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Structure of a Novel Neutral Lead(II) Complex with Dipropyldithiocarbamate

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Abstract

The synthesis and X-ray structure of a novel tetramer of Pb(II) with the dipropyldithiocarbamato ligand is described. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.576(2)$, $b = 14.151(4)$, $c = 16.175(4)$ Å, $\alpha = 104.84(2)$, $\beta = 102.26(2)$, $\gamma = 90.62(2)°$, $V = 2065(1)$ Å^3. Unit cell dimensions and data collection were done at 130(1) K using graphite-monochromated Mo Kα radiation. The conventional R factor is 0.030 for 5323 unique observed reflections with the goodness-of-fit parameter = 1.35. The structure consists of a sulfur-bridged neutral tetrameric species where each Pb(II) ion is pentacoordinated.

Introduction

There is much interest in determining when the size of the ligand causes the typical coordination geometry of a metal to change to give a species having either a higher or a lower coordination number. For simple ligands substituents on the atom next to the donor can be increased in size, but with 1,1-dithioligands the substituents on the atom at least two atoms away from the donor must be increased in size to achieve the desired result. Pb(II) complexes of both dimethyldithiocarbamate [1] and diethyldithiocarbamate [2] have been prepared and found to be monomeric with a distorted four-coordinated square pyramidal geometry. However, a weak intermolecular interaction with an adjacent molecule occurs giving an overall coordination number of six to the Pb(II) ion. For the dimethyldithiocarbamate complex, the nearest intermolecular S atoms are 3.361(6) Å away from Pb(II) while for diethyldithiocarbamate this distance is an average of about 3.50 Å. When we increased the length of the hydrocarbon chain by one methylene group, we found that the coordination number of Pb(II) had been changed from four to five resulting in a novel tetrameric species. This work is part of a research program to develop an α-emitting radiopharmaceutical that binds strongly to Pb(II) and Bi(III). Crystalline dipropyldithiocarbamate complexes of both Pb(II) and Bi(III) have now been prepared and we wish to report here the structure of the lead complex. Structure elucidation of the Bi(III) complex is in progress.

Experimental

The ligand was synthesized following a published procedure [3] as the potassium salt. In a typical preparation of the Pb(II) complex, an aqueous solution of $Pb(NO)_3 \cdot 6H_2O$ was allowed to react with an aqueous solution of the ligand in 1:2 molar ratio at room temperature (r.t.) under nitrogen whereupon a light yellow solid precipitated in 93% yield. Single crystals of $[Pb(C_{14}H_{28}N_2S_4)]_2$ was obtained as light yellow rectangular parallelopipeds on slow evaporation of an acetone solution at r.t. IR data showed that the powder was identical to the crystalline form.

X-ray Diffraction Studies

A crystal of the title compound was mounted at the end of a glass fibre. All diffraction measurements were made at 130(1) K with a Syntex $P2_1$ diffractometer using graphite monochromated Mo Kα radiation. Details of data collection and refinement are presented in Table I. Data were corrected for decay, absorption and L_p effects.

The structure was solved by the heavy atom method and refined on F using full matrix least-squares techniques with the SHELXTL (version 5.1) program package [4]. Details of the structure solution technique used have been described earlier [5]. Anisotropic refinement of all non-hydrogen atoms led to the convergence with $R_f = 0.030$ and $R_{wf} = 0.032$ with the goodness of fit parameter = 1.345. Neutral atom scattering factors including anomalous dispersion effects were taken from the 'International Tables for X-ray Crystallography' [6]. Final atomic parameters are listed in Table II and a view of the structure is given in Figs. 1 and 2. See also 'Supplementary Material'.

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TABLE I. Crystal and Refinement Data

Formula	$2(C_{14}H_{28}N_2S_4Pb)$
Formula weight (a.u.)	1119.66
a (Å)	9.576(2)
b (Å)	14.151(4)
c (Å)	16.175(4)
α (°)	104.84(2)
β (°)	102.26(2)
γ (°)	90.62(2)
V (Å^3)	2065(1)
Space group	$P\bar{1}$
Z	2
No. of reflections used to determine cell constants	$15(9.65 < \theta < 13.55)$
Diffractometer	Syntex $P2_1$
Temperature (K)	130(1)
Radiation used	graphite monochromated Mo Kα (0.71073 Å)
D_{calc} (g cm^{-3})	1.80
Crystal dimensions (mm)	0.13 × 0.16 × 0.18
Linear absorption coefficient (cm^{-1})	84.31
Data collection method	ω-scan
2θ range (°)	$0 < 2\theta < 50$
ω-scan range (°)	1.0
Scan rate (°)	variable
No. of standard reflections	2
% Variation in standard intensity	<0.1
Octants collected ($+h, \pm k, \pm l$)	11, ±16, ±18
R(Merge)[a]	0.0001
No. of data used in refinement	$5323\ (F_o > 3\sigma(F_o))$
Data:parameter ratio	~14
Weighting scheme[b]	$w = 1/[(\sigma^2(F_o) + gF_o{}^2]$
Systematic absences	none
Final *GOF*	1.35
Final R_f	0.030
Final R_{wf}	0.032
Final largest shift/e.s.d.	0.013
Highest peak[c] in final difference map (e/Å^3)	1.67

[a] $R(\text{merge}) = (\Sigma(N\Sigma(\text{weight}(F(\text{mean}) - F)^2))/\Sigma((N - 1)\Sigma(\text{weight}FF)))^{1/2}$, where the inner summations are over the *N* equivalent reflections averaged to give *F*(mean) and the outer summations are over all unique observed reflections. [b] *g* was refined by fitting $(F_o - F_c)^2$ to $(\Sigma^2(F) + \text{abs}(g)FF)/K$ (where *K* is a scale factor) to put weight on an approximately absolute scale. For the present structure $g = 0.00018$. [c] Large peaks near the Pb atoms may be due to inadequate absorption corrections.

TABLE II. Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U[a]
Pb(A)	−5(1)	1679(1)	250(1)	18(1)*
S(1A)	−1120(3)	1104(2)	1464(2)	19(1)*
S(2A)	2148(2)	202(2)	344(2)	19(1)*
S(3A)	−383(3)	3630(2)	1311(2)	32(1)*
S(4A)	2122(3)	2472(2)	1728(2)	24(1)*
N(1A)	−3317(8)	−230(5)	1011(5)	18(3)*
N(2A)	966(9)	3657(6)	2937(5)	25(3)*
C(1A)	−2302(9)	158(7)	730(6)	17(3)*
C(2A)	−4411(10)	−969(7)	414(6)	19(3)*
C(3A)	−4035(11)	−2020(7)	371(7)	28(4)*
C(4A)	−5214(12)	−2739(8)	−260(7)	37(4)*
C(5A)	−3441(10)	77(7)	1938(6)	22(3)*
C(6A)	−4281(11)	1008(8)	2125(7)	28(4)*
C(7A)	−4251(13)	1378(10)	3107(7)	47(5)*
C(8A)	897(11)	3321(7)	2072(7)	24(3)*
C(9A)	2026(11)	3343(8)	3614(7)	31(4)*
C(10A)	3461(14)	3940(9)	3880(8)	48(5)*
C(11A)	4416(13)	3692(9)	4642(8)	47(5)*
C(12A)	−43(13)	4337(8)	3269(7)	38(4)*
C(13A)	−1372(14)	3788(10)	3348(9)	53(6)*
C(14A)	−2407(17)	4515(12)	3708(12)	83(8)*
Pb(B)	1712(1)	178(1)	2391(1)	19(1)*
S(1B)	−138(3)	−1405(2)	2037(2)	22(1)*
S(2B)	2794(3)	−1787(2)	1726(2)	29(1)*
S(3B)	2948(3)	123(2)	4072(2)	35(1)*
S(4B)	187(3)	1027(2)	3647(2)	22(1)*
N(1B)	838(8)	−3167(6)	1634(5)	22(3)*
N(2B)	1470(9)	987(6)	5257(5)	28(3)*
C(1B)	1152(10)	−2225(7)	1785(6)	18(3)*
C(2B)	−535(10)	−3583(7)	1699(7)	24(4)*
C(3B)	−1579(11)	−3977(8)	808(7)	32(4)*
C(4B)	−2997(12)	−4394(8)	933(9)	46(5)*
C(5B)	1853(11)	−3925(7)	1377(7)	28(3)*
C(6B)	2770(11)	−4175(8)	2155(8)	36(4)*
C(7B)	3821(13)	−4924(10)	1889(10)	57(6)*
C(8B)	1547(11)	736(7)	4408(7)	26(4)*
C(9B)	2605(13)	777(9)	5945(7)	41(5)*
C(10B)	4047(24)	2335(19)	6149(15)	177(15)*
C(11B)	3486(19)	1710(13)	6591(11)	88(8)*
C(12B)	184(12)	1407(8)	5539(7)	33(4)*
C(13B)	79(14)	2505(8)	5677(7)	44(4)*
C(14B)	−1392(16)	2741(11)	5794(10)	65(7)*

[a] Starred items: equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

Results and Discussion

The structure of the Pb(II) complex consists of neutral discrete tetrameric species (Fig. 2; a and a′; b and b′) where each Pb(II) atom in the tetramer is pentacoordinated. Only a and b are present in the asymmetric unit; a′ and b′ are related by a center of inversion. Several transition metal complexes of 1,1-dithio ligands are known where S acts as a bridge between two metal ions [7] but this structure is the first example in whicn a Pb(II) ion is involved. When 1,1-dithio ligands act as chelates, they make four-membered rings which are under strain. One way to relieve the strain is by making the M–S bonds slightly unequal in length [7]. However, the extent of the asymmetric binding (Table III) also suggests that the lone-pair on Pb(II) is stereochemically active.

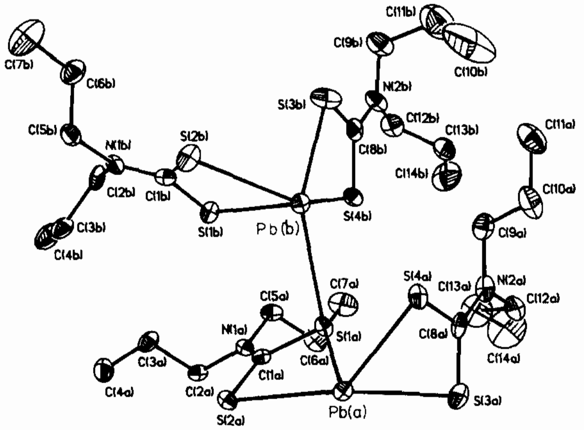

Fig. 1. View of the title compound showing the atom numbering scheme. H atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

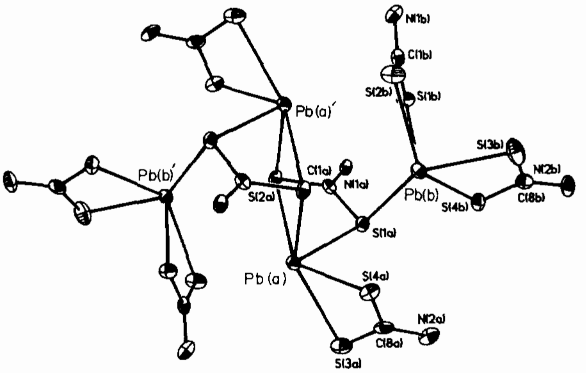

Fig. 2. View of the tetramer. Alkyl groups have been omitted for clarity. Thermal ellipsoids are at the 50% probability level.

TABLE III. Bond Lengths (Å)

Pb(A)–S(1A)	2.711(3)	Pb(A)–S(2A)	2.960(2)
Pb(A)–S(3A)	2.926(3)	Pb(A)–S(4A)	2.763(2)
S(1A)–C(1A)	1.751(8)	S(2A)–C(1A)	1.719(10)
S(3A)–C(8A)	1.690(10)	S(4A)–C(8A)	1.759(10)
N(1A)–C(1A)	1.325(13)	N(1A)–C(2A)	1.468(10)
N(1A)–C(5A)	1.481(12)	N(2A)–C(8A)	1.345(13)
N(2A)–C(9A)	1.488(14)	N(2A)–C(12A)	1.457(14)
C(2A)–C(3A)	1.523(14)	C(3A)–C(4A)	1.518(13)
C(5A)–C(6A)	1.548(15)	C(6A)–C(7A)	1.534(16)
C(9A)–C(10A)	1.525(16)	C(10A)–C(11A)	1.492(18)
C(12A)–C(13A)	1.529(19)	C(13A)–C(14A)	1.530(22)
Pb(B)–S(1B)	2.704(2)	Pb(B)–S(2B)	2.994(3)
Pb(B)–S(3B)	2.747(3)	Pb(B)–S(4B)	2.784(3)
S(1B)–C(1B)	1.744(10)	S(2B)–C(1B)	1.714(10)
S(3B)–C(8B)	1.714(11)	S(4B)–C(8B)	1.723(10)
N(1B)–C(1B)	1.312(12)	N(1B)–C(2B)	1.470(13)
N(1B)–C(5B)	1.495(13)	N(2B)–C(8B)	1.346(13)
N(2B)–C(9B)	1.473(14)	N(2B)–C(12B)	1.481(15)
C(2B)–C(3B)	1.534(13)	C(3B)–C(4B)	1.548(17)
C(5B)–C(6B)	1.499(16)	C(6B)–C(7B)	1.515(17)
C(9B)–C(11B)	1.563(18)	C(10B)–C(11B)	1.435(35)
C(12B)–C(13B)	1.520(16)	C(13B)–C(14B)	1.491(21)

Normally, with 1,1-dithio ligands, Pb(II) makes a distorted four-coordinate pyramidal PbS_4 unit and then increases its coordination number to six by weakly binding to two sulfur atoms on an adjacent molecule. In the present structure, the combined effects of an additional methylene group and the lone pair on Pb(II) have distorted the coordination geometry even further causing a considerable gap in the PbS_4 coordination sphere. However, only one sulfur atom, S(1a), from the nearest neighbour comes close enough to bind to Pb(b) (Pb(B)...S(1a) = 3.268(6)

TABLE IV. Bond Angles (°)

S(1A)–Pb(A)–S(2A)	89.7(1)	S(1A)–Pb(A)–S(3A)	82.4(1)
S(2A)–Pb(A)–S(3A)	136.2(1)	S(1A)–Pb(A)–S(4A)	80.3(1)
S(2A)–Pb(A)–S(4A)	73.2(1)	S(3A)–Pb(A)–S(4A)	63.0(1)
Pb(A)–S(1A)–C(1A)	96.9(4)	Pb(A)–S(2A)–C(1A)	101.0(3)
Pb(A)–S(3A)–C(8A)	82.9(3)	Pb(A)–S(4A)–C(8A)	86.9(3)
C(1A)–N(1A)–C(2A)	121.7(8)	C(1A)–N(1A)–C(5A)	122.1(7)
C(2A)–N(1A)–C(5A)	116.1(8)	C(8A)–N(2A)–C(9A)	123.1(8)
C(8A)–N(2A)–C(12A)	121.3(9)	C(9A)–N(2A)–C(12A)	115.6(8)
S(1A)–C(1A)–N(1A)	119.0(7)	S(1A)–C(1A)–S(2A)	118.6(6)
N(1A(–C(1A)–S(2A)	122.3(6)	N(1A)–C(2A)–C(3A)	113.9(7)
C(2A)–C(3A)–C(4A)	110.7(8)	N(1A)–C(5A)–C(6A)	111.8(8)
C(5A)–C(6A)–C(7A)	110.8(9)	S(3A)–C(8A)–S(4A)	119.3(6)
S(3A)–C(8A)–N(2A)	122.4(8)	S(4A)–C(8A)–N(2A)	118.2(7)
N(2A)–C(9A)–C(10A)	113.0(10)	C(9A)–C(10A)–C(11A)	111.0(11)
N(2A)–C(12A)–C(13A)	111.1(9)	C(12A)–C(13A)–C(14A)	110.2(11)
S(1B)–Pb(B)–S(2B)	63.0(1)	S(1B)–Pb(B)–S(3B)	95.7(1)
S(2B)–Pb(B)–S(3B)	89.0(1)	S(1B)–Pb(B)–S(4B)	85.1(1)
S(2B)–Pb(B)–S(4B)	137.0(1)	S(3B)–Pb(B)–S(4B)	65.1(1)
Pb(B)–S(1B)–C(1B)	93.0(3)	Pb(B)–S(2B)–C(1B)	84.1(3)
Pb(B)–S(3B)–C(8B)	88.2(4)	Pb(B)–S(4B)–C(8B)	86.8(4)

(continued)

TABLE IV. *(continued)*

C(1B)–N(1B)–C(2B)	123.8(8)	C(1B)–N(1B)–C(5B)	122.8(8)
C(2B)–N(1B)–C(5B)	113.4(8)	C(8B)–N(2B)–C(9B)	121.6(9)
C(8B)–N(2B)–C(12B)	121.8(8)	C(9B)–N(2B)–C(12B)	116.3(9)
S(1B)–C(1B)–S(2B)	119.5(6)	S(1B)–C(1B)–N(1B)	119.1(7)
S(2B)–C(1B)–N(1B)	121.4(7)	N(1B)–C(2B)–C(3B)	113.4(9)
C(2B)–C(3B)–C(4B)	110.2(10)	N(1B)–C(5B)–C(6B)	112.3(8)
C(5B)–C(6B)–C(7B)	111.8(10)	S(3B)–C(8B)–S(4B)	119.8(6)
S(3B)–C(8B)–N(2B)	121.5(8)	S(4B)–C(8B)–N(2B)	118.7(8)
N(2B)–C(9B)–C(11B)	114.0(11)	C(9B)–C(11B)–C(10B)	112.9(14)
N(2B)–C(12B)–C(13B)	117.0(10)	C(12B)–C(13B)–C(14B)	108.1(11)

Å). Thus, the Pb(b) achieves only five coordination (Fig. 1).

For Pb(a), the two CS_2 groups are twisted significantly resulting in a staggered configuration of the four S atoms [S(1a), S(2a), S(3a), S(4a)]. S(2a)′, one of the sulfur atoms bound to Pb(a)′, comes even closer to bind Pb(a) [Pb(a)...S(2a)′, 3.155(5) Å] (Fig. 2) than S(1a) approaches Pb(b) (Fig. 1). For the CS_2 group, the S–C–S bond angles are very close to 120° (Table IV). Except for the S(1a)–Pb(a)–S(2a) angle [89.7(1)°], the other S–Pb–S angles [S(3a)–Pb(a)–S(4a), 63.0(1)°; S(1b)–Pb(b)–S(2b), 63.0(1)°; S(3b)–Pb(b)–S(4b), 65.1(1)°] are significantly smaller here than in related Ni and Pd complexes but similar to other Pb(II) structures. For Pb(a) and Pb(a)′, each of the C_2N–CS_2 units is planar to within ±0.005 Å, while for Pb(b) and Pb(b)′, they are significantly distorted from planarity to within ±0.02 Å. The C–N bond lengths (Table III) show appreciable double bond character which is also supported by higher C–N stretching frequency. The C–C bond lengths and C–C–C bond angles are within normal ranges (Table IV).

Supplementary Material

Listing of anisotropic thermal parameters, hydrogen atom coordinates and structure factors are available from the authors on request.

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