quasi-reversible behaviour. Peak potential varied little with scan rate, however the peak separation was *ca* 0.3 V, which is much

Table 2. Selected bond lengths (Å), bond and torsion angles ( ) and non-bonded intramolecular distances (Å) for $(Ph_3Pb)_2(dmit)$ (**4**)

Bond distances (Å)			
Pb(1)—S(1)	2.523 (5)	Pb(1)—C(4)	2.220 (8)
Pb(1)—C(10)	2.166 (7)	Pb(1)—C(16)	2.190 (9)
Pb(2)—S(4)	2.580 (4)	Pb(2)—C(22)	2.193 (8)
Pb(2)—C(28)	2.209 (8)	Pb(2)—C(34)	2.229 (9)
S(1)—C(1)	1.75 (1)	S(2)—C(1)	1.75 (1)
S(2)—C(3)	1.73 (1)	S(3)—C(2)	1.75 (1)
S(3)—C(3)	1.73 (1)	S(4)—C(2)	1.74 (1)
S(5)—C(3)	1.66 (1)	C(1)—C(2)	1.35 (2)
Non-bonded intramolecular distances (Å)			
C(15)—C(2)	3.53 (2)	C(22)—C(1)	3.54 (2)
C(10)—C(2)	3.54 (2)	C(23)—C(1)	3.74 (2)
C(27)—C(1)	3.90 (2)	C(27)—C(2)	3.60 (2)
S(1)—C(23)	3.69 (1)	S(4)—C(15)	3.36 (1)
Pb(1)—Pb(2)	5.79(1)		
Bond angles ( )			
C(10)—Pb(1)—C(16)	120.2 (3)	C(4)—Pb(1)—C(16)	109.1 (3)
C(4)—Pb(1)—C(10)	110.5 (3)	S(1)—Pb(1)—C(16)	106.3 (3)
S(1)—Pb(1)—C(10)	106.6 (3)	S(1)—Pb(1)—C(4)	102.5 (2)
C(28)—Pb(2)—C(34)	112.0 (3)	C(22)—Pb(2)—C(34)	117.4 (4)
C(22)—Pb(2)—C(28)	120.1 (3)	S(4)—Pb(2)—C(34)	98.8 (3)
S(4)—Pb(2)—C(28)	102.6 (2)	S(4)—Pb(2)—C(22)	101.6 (5)
Pb(1)—S(1)—C(1)	99.5 (4)	C(1)—S(2)—C(3)	98.3 (6)
C(2)—S(3)—C(3)	98.7 (6)	Pb(2)—S(4)—C(2)	101.6 (5)
S(1)—C(1)—S(2)	117.0 (7)	S(2)—C(1)—C(2)	116 (1)
S(1)—C(1)—C(2)	127 (1)	S(4)—C(2)—C(1)	128 (1)
S(3)—C(2)—C(1)	115 (1)	S(3)—C(2)—S(4)	117.3 (7)
S(3)—C(3)—S(5)	124.2 (7)	S(2)—C(3)—S(5)	123.9 (7)
S(2)—C(3)—S(3)	111.8 (7)	Pb(1)—C(4)—C(9)	119.5 (5)
Pb(1)—C(4)—C(5)	120.4 (6)	Pb(1)—C(10)—C(15)	122.9 (6)
Pb(1)—C(10)—C(11)	117.1 (6)	Pb(1)—C(16)—C(21)	122.3 (7)
Pb(1)—C(16)—C(17)	117.5 (6)	Pb(2)—C(22)—C(27)	121.1 (6)
Pb(2)—C(22)—C(23)	118.8 (7)	Pb(2)—C(28)—C(33)	118.2 (5)
Pb(22)—C(28)—C(29)	121.3 (6)	Pb(2)—C(34)—C(39)	121.0 (7)
Pb(2)—C(34)—C(35)	118.8 (7)		
Torsion angles ( )			
S(2)—C(1)—S(1)—Ph(1)	105	S(3)—C(2)—S(4)—Pb(2)	103
C(1)—S(1)—Pb(1)—C(10)	3	C(2)—S(4)—Pb(2)—C(22)	−2
S(1)—Pb(1)—C(10)—C(15)	(6)	S(4)—Pb(2)—C(22)—C(23)	102

greater than the ideal reversible value. Scanning anodically from −0.7 V_{Ag/Ag^+}, an oxidation peak was observed at *ca* −0.1 V, and on the reverse scan, a reduction peak was seen at *ca* −0.4 V (Fig. 2). Scanning cathodically from −0.2 V, no reduction peak was detected, confirming that the two peaks were related. As the scan rate was increased, the peak separation increased. Both the oxidation and reduction peak currents were proportional to the square root of the scan rate $(\nu)^{0.5}$ indicating that both events were due to an electron transfer rather than an absorption process (Fig. 4). The electrochemical mechanism is considered to involve an electron transfer oxidation, followed by a chemical reaction. The chemical reaction is possibly a change in coordination at the metal centre, which gives rise to the large peak separation. The reversal of the oxidation process for **4** does not result in the characteristic sharp reduction peak, observed for **3** and most other dmits so far studied[20] and which has

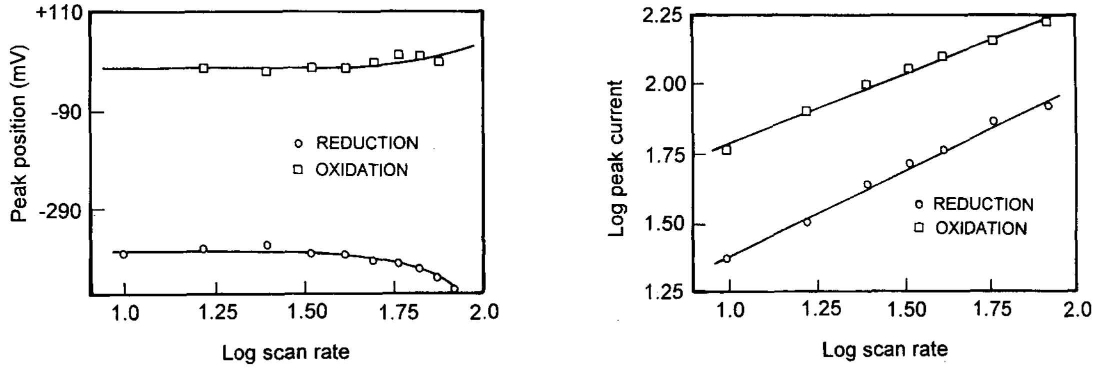


Fig. 4. Summary of cyclic voltammetry results for $(Ph_3Pb)_2(dmit)$.

been abscribed to a reorganisation of the dmit ligand. This electrochemical stability of the dmit ligand in **4** probably arises because the dmit ligand in **4** is acting as a bridging rather than as a chelating ligand.

Inorganic lead compounds

The only inorganic lead dmit compound obtained in this study was $Pb^{II}(dmit)$ (**6**), which was produced from $[NEt_4]_2[Zn(dmit)_2]$ and either $Pb(OAc)_2$ or $Pb(NO_3)_2$. Attempts to prepare $[Pb^{IV}(dmit)_2]$ and $[Pb^{II}(dmit)_2]^{2-}$ or $[Pb^{IV}(dmit)_3]^{2-}$ salts failed. Previously reported lead(II) dithiolate species include $Pb^{II}L_2$ (L_2 = tdt,[14,22] edt[23]), $[Pb^{II}(mnt)_nBr_{2-n}]^{n-}$ ($n = 1, 2$)[24] and $[Pb^{IV}(tdt)_2]$.[22]

Compound **6** was obtained as a dark-violet- to black-coloured amorphous material, highly insoluble in all the usual organic solvents, and was only characterized by elemental analysis and IR spectroscopy. The IR spectrum showed only two major peaks, 1410 (C=C) and 1015 cm^{-1} (C=S). Crystals suitable for X-ray crystallography could not be grown. It is assumed to have a polymeric structure from its solubility behaviour and also by comparison with another lead(II) dithiolate,[23] $Pb^{II}(edt)$, which has been shown to possess a three-dimensional polymeric structure with intermolecular $Pb\cdots S$ interactions. Only with bulky organic groups can $Pb^{II}(SR)_2$ compounds exist as small aggregates, *eg*. $Pb^{II}(SC_6H_2Bu^t_3-2,4,6)_2$ is trimeric in the solid state.[25] No evidence was found for the formation of $[NR_4]_2[Pb^{II}(dmit)_2]$ in the reactions between $[NR_4]_2[Zn(dmit)_2]$ and lead(II) salts; this matches the finding by Dean *et al.*[23] that only Pb(edt) was isolated from a reaction mixture containing $Pb^{II}(NO_3)_2$, $Na_2(edt)$ and excess $[NMe_4]Cl$, but contrasts with the isolation of $[Pb^{II}(mnt)_2]^{2-}$ and $[Pb^{II}(mnt)Br]^-$ salts from reactions involving $Pb^{II}(OAc)_2$ [or $Pb^{IV}(OAc)_4$], $Na_2(mnt)$ and an onium bromide.[24]

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