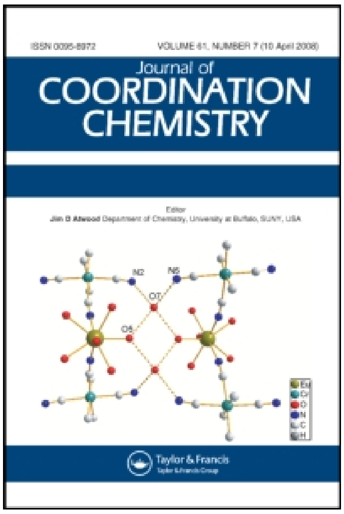

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SYNTHESES AND STRUCTURES OF $[Et_4N]_2[Sn(DMIT)_3]$ AND $[Pb(DMIT)(DMF)]_n$ (DMIT = 2-THIOXO-1,3-DITHIOLE-4,5-DITHIOLATO)

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SYNTHESES AND STRUCTURES OF $[Et_4N]_2[Sn(DMIT)_3]$ AND $[Pb(DMIT)(DMF)]_n$ (DMIT = 2-THIOXO-1,3-DITHIOLE-4,5-DITHIOLATO)

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(Received 30 July 1998)

Two complexes, $[Et_4N]_2[Sn(dmit)_3]$, **1**, and $[Pb(dmit)(DMF)]_n$, **2**, have been obtained and their structures crystallographically determined. In complex **1**, the Sn atom is six-coordinated to six sulfur atoms from three dmit ligands; the anions form a one-dimensional network through S···S contacts shorter than 3.7 Å. Complex **2** forms a two-dimensional polymer, achieved through Pb atom coordinating not only to the chelating sulfur atoms of the dithiolate fragment of dmit, but also to the sulfur atom of the thiocarbonyl group of a dmit ligand. In complex **2**, the central Pb atom is six-coordinated by four sulfur atoms from dmit ligands and two oxygen atoms of *N,N*-dimethylformamide ligands, exhibiting a distorted octahedral structure.

Keywords: Metal-dmit complexes; tin; lead; X-ray structure

INTRODUCTION

In the last two decades, the chemistry of compounds involving dmit (dmit is 2-thioxo-1,3-dithiole-4,5-dithiolate) has been a research focus[1] due to the presence of good electrical conductivity (even superconductivity) in many planar *bis*(dmit)-metal complexes. After the discovery in 1986 of the first formally inorganic molecular superconductor $(TTF)[Ni(dmit)_2]$ (TTF = tetrathiafulvalene),[2(a)] research activity in this area increased and a large

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* Corresponding author.

number of homoleptic and heteroleptic complexes with dmit have been synthesized and structurally characterized.[1–11] These include seven charge transfer salts of dmit, $(NMe_4)_{0.5}[Ni(dmit)_2]$,[3] β-$(NMe_4)_{0.5}[Pd(dmit)_2]$,[4] $(NMe_2Et_2)_{0.5}[Pd(dmit)_2]$,[5] $(TTF)[Ni(dmit)_2]$,[2] α- and α'-$(TTF)[Pd(dmit)_2]$,[6,7] and α-$(EDT\text{-}TTF)[Ni(dmit)_2]$,[8] in which superconductivity has been observed. However, main-group metal complexes with dmit are rare. Herein, two new complexes with dmit, $[Et_4N]_2[Sn(dmit)_3]$, **1**, and $[Pb(dmit)(DMF)]_n$, **2**, are reported.

EXPERIMENTAL

The procedures for preparing **1** and **2** were carried out under nitrogen atmosphere using standard Schlenk techniques, but work up as carried out in air. The chemicals used were of A.R. grade and used without purification; 4,5-*bis*(benzoylthio)-1,3-dithiole-2-thione was prepared following the detailed procedure described by Steimecke.[12] Elemental analysis was performed by the Elemental Analysis Laboratory in our Institute. IR spectra of **1** and **2** were recorded on an FT-IR spectrometer for **1** and on an F750 spectrometer for **2**.

Preparation of $[Et_4N]_2[Sn(dmit)_3]$, 1

Some 0.408 g (1.0 mmol) of 4,5-*bis*(benzoylthio)-1,3-dithiole-2-thione was dissolved in methanol (30 cm^3) containing 0.046 g (2 mmol) of sodium metal. To the resulting purple solution of $Na_2[C_3S_5]$ was added with stirring 0.295 g (0.5 mmol) of $SnCl_2$. After 2 h at room temperature, 25 cm^3 of methanol solution containing an excess of Et_4NBr (0.32 g, 1.5 mmol) was added, precipitating the red product. This was collected by filtration and redissolved in 10 cm^3 of MeCN. It was filtered after stirring for a while at room temperature, the filtrate covered with Et_2O and left to stand in the refrigerator overnight to yield red crystals of complex **1**. Yield: 0.16 g. *Anal.* calcd. for $C_{25}H_{40}N_2S_{15}Sn$: C, 31.01; H, 4.16; N, 2.89%. Found: C, 30.65; H, 4.57; N, 2.85%. IR (KBr pellet, cm^{-1}): 262.6(s), 280.0(s), 309.0(s), 320.8(vs), 334.8(s), 387.6(w), 483.3(vs), 521.7(vs), 780.6(vs), 883.8(s), 1001.3(vs), 1032.5(vs), 1063.3(vs), 1170.8(w).

Preparation of $[Pb(dmit)(DMF)]_n$, 2

To 5 cm^3 of a DMF solution containing 0.38 g (0.5 mmol) of $[Et_4N]_2[MoO(dmit)_2]$[13] was added 0.14 g (0.5 mmol) of $Pb(NO_3)_2$. After stirring for a while at room temperature, the reaction solution was filtered and allowed to stand in air for several days to yield black crystals of complex **2**. Yield: 0.06 g. *Anal.* calcd. for $C_6H_7NOPbS_5$: C, 15.12; H, 1.48; N, 2.94%. Found: C, 14.83; H, 1.52, N, 2.81%. IR (KBr pellet, cm^{-1}): 416.6(w), 443.6(s), 462.8(vs), 538.0(m), 663.4(vs), 881.3(s), 937.2(w), 1018.2(vs), 1056.8(m), 1107.0(s).

X-ray Structure Determinations

Single crystals of complexes **1** and **2** were mounted in glass tubes. X-ray intensity data were collected on a Siemens SMART-CCD diffractometer for **1** and on an Enraf-Nonius CAD4 diffractometer for **2**. The radiation used was graphite-monochromatized MoKα. Complex **1** crystallizes in the monoclinic space group *Cc* (No. 15), while complex **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2). Both structures were solved by direct methods. Crystal data and details of data collection for complexes **1** and **2** are given in Table I. Atomic coordinates are given in Tables II and III. The structures of complexes **1** and **2** are given in Figures 1–4. Full lists of crystallographic data are available from the authors upon request.

$[Et_4N]_2[Sn(dmit)_3]$, 1

The crystal chosen for data collection had dimensions 0.07 × 0.10 × 0.6 mm. Intensities were corrected for Lorentz and polarization effects, some 3303

TABLE I Crystallographic data for complexes **1** and **2**

	1	**2**
Chemical formula	C25H40N2S15Sn	C6H7OPbS5
Formula weight	968.18	476.63
Crystal system:	Monoclinic, *Cc* (No. 15)	Triclinic, $P\bar{1}$(No. 2)
a (Å)	21.721(7)	8.2628(2)
b (Å)	15.589(4)	8.5254(1)
c (Å)	16.275(6)	8.9832(2)
α (°)		97.466(2)
β (°)	131.31(3)	104.013(2)
γ (°)		86.296(2)
V (Å^3)	4139(2)	608.4(2)
Dcalc (g cm^{-3})	1.554	2.60
Z	4	2
Diffractometer	Siemens Smart-CCD	Enraf-Nonius CAD4
Radiation	MoKα (γ = 0.71073 Å)	MoKα (γ = 0.71073 Å)
θ_{max} (°):	23.27	25
T(K):	293	293
Independent reflections	5099	2147
Observed reflections	3303 [$I > 2.0\sigma(I)$]	1972 [$I > 2.0\sigma(I)$]
R	0.0327	0.0324
R_w	0.0703[a]	0.0376[b]

[a] $w = [\sigma^2(Fo)^2 + (0.0331P)^2]^{-1}$, where $P = ((Fo)^2 + 2(Fc)^2)/3$;
[b] $w = [\sigma^2(Fo)^2 + (0.020Fo) + 1.000]^{-1}$.

TABLE II Atomic coordinates and Ueq values (Å^2) for complex **1**

Atom	x/a	y/b	z/c	Ueq
Sn	0.8637(2)	0.25088(3)	1.2365(3)	0.0405(2)
S1	1.0186(4)	0.2392(4)	1.3697(6)	0.050(2)
S2	0.8745(4)	0.1371(4)	1.3594(6)	0.051(2)
S3	1.1114(4)	0.0740(4)	1.4647(6)	0.058(2)
S4	0.9873(4)	−0.0141(4)	1.4469(6)	0.052(2)
S5	1.1451(5)	−0.1032(5)	1.5480(6)	0.067(2)
S6	0.8543(5)	0.1345(4)	1.1160(6)	0.050(2)
S7	0.7102(4)	0.2384(4)	1.1023(5)	0.046(2)
S8	0.7398(4)	−0.0152(4)	1.0272(6)	0.051(2)
S9	0.6166(4)	0.0739(4)	1.0102(5)	0.042(2)
S10	0.5820(5)	−0.1049(4)	0.9259(6)	0.062(2)
S11	0.8596(5)	0.3700(4)	1.3386(6)	0.055(2)
S12	0.8658(5)	0.3697(4)	1.1309(6)	0.057(2)
S13	0.8613(5)	0.5586(4)	1.3226(6)	0.071(2)
S14	0.8656(4)	0.5601(4)	1.1509(6)	0.057(2)
S15	0.8635(11)	0.72709(13)	1.2361(15)	0.1092(10)
C1	1.0240(15)	0.1303(13)	1.4138(19)	0.044(7)
C2	0.9670(11)	0.0884(12)	1.4043(17)	0.035(5)
C3	1.0832(16)	−0.0221(14)	1.4891(20)	0.044(7)
C4	0.7640(15)	0.0964(13)	1.0690(18)	0.049(7)
C5	0.7039(14)	0.1372(12)	1.0643(16)	0.033(6)
C6	0.6429(15)	−0.0178(14)	0.9855(18)	0.042(7)
C7	0.8669(15)	0.4548(14)	1.2768(20)	0.058(8)
C8	0.8687(13)	0.4619(14)	1.1967(18)	0.036(5)
C9	0.8598(23)	0.6202(5)	1.2284(34)	0.066(4)
N1	1.1371(9)	0.3231(10)	1.2334(12)	0.046(5)
N2	1.0993(10)	−0.1726(10)	1.2505(13)	0.047(5)
C11	1.1927(11)	0.3582(9)	1.2195(13)	0.057(5)
C12	1.2512(8)	0.4342(8)	1.3117(10)	0.072(4)
C21	1.0850(11)	0.3897(11)	1.2363(14)	0.050(5)
C22	1.0359(10)	0.4575(11)	1.1416(13)	0.096(7)
C31	1.0692(13)	0.2731(13)	1.1217(18)	0.060(7)
C32	1.0143(9)	0.2175(9)	1.1224(12)	0.072(4)
C41	1.1838(10)	0.2697(9)	1.3318(13)	0.048(5)
C42	1.2164(11)	0.1908(11)	1.3213(14)	0.083(6)
C51	1.0568(11)	−0.2374(10)	1.1544(14)	0.060(6)
C52	0.9928(10)	−0.3011(11)	1.1399(14)	0.074(6)
C61	1.1306(12)	−0.1076(12)	1.2201(16)	0.065(6)
C62	1.1774(10)	−0.0388(9)	1.3002(13)	0.074(5)
C71	1.0359(10)	−0.1249(10)	1.2517(13)	0.055(5)
C72	0.9602(8)	−0.0924(8)	1.1500(10)	0.069(4)
C81	1.1557(12)	−0.2191(13)	1.3532(17)	0.053(7)
C82	1.2288(8)	−0.2614(8)	1.3756(11)	0.069(4)

reflections with $I > 2\sigma(I)$ of 5099 unique reflections were used to solve the structure using the SHELXTL program.[14] The atoms of the anion were refined with anisotropic temperature factors. The positions of the hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinement.

TABLE III Atomic coordinates and *U*eq values (Å^2) for complex **2**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*eq
Pb	1.00028(4)	0.24357(4)	−0.05193(4)	0.03168(8)
S1	0.9596(3)	0.3494(3)	−0.3232(3)	0.0324(5)
S2	1.2236(3)	0.0536(3)	−0.1549(2)	0.0310(5)
S4	1.2975(3)	−0.0166(3)	−0.4639(2)	0.0282(5)
S3	1.0850(3)	0.2279(3)	−0.6007(2)	0.0318(5)
S5	1.2668(3)	0.0108(3)	−0.7969(2)	0.0358(6)
O	1.2334(8)	0.4417(9)	0.0794(9)	0.050(2)
N	1.505(1)	0.4612(9)	0.212(1)	0.042(2)
C1	1.087(1)	0.2156(9)	−0.4087(9)	0.025(2)
C2	1.190(1)	0.0979(9)	−0.3444(9)	0.026(2)
C3	1.218(1)	0.071(1)	−0.6284(9)	0.026(2)
C4	1.671(1)	0.386(1)	0.248(2)	0.067(4)
C5	1.484(2)	0.622(2)	0.283(2)	0.095(5)
C6	1.380(1)	0.388(1)	0.117(1)	0.043(3)

[Pb(dmit)(DMF)]$_n$, 2

The crystal chosen for data collection had dimensions 0.075 × 0.125 × 0.20 mm. A total of 2147 reflections were collected, of which 2147 were unique and 1972 observed, $I > 2.0\sigma(I)$. Intensities were corrected for Lorentz and polarization effects, and a DIFABS[15] empirical absorption correction was applied. The Pb atom was located by direct methods using MULTAN[16] and the remaining non-H atoms were located in the succeeding Fourier syntheses. H atoms were placed in geometrically calculated positions, with C–H distance 0.95 Å, but their parameters were not included in the refinement. All calculation were performed on a Compaq PL4/50 computer using the MolEN program package.[17]

RESULTS AND DISCUSSION

The syntheses of complexes **1** and **2** can be described as follows:

$$\mathrm{Na_2dmit + SnCl_2 + Et_4NBr \xrightarrow{O_2} [Et_4N]_2[Sn(dmit)_3]} \qquad (1)$$

$$n\mathrm{[Et_4N]_2[MoO(dmit)_2]} + n\mathrm{Pb(NO_3)_2 \xrightarrow{DMF} [Pb(dmit)(DMF)]}_n \qquad (2)$$

The reaction of Na_2dmit with $SnCl_2$ leads to the formation of $[Sn^{IV}(dmit)_3]^{2-}$ instead of $[Sn^{II}(dmit)_3]^{4-}$, which may be because $[Sn(dmit)_3]^{4-}$ is easily oxidized to $[Sn(dmit)_3]^{2-}$ by atmospheric oxygen. The synthesis of complex **2** reported here is based on equation (2). An attempt has been made to synthesize complex **2** by the reaction of Na_2dmit with $Pb(NO_3)_2$, but it failed. Complexes **1** and **2** are stable and remain unaffected by atmospheric oxygen and moisture for long times.

The structure of **1** consists of two anions and four cations in the unit cell. Selected bond lengths and angles for **1** are listed in Table IV. The numbering scheme and coordination geometry of **1** are shown in Figure 1; the tin atom

TABLE IV Selected bond distances (Å) and angles (°) for complex **1**

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Sn	S7	2.512(8)	S8	C6	1.73(3)
Sn	S11	2.533(6)	S8	C4	1.82(2)
Sn	S1	2.534(7)	S9	C6	1.68(2)
Sn	S12	2.547(7)	S9	C5	1.77(2)
Sn	S2	2.565(7)	S10	C6	1.68(2)
Sn	S6	2.579(7)	S11	C7	1.73(2)
S1	C1	1.82(2)	S12	C8	1.77(2)
S2	C2	1.79(2)	S13	C9	1.79(3)
S3	C1	1.73(2)	S13	C7	1.82(2)
S3	C3	1.76(2)	S14	C9	1.64(3)
S4	C2	1.68(2)	S14	C8	1.68(2)
S4	C3	1.72(3)	S15	C9	1.669(9)
S5	C3	1.62(2)	C1	C2	1.32(3)
S6	C4	1.67(3)	C4	C5	1.41(3)
S7	C5	1.67(2)	C7	C8	1.334(12)

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
S7	Sn	S11	91.5(2)	C2	C1	S3	117.1(16)
S7	Sn	S1	171.40(6)	C2	C1	S1	127.4(18)
S11	Sn	S1	95.3(2)	S3	C1	S1	115.4(15)
S7	Sn	S12	94.2(2)	C1	C2	S4	117.0(15)
S11	Sn	S12	86.19(6)	C1	C2	S2	123.5(16)
S1	Sn	S12	91.4(3)	S4	C2	S2	119.3(11)
S7	Sn	S2	90.6(2)	S5	C3	S4	127.5(15)
S11	Sn	S2	91.1(2)	S5	C3	S3	121.4(16)
S1	Sn	S2	84.0(2)	S4	C3	S3	111.1(13)
S12	Sn	S2	174.5(3)	C5	C4	S6	129.0(17)
S7	Sn	S6	83.8(2)	C5	C4	S8	112.5(17)
S11	Sn	S6	174.5(3)	S6	C4	S8	118.2(14)
S1	Sn	S6	89.7(2)	C4	C5	S7	124.1(17)
S12	Sn	S6	91.5(2)	C4	C5	S9	115.2(16)
S2	Sn	S6	91.56(7)	S7	C5	S9	120.7(14)
C1	S1	Sn	96.3(8)	S9	C6	S10	124.0(15)
C2	S2	Sn	96.5(7)	S9	C6	S8	113.7(13)
C1	S3	C3	96.1(12)	S10	C6	S8	122.3(14)
C2	S4	C3	98.8(10)	C8	C7	S11	134.8(23)
C4	S6	Sn	94.4(8)	C8	C7	S13	112.3(23)
C5	S7	Sn	97.6(8)	S11	C7	S13	112.6(14)
C6	S8	C4	98.4(11)	C7	C8	S14	119.3(23)
C6	S9	C5	99.8(11)	C7	C8	S12	120.8(22)
C7	S11	Sn	97.0(8)	S14	C8	S12	119.7(12)
C8	S12	Sn	101.1(7)	S14	C9	S15	127.1(21)
C9	S13	C7	95.4(12)	S14	C9	S13	112.6(4)
C9	S14	C8	100.4(11)	S15	C9	S13	119.9(22)

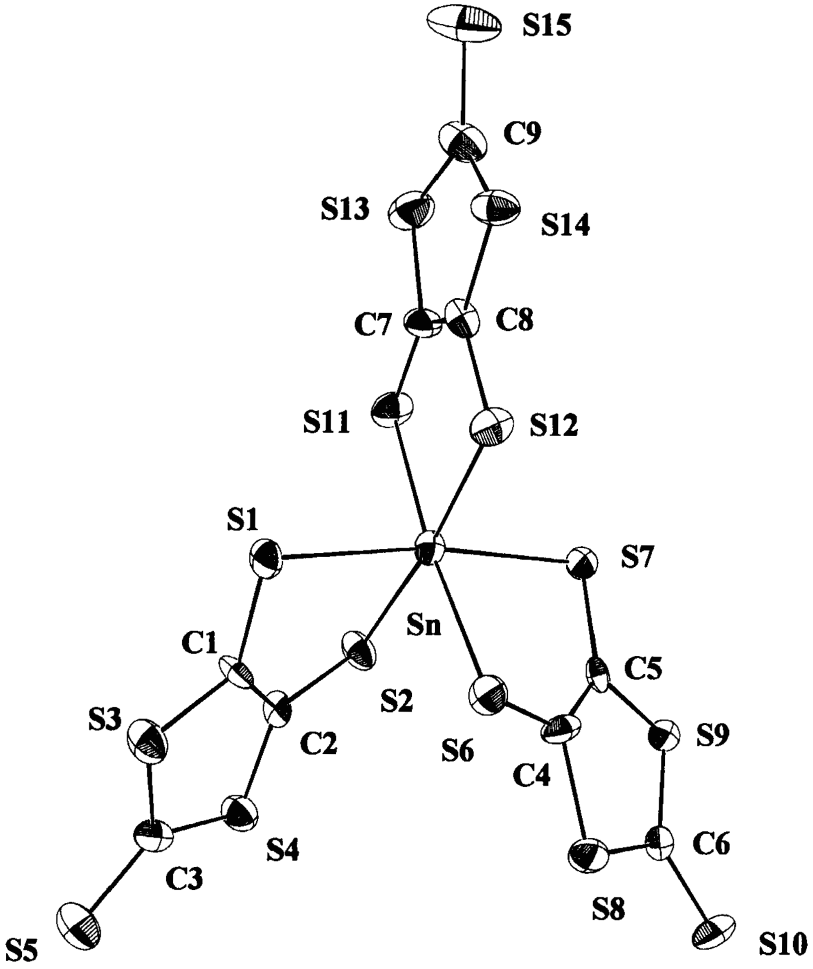

FIGURE 1 The structure of complex **1**.

is six-coordinated by six sulfur atoms from three dmit ligands to form an octahedral geometry. The six sulfur donor atoms are located around tin at an average distance of 2.545(7) Å, which is in quite good accordinance with the value 2.535(2) Å reported for the internuclear distances in $[(C_2H_5)_2PS_2]_2$-SnI_2,[18] but slightly longer than the value 2.471(2) Å reported for $Sn(CH_2$-$CH_2CO_2Me)_2(C_3S_5)$[19] and 2.484(1) Å (av.) for MePhSn(dmit).[20] All three $SnS_2C_2S_2CS$ units are nearly planar. The average C–S (1.73(2) Å) and C–C (1.35(3) Å) distances in the chelate rings are similar to those found for $Sn(CH_2CH_2CO_2Me)_2(C_3S_5)$[19] and MePhSn(dmit).[20] As shown in Figure 2, in complex **1**, interanionic S···S contacts shorter than 3.7 Å involve S1···S7′

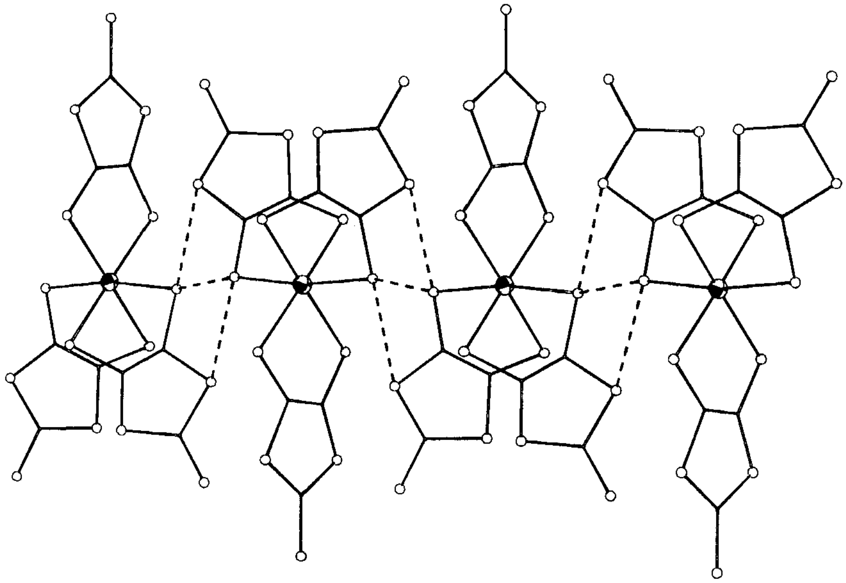

FIGURE 2 The one-dimensional network formed by complex **1** through S···S contacts less than 3.7 Å viewed down the *c* axis.

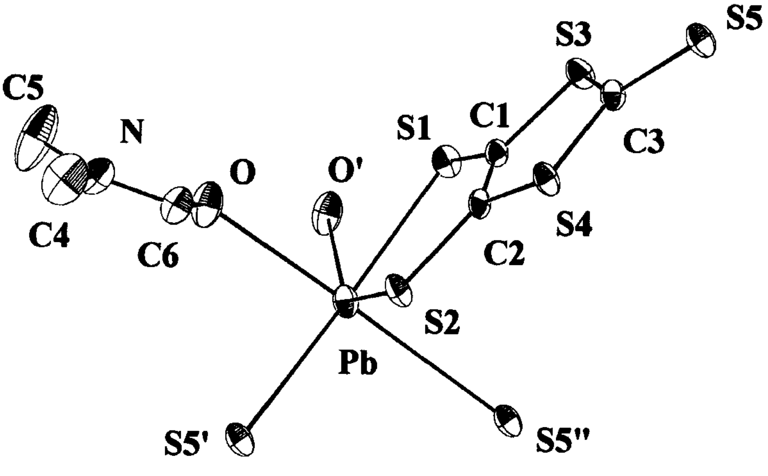

FIGURE 3 Environment of the Pb atom in complex **2**.

(3.44(1) Å), S1···S9′ (3.31(1) Å) and S3···S7′ (3.44(2) Å), through which the anions in complex **1** form a one-dimensional network.

Complex **2** consists of repeating units of Pb(dmit)(DMF). Figure 3 shows the geometry around the Pb atom in complex **2**. As shown in Figure 3, the lead atom is six-coordinated to two S atoms of the dithiolate fragment of dmit ligands and two S atoms of thiocarbonyl groups of dmit ligands in adjacent units, together with two O atoms of DMF ligands. The geometry around the lead can be described as a distorted octahedral structure. In complex **2**, the Pb–S_{C-S} (S_{C-S} stands for the sulfur atom of the dithiolate fragment of dmit ligand) bond distances in the repeating unit range from 2.633(2) to 2.648(2) Å, slightly longer than those (from 2.523(5) to 2.580(4) Å) in $(Ph_3Pb)_2(dmit)$,[21] whereas the Pb–$S_{C=S}$ ($S_{C=S}$ stands for the sulfur atom

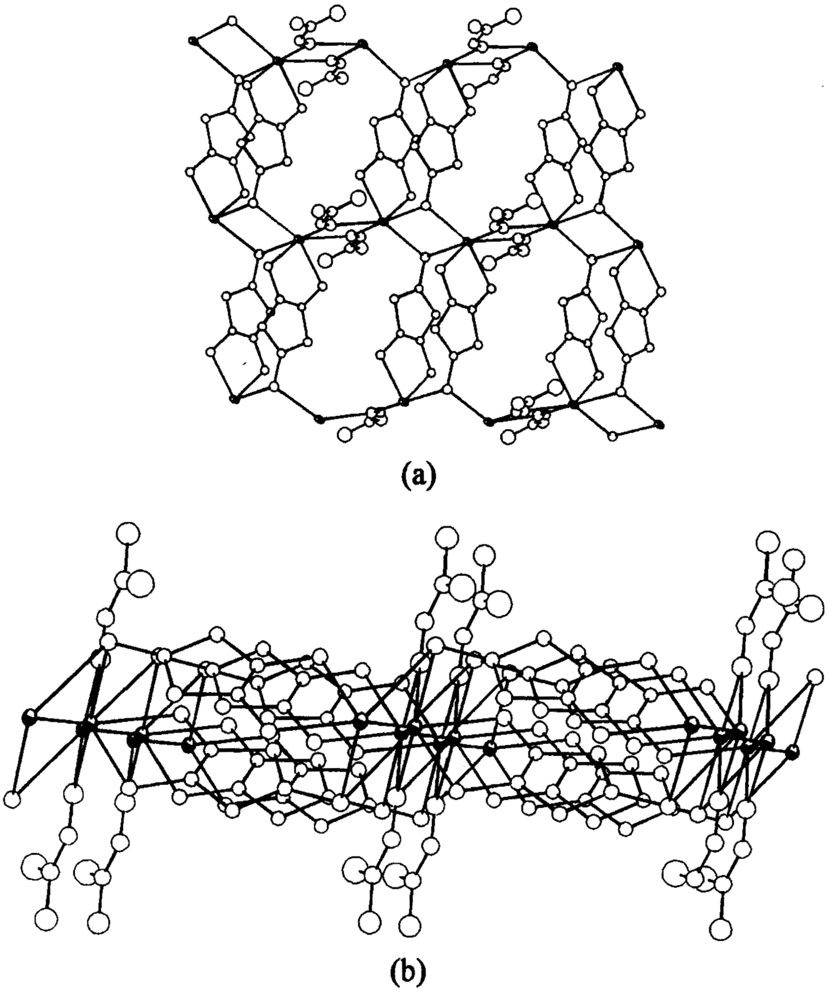

FIGURE 4 Part of the two-dimensional polymer of complex **2**, (a) viewed down *a* axis; (b) viewed down *b* axis.

TABLE V Selected bond distances (Å) and angles (°) for complex **2**

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Pb	S1	2.648(2)	S2	C2	1.748(8)
Pb	S2	2.633(2)	S4	C2	1.727(8)
Pb	S5′[a]	3.495(2)	S4	C3	1.711(8)
Pb	S5″[b]	3.133(2)	S3	C1	1.734(8)
Pb	O	2.610(7)	S3	C3	1.707(8)
Pb	O′[c]	3.201(7)	S5	C3	1.669(9)
S1	C1	1.734(8)	C1	C2	1.36(2)

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
S1	Pb	S2	82.35(7)	Pb	S1	C1	100.8(3)
S1	Pb	S5′	142.68(6)	Pb	S2	C2	101.4(3)
S1	Pb	S5″	89.51(6)	C2	S4	C3	98.2(4)
S1	Pb	O	92.5(2)	C1	S3	C3	98.5(4)
S1	Pb	O′	67.6(2)	Pb	O	C6	118.0(6)
S2	Pb	S5′	61.43(6)	S1	C1	S3	117.4(4)
S2	Pb	S5″	88.37(6)	S1	C1	C2	128.0(7)
S2	Pb	O	89.4(2)	S3	C1	C2	114.6(6)
S2	Pb	O′	148.7(2)	S2	C2	S4	117.3(4)
S5′	Pb	S5″	97.62(6)	S2	C2	C1	126.7(7)
S5′	Pb	O	79.3(2)	S4	C2	C1	116.0(7)
S5′	Pb	O′	145.2(1)	S4	C3	S3	112.6(5)
S5″	Pb	O	176.8(2)	S4	C3	S5	123.7(5)
S5″	Pb	O′	99.6(1)	S3	C3	S5	123.7(5)
O	Pb	O′	83.6(2)				

[a] $x, y, 1+z$; [b] $2-x, -y, -1-z$; [c] $2-x, 1-y, -z$.

of the thiocarbonyl group of dmit ligand) distances between the repeating units (Pb–S5′, 3.133(2) Å, Pb–S5″, 3.495(2) Å) are relatively longer and close to corresponding Pb–S distances found in $[Pb\{S_2(i\text{-}C_3H_7O)_2\}_2]$[22] and found in $[Pb(S_2COC_2H_5)_2]$.[23] It is noted that in **2** the sulfur atom of the thiocarbonyl group is able to coordinate and it does so. Through $Pb-S_{C=S}$ and Pb–O interactions between repeating units, complex **2** form a two-dimensional structural polymer as shown in Figure 4. The Pb···Pb distances in PbS_2Pb four-membered rings and PbO_2Pb four-membered rings of complex **2** are 4.35 and 4.37 Å, respectively, close to those (range from 4.30 to 4.52 Å) found in $Pb[(CH_3)_2NC_4O_3]_2(OH_2)_2 \cdot H_2O$, $Pb[(C_2H_5)_2NC_4O_3]_2(H_2O)$ and $Pb(C_4O_4)_2(H_2O)_4$.[24] Contrary to complex **1**, no S···S contacts less than 3.7 Å are found in complex **2** (see Table V).

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