Structural Studies in Metal–Purpurate Complexes. Part 4.† The Crystal Structures of Aquabis(purpurato)lead(II) and Aquabis(purpurato)lead(II) Trihydrate

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The crystal structures of two purpurate complexes of stoicheiometry $[PbL_2]\cdot4H_2O$ (1) and $[PbL_2]\cdot H_2O$ (2) (L = purpurate) have been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.063 (3 405 'observed' reflections) and 0.083 (2 164 'observed' reflections) respectively. Crystals of (1) are triclinic, space group $P\bar{1}$, $a = 12.593(7)$, $b = 11.393(5)$, $c = 10.274(3)$ Å, $\alpha = 115.38(3)$, $\beta = 102.98(4)$, $\gamma = 103.67(4)°$, $Z = 2$. Crystals of (2) are monoclinic, space group $P2_1/n$, $a = 16.63(1)$, $b = 18.72(2)$, $c = 6.981(2)$ Å, $\beta = 100.16(5)°$, $Z = 4$. In each case, the lead atom is eight-co-ordinated by two tridentate purpurate ligand sites, a water molecule, and an oxygen atom from a neighbouring ligand so that dimers are formed in (1) and a polymeric lattice in (2). In (1), the two non-tridentate oxygen atoms are tolerably *trans* in the co-ordination sphere [Pb–OH$_2$, 2.52(1); Pb–O(purpurate), 2.74(1) Å; O–Pb–O, 145.1(5)°] with the two tridentate ligands opposed [Pb–N, 2.83(1), 2.75(1) Å, N–Pb–N, 176.2(4)°; Pb–O, 2.55(1)—2.74(1) Å]. In (2), the two non-tridentate oxygen atoms are more nearly *cis* [Pb–OH$_2$, 2.92(2), Pb–O(purpurate), 2.77(2) Å; O–Pb–O, 98.3 (5)°] as are the two tridentate ligand sites [Pb–N, 2.66(2), 2.67(2) Å, N–Pb–N, 93.6(5)°; Pb–O, 2.48(2)—2.78 (1) Å].

ADDITION of murexide {ammonium purpurate, $[NH_4][L]$, ($L = [C_8H_4N_5O_6]^-$)} to an aqueous lead(II) solution precipitates a red powder unless the solutions are very dilute; interdiffusion of a concentrated murexide suspension and a very dilute lead nitrate solution produced at the interface a dark red efflorescent crystalline solid with a green dichroism (1); analysis (below) suggested the complex to be $[PbL_2]\cdot$*ca.* $5H_2O$ but structure determination subsequently showed it to be $[PbL_2]\cdot4H_2O$. A further derivative (2) was obtained as minute needles by mixing dilute solutions of lead nitrate and murexide, filtering off the precipitate immediately, and allowing the filtrate to stand whereupon a dark red

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† Part 3 is the preceding paper.

crystalline solid crystallized on the walls of the vessel. Analysis suggested it to be $[PbL_2]\cdot6H_2O$, but the structure determination showed subsequently that it was $[PbL_2]\cdot H_2O$.

EXPERIMENTAL

Analyses: (1) (Found, calc. for $[PbL_2]\cdot4H_2O$): C, 24.8, 23.68; H, 1.85, 1.99; N, 17.2, 17.26; Pb, 25.0, 25.5%.

(2) (Found, calc. for $[PbL_2]\cdot H_2O$, calc. for $[PbL_2]\cdot6H_2O$):

TABLE 1

Atomic fractional cell co-ordinates [(*x*, *y*, *z*); Pb × 10^5, others × 10^3) and thermal parameters (U_{ij} × 10 Å) with least-squares estimated standard deviations in parentheses

Compound (1), $[PbL_2]\cdot4H_2O$

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	65 807(5)	73 186(6)	53 465(7)	24.0(2)	30.7(3)	30.0(3)	11.4(2)	10.9(2)	21.8(2)
The purpurate ligand ' a ' [r(Å) is N–H; γ, δ(°) are H(nm)–N(nm)–C($n,m-1,m+1$)]									
N(0)	549(1)	636(1)	702(1)	24(6)	19(6)	22(6)	13(5)	2(5)	9(5)
C(11)	610(1)	595(1)	785(2)	27(7)	29(8)	29(8)	14(6)	17(6)	17(7)
C(12)	735(1)	635(1)	804(2)	26(7)	30(8)	22(7)	12(6)	3(6)	16(6)
O(12)	780(1)	694(1)	744(1)	26(5)	62(7)	59(7)	23(5)	21(5)	49(7)
N(13)	803(1)	601(1)	896(1)	17(6)	37(7)	33(7)	12(5)	11(5)	24(6)
H(13)	888(—)	628(—)	910(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(14)	766(1)	535(2)	973(2)	23(7)	40(9)	31(8)	18(7)	2(6)	22(7)
O(14)	832(1)	520(1)	1 062(1)	35(6)	68(8)	40(7)	19(6)	4(5)	39(6)
N(15)	645(1)	483(1)	932(1)	40(7)	34(7)	30(7)	10(6)	6(6)	25(6)
H(15)	615(—)	430(—)	980(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(16)	564(1)	496(1)	833(1)	34(8)	28(8)	17(7)	19(6)	1(6)	10(6)
O(16)	458(1)	421(1)	780(1)	26(5)	43(6)	45(6)	9(5)	8(5)	31(6)
C(21)	438(1)	633(1)	692(2)	23(7)	28(8)	43(9)	12(6)	15(6)	29(7)
C(22)	382(1)	656(1)	568(2)	30(3)	9(6)	41(9)	6(6)	12(7)	14(6)
O(22)	423(1)	672(1)	477(1)	34(5)	46(6)	33(6)	19(5)	17(5)	31(5)
N(23)	268(1)	654(1)	552(1)	16(5)	46(7)	30(7)	11(5)	6(5)	28(6)
H(23)	224(—)	661(—)	462(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(24)	210(1)	644(2)	648(2)	29(8)	60(11)	42(9)	16(8)	18(7)	40(9)
O(24)	110(1)	636(1)	624(1)	32(6)	99(10)	71(9)	37(7)	29(6)	61(8)
N(25)	279(1)	647(1)	778(1)	27(7)	62(9)	43(8)	22(6)	21(6)	36(7)
H(25)	244(—)	651(—)	857(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(26)	391(1)	646(1)	809(2)	34(8)	24(7)	44(9)	17(6)	21(7)	22(7)
O(26)	444(1)	665(1)	935(1)	33(5)	45(6)	29(5)	15(5)	13(5)	23(5)
The purpurate ligand ' b '									
N(0)	759(1)	839(1)	378(1)	14(5)	31(7)	29(6)	8(5)	8(5)	19(6)
C(11)	852(1)	816(1)	359(1)	25(7)	19(7)	25(7)	10(6)	9(6)	11(6)
C(12)	888(1)	729(1)	420(2)	27(7)	28(7)	33(8)	12(6)	12(6)	26(7)
O(12)	831(1)	674(1)	476(1)	37(6)	48(7)	51(7)	22(5)	23(5)	32(6)
N(13)	987(1)	705(1)	408(1)	20(6)	45(8)	51(8)	24(6)	20(6)	35(7)
H(13)	1 007(—)	639(—)	441(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(14)	1 063(1)	763(2)	356(2)	41(9)	46(9)	30(8)	31(8)	18(7)	23(8)
O(14)	1 153(1)	739(1)	354(1)	33(6)	80(9)	68(8)	35(6)	32(6)	59(7)
N(15)	1 034(1)	852(1)	312(1)	30(6)	52(8)	24(6)	15(6)	8(4)	27(6)
H(15)	1 087(—)	893(—)	270(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(16)	940(1)	891(1)	320(2)	31(8)	28(8)	25(8)	6(6)	1(6)	20(7)
O(16)	940(1)	996(1)	313(1)	26(5)	26(5)	40(6)	5(4)	8(5)	19(5)
C(21)	698(1)	899(1)	321(1)	18(6)	16(6)	19(7)	7(5)	4(5)	9(6)
C(22)	615(1)	936(1)	391(2)	24(7)	26(7)	23(7)	11(6)	9(6)	14(6)
O(22)	603(1)	923(1)	501(1)	54(7)	54(7)	40(6)	35(6)	32(6)	37(6)
N(23)	545(1)	992(1)	332(1)	36(7)	39(7)	41(7)	26(6)	20(6)	29(6)
H(23)	492(—)	1 027(—)	388(—)	100(—)	r = 1.00(—); γ = 117(—); δ = 117(—)				
C(24)	539(1)	1 003(2)	204(2)	38(8)	39(9)	25(8)	22(7)	14(7)	21(7)
O(24)	468(1)	1 047(1)	156(1)	44(6)	53(7)	40(6)	39(6)	18(5)	30(6)
N(25)	615(1)	963(1)	136(1)	26(6)	35(7)	23(6)	14(5)	4(5)	18(6)
H(25)	619(—)	980(—)	050(—)	100(—)	r = 1.00(—); γ = 118(—); δ = 118(—)				
C(26)	687(1)	901(1)	178(1)	23(7)	22(7)	16(7)	6(6)	7(6)	4(6)
O(26)	736(1)	847(1)	091(1)	28(5)	41(6)	38(6)	16(5)	12(5)	25(5)
The co-ordinated water molecule									
O(1)	787(1)	972(1)	765(1)	67(8)	50(7)	49(8)	23(7)	23(7)	26(6)
The lattice water molecules									
O(2)	265(2)	795(2)	160(3)	128(16)	66(11)	176(12)	38(11)	99(16)	47(13)
O(3)	964(1)	340(2)	114(2)	51(9)	181(20)	90(13)	46(11)	31(9)	57(13)
O(4)	920(2)	056(2)	062(2)	123(15)	126(15)	96(13)	25(12)	48(12)	82(13)

Compound (2), $[PbL_2]\cdot H_2O$

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	16 434(6)	16 455(6)	32 268(14)	22.8(5)	29.2(5)	16.4(4)	2.6(8)	6.8(3)	1.4(7)

TABLE 1 (*Continued*)

The purpurate ligands

	ligand ' a '				ligand ' b '			
Atom	*x*	*y*	*z*	*U*	*x*	*y*	*z*	*U*
N(0)	119(1)	086(1)	006(3)	23(5)	309(1)	197(1)	230(3)	21(5)
C(11)	043(1)	085(1)	−086(3)	22(6)	375(1)	164(2)	334(3)	25(5)
C(12)	−016(1)	131(1)	−011(3)	17(5)	364(1)	146(1)	534(3)	26(6)
O(12)	003(1)	173(1)	132(2)	25(4)	302(1)	156(1)	603(2)	31(4)
N(13)	−096(1)	131(1)	−113(3)	23(5)	435(1)	116(1)	651(3)	21(5)
C(14)	−124(2)	089(1)	−275(4)	31(7)	505(2)	097(2)	586(4)	45(8)
O(14)	−190(1)	099(1)	−362(2)	23(4)	565(1)	076(1)	693(3)	69(7)
N(15)	−070(1)	040(1)	−323(3)	35(6)	505(1)	104(1)	388(3)	29(5)
C(16)	010(1)	031(1)	−227(3)	27(6)	441(1)	133(1)	251(3)	17(5)
O(16)	045(1)	−024(1)	−265(2)	37(5)	439(1)	125(1)	079(2)	29(4)
C(21)	182(1)	053(1)	−052(3)	18(6)	308(1)	231(1)	073(3)	27(6)
C(22)	247(1)	034(1)	098(3)	20(6)	227(1)	253(1)	−029(3)	23(6)
O(22)	251(1)	049(1)	275(2)	30(4)	161(1)	240(1)	029(2)	33(4)
N(23)	311(1)	−007(1)	054(2)	17(4)	221(1)	283(1)	−212(3)	25(5)
C(24)	315(2)	−025(1)	−135(4)	31(7)	285(2)	304(1)	−295(4)	29(6)
O(24)	371(1)	−063(1)	−177(3)	45(5)	274(1)	325(1)	−455(2)	46(5)
N(25)	255(1)	002(1)	−280(3)	21(5)	364(1)	295(1)	−179(3)	26(5)
C(26)	189(2)	037(1)	−250(4)	34(7)	377(1)	263(1)	003(3)	19(6)
O(26)	143(1)	066(1)	−395(2)	25(4)	448(1)	265(1)	090(2)	32(4)
The water molecule								
O(1)	089(1)	287(1)	477(2)	35(5)				

C, 22.5, 25.37, 22.67; H, 2.35, 1.33, 2.38; N, 16.7, 18.49, 16.50; Pb, 27.7, 27.35, 24.45%.

The only previous report in the literature on lead–murexide systems concerns the formation constants of complexes in solution (these being shown to be 1 : 1) and their kinetics.[1-3]

The definition of the atom numbering scheme within the purpurate anion together with other details common to all structure determinations in this series is given in Part 1.[4] Observed and calculated structure factors have been deposited.*

Crystallographic Data and Procedure.—Compound (1). $C_{16}H_{16}N_{10}O_{16}Pb$, $M = 811.6$, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 12.593(7)$, $b = 11.393(5)$, $c = 10.274(3)$ Å, $\alpha = 115.38(3)$, $\beta = 102.98(4)$, $\gamma = 103.67(4)°$, $U = 1\,202(1)$ Å^3, $D_m = 2.24(1)$ g cm^{-3}, $Z = 2$, $D_c = 2.24$ g cm^{-3}, $F(000) = 784$, crystal size $0.08 \times 0.08 \times 0.14$ mm (coated prism), $\mu(\text{Mo-}K_\alpha) = 68.2$ cm^{-1} (data corrected for absorption), data range $2\theta < 50°$, yielding 4 262 independent reflections (3 405 ' observed '), final $R = 0.063$, $R' = 0.071$ ($n = 10$).

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least squares; in the final refinement stages, the parameters of the metal atom and the atoms in its immediate environment were refined as a single block, the atom parameters of each of the purpurate-ligand ring systems being refined similarly. Non-hydrogen-atom thermal motion was refined anisotropically. Hydrogen atoms were located geometrically about the ligand and included in the refinement with $r_{\text{N-H}}$ held invariant at 1.00 Å.

Compound (2). $C_{16}H_{10}N_{10}O_{13}Pb$, $M = 757.5$, Monoclinic, space group $P2_1/n$ (variant of C_{2h}^5, No. 14), $a = 16.63(1)$, $b = 18.72(2)$, $c = 6.981(2)$ Å, $\beta = 100.16(5)°$, $U = 2\,140(3)$ Å^3, $Z = 4$, $D_c = 2.35$ g cm^{-3}, $F(000) = 1\,448$, crystal size $0.03 \times 0.03 \times 0.11$ mm (needle), $\mu(\text{Mo-}K_\alpha) = 76.4$ cm^{-1} (data corrected for absorption), data range $2\theta < 50°$ yielding 3 746 independent reflections (2 164 ' observed '), final $R = 0.083$, $R' = 0.069$ ($n = 1$).

The minute crystal size presented considerable difficulty in orientation and cell determination and a correspondingly weak data set resulted. The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least squares; in the final refinement stages the parameters of the metal atom and the atoms in its immediate environment were refined as a single block, the atom parameters of each of the purpurate-ligand ring systems being refined similarly. Only the lead-atom thermal parameters could be refined anisotropically in a meaningful manner, and hydrogen atoms were ignored, except for the purpose of determining hydrogen bonding from the ligand in which case they were calculated as above.

For both (1) and (2), the ligand atom numbering is suffixed ' a ' or ' b ' to denote which ligand is referred to.

DISCUSSION

Crystal structure determination has shown the two complexes (1) and (2) to be the tetra- and mono-hydrates of lead(II) purpurate respectively. In each case the formula unit $PbL_2 \cdot nH_2O$ comprises the asymmetric unit and in each case the lead atom is eight-co-ordinated by the two tridentate ligand centres and two other oxygen atoms. Throughout the two complexes metal–ligand distances span a very wide range, Pb–O varying between 2.48 and 2.78 and Pb–N between 2.66 and 2.83 Å. In view of this wide and somewhat unsystematic variation, and in view of the few structural data available on complexes of lead(II) with organic nitrogen or oxygen ligands, either mono- or poly-dentate, little that is meaningful can be said about metal–ligand interactions, the more so since co-ordination types and numbers vary widely and are often irregular as in the present case. Only two compounds have been previ-

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* Supplementary Publication No. SUP 21990 (28 pp., 1 microfiche). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[1] C. B. Riolo, T. F. Soldi, and G. Spini, *Acta Chim. Acad. Sci. Hung.*, 1972, **71**, 11.

[2] G. Geier, *Helv. Chim. Acta*, 1967, **50**, 1879.

[3] G. Geier, *Helv. Chim. Acta*, 1968, **51**, 94.

[4] R. L. Martin, A. H. White, and A. C. Willis, Part 1, *J.C.S. Dalton*, 1977, 1336.

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses

(1)

(*a*) The purpurate geometry; as in previous papers in this series, the geometries of the two halves of the barbiturate ring are tabulated in parallel columns. The two components with each entry are for the two barbiturate segments *n* = 1,2 respectively of the purpurate species

Ligand	‘ a ’	‘ b ’
Segment *n*	1 2	1 2
N(0)–C(*n*1)	1.32(2), 1.37(2)	1.29(2), 1.33(2)
C(*n*1)–C(*n*2)	1.47(2), 1.47(3)	1.48(3), 1.44(2)
C(*n*2)–O(*n*2)	1.22(2), 1.22(2)	1.24(2), 1.23(2)
C(*n*2)–N(*n*3)	1.37(2), 1.40(2)	1.36(2), 1.38(2)
N(*n*3)–C(*n*4)	1.38(3), 1.37(3)	1.37(3), 1.36(2)
C(*n*4)–O(*n*4)	1.20(2), 1.21(2)	1.22(2), 1.25(2)
C(11)–N(0)–C(21)	124(1)	129(1)
N(0)–C(*n*1)–C(*n*2)	114(2), 133(2)	116(2), 115(1)
C(*n*1)–C(*n*2)–O(*n*2)	125(2), 127(2)	123(1), 125(2)
O(*n*2)–C(*n*2)–N(*n*3)	119(1), 118(2)	118(2), 118(1)
C(*n*1)–C(*n*2)–N(*n*3)	116(2), 115(2)	119(2), 117(2)
C(*n*2)–N(*n*3)–C(*n*4)	126(1), 126(2)	125(2), 126(1)
N(*n*3)–C(*n*4)–O(*n*4)	123(1), 123(2)	121(2), 120(2)
N(*n*3)–C(*n*4)–N(*n*5)	114(1), 114(1)	116(2), 116(2)
C(*n*2)–C(*n*1)–C(*n*6)	118(2), 120(1)	115(1), 117(1)
Pb–N(0)–C(*n*1)	116(1), 119(1)	117(1), 114(1)
Pb–O(*n*2)–C(*n*2)	123(1), 120(1)	122(1), 117(1)
also: Pb–O(16a$^{\mathrm{I}}$)–C(16a$^{\mathrm{I}}$)	118(1)	

	‘ a ’	‘ b ’
	1 2	1 2
C(*n*1)–C(*n*6)	1.46(3), 1.42(3)	1.48(2), 1.46(2)
C(*n*6)–O(*n*6)	1.24(2), 1.22(2)	1.23(2), 1.24(2)
C(*n*6)–N(*n*5)	1.36(2), 1.38(2)	1.37(2), 1.37(2)
N(*n*5)–C(*n*4)	1.38(2), 1.41(3)	1.37(3), 1.35(2)
O(16) · · · O(26)	2.62(2)	2.58(1)
N(0)–C(*n*1)–C(*n*6)	127(1), 125(1)	127(2), 127(1)
C(*n*1)–C(*n*6)–O(*n*6)	124(2), 125(1)	123(2), 123(2)
O(*n*6)–C(*n*6)–N(*n*5)	120(2), 118(2)	119(2), 119(2)
C(*n*1)–C(*n*6)–N(*n*5)	116(1), 116(2)	117(2), 118(1)
C(*n*6)–N(*n*5)–C(4)	127(2), 126(2)	126(2), 125(2)
N(*n*5)–C(*n*4)–O(*n*4)	122(2), 122(2)	123(2), 124(2)

(*b*) The metal environment

Pb–O(1)	2.52(1)	Pb–O(16a$^{\mathrm{I}}$)	2.74(1)
Pb–N(0a)	2.83(1)	Pb–N(0b)	2.75(1)
Pb–O(12a)	2.60(1)	Pb–O(12b)	2.55(1)
Pb–O(22a)	2.74(1)	Pb–O(22b)	2.57(1)
O(1)–Pb–O(16a$^{\mathrm{I}}$)	145.1(5)	N(0a)–Pb–O(12a)	59.8(4)
O(1)–Pb–N(0a)	95.2(4)	N(0a)–Pb–O(12b)	121.8(4)
O(1)–Pb–N(0b)	82.8(4)	N(0a)–Pb–O(22a)	59.0(4)
O(1)–Pb–O(12a)	73.3(4)	N(0a)–Pb–O(22b)	115.2(4)
O(1)–Pb–O(12b)	93.7(4)	N(0b)–Pb–O(12a)	122.3(4)
O(1)–Pb–O(22a)	113.2(4)	N(0b)–Pb–O(12b)	61.7(4)
O(1)–Pb–O(22b)	69.0(4)	N(0b)–Pb–O(22a)	118.9(4)
O(16a$^{\mathrm{I}}$)–Pb–N(0a)	115.1(3)	N(0b)–Pb–O(22b)	61.1(4)
O(16a$^{\mathrm{I}}$)–Pb–N(0b)	65.9(3)	O(12a)–Pb–O(12b)	68.3(4)
O(16a$^{\mathrm{I}}$)–Pb–O(12a)	136.3(4)	O(12a)–Pb–O(22a)	118.8(4)
O(16a$^{\mathrm{I}}$)–Pb–O(12b)	85.1(3)	O(12a)–Pb–O(22b)	141.3(3)
O(16a$^{\mathrm{I}}$)–Pb–O(22a)	72.5(3)	O(12b)–Pb–O(22a)	153.0(3)
O(16a$^{\mathrm{I}}$)–Pb–O(22b)	82.1(4)	O(12b)–Pb–O(22b)	121.6(4)
N(0a)–Pb–N(0b)	176.2(4)	O(22a)–Pb–O(22b)	70.7(3)

(*c*) Ligand-hydrogen-bonded contacts (O · · · H <2.5 Å); the angle subtended at the hydrogen is given in parentheses.

H(13a) · · · O(3$^{\mathrm{II}}$)	1.9(167)	H(15a) · · · O(26a$^{\mathrm{III}}$)	1.8(178)
H(23a) · · · O(14b$^{\mathrm{IV}}$)	1.9(159)	H(25a) · · · O(14a$^{\mathrm{III}}$)	2.5(134)
H(13b) · · · O(24$^{\mathrm{V}}$)	2.0(142)	H(15b) · · · O(1$^{\mathrm{VI}}$)	2.1(166)
H(23b) · · · O(22b$^{\mathrm{VII}}$)	1.9(173)	H(25b) · · · O(24b$^{\mathrm{VIII}}$)	2.0(147)

Transformations of the asymmetric unit (x, y, z) are denoted by the following Roman superscripts.

I	($1 - x, 1 - y, 1 - z$)	V	($1 + x, y, z$)
II	($2 - x, 1 - y, 1 - z$)	VI	($2 - x, 2 - y, 1 - y$)
III	($1 - x, 1 - y, 2 - z$)	VII	($1 - x, 2 - y, 1 - z$)
IV	($x - 1, y, z$)	VIII	($1 - x, 2 - y, \bar{z}$)

(2)

(*a*) The purpurate geometry, tabulated as for (1) above.

Ligand	‘ a ’	‘ b ’
Segment *n*	1 2	1 2
N(0)–C(*n*1)	1.31(3), 1.34(3)	1.36(3), 1.27(3)
C(*n*1)–C(*n*2)	1.48(2), 1.42(3)	1.49(3), 1.47(3)
C(*n*2)–O(*n*2)	1.26(3), 1.26(3)	1.23(3), 1.25(3)
C(*n*2)–N(*n*3)	1.40(3), 1.39(3)	1.43(3), 1.38(3)
N(*n*3)–C(*n*4)	1.39(3), 1.37(3)	1.37(4), 1.36(3)
C(*n*4)–O(*n*4)	1.17(3), 1.24(3)	1.20(3), 1.17(3)
C(11)–N(0)–C(21)	126(2)	125(2)
N(0)–C(*n*1)–C(*n*2)	117(2), 116(2)	112(2), 116(2)
C(*n*1)–C(*n*2)–O(*n*2)	124(2), 125(2)	126(2), 125(2)
O(*n*2)–C(*n*2)–N(*n*3)	119(2), 115(2)	120(2), 116(2)

	‘ a ’	‘ b ’
	1 2	1 2
C(*n*1)–C(*n*6)	1.45(3), 1.44(4)	1.44(3), 1.46(4)
C(*n*6)–O(*n*6)	1.24(3), 1.27(3)	1.21(3), 1.22(3)
C(*n*6)–N(*n*5)	1.38(3), 1.33(3)	1.41(3), 1.39(3)
N(*n*5)–C(*n*4)	1.38(4), 1.38(3)	1.39(4), 1.42(3)
O(16) · · · O(26)	2.61(2)	2.62(2)
N(0)–C(*n*1)–C(*n*6)	124(2), 126(2)	125(2), 127(2)
C(*n*1)–C(*n*6)–O(*n*6)	126(2), 122(2)	124(2), 126(2)
O(*n*6)–C(*n*6)–N(*n*5)	117(2), 119(2)	121(2), 116(2)

TABLE 2 (*Continued*)

Ligand	'a'		'b'	
Segment *n*	1	2	1	2
C(*n*1)–C(*n*2)–N(*n*3)	117(2),	120(2)	114(2),	118(2)
C(*n*2)–N(*n*3)–C(*n*4)	125(2),	121(2)	125(2),	125(2)
N(*n*3)–C(*n*4)–O(*n*4)	120(2),	122(1)	122(3),	120(2)
N(*n*3)–C(*n*4)–N(*n*5)	116(1),	117(1)	117(2),	116(2)
C(*n*2)–C(*n*1)–C(*n*6)	117(2),	118(2)	121(2),	116(2)
Pb–N(0)–C(*n*1)	122(1),	112(1)	117(1),	117(1)
Pb–O(*n*2)–C(*n*2)	115(1),	111(1)	113(1),	119(1)
C(*n*1)–C(*n*6)–N(*n*5)	117(2),	117(2)	115(2),	118(2)
C(*n*6)–N(*n*5)–C(*n*4)	125(2),	125(2)	125(2),	124(2)
N(*n*5)–C(*n*4)–O(*n*4)	125(2),	120(2)	121(3),	123(2)

also: Pb–O(26a^{I})–C(26a^{I}) 135(2)

(*b*) The metal environment

Pb–O(1)	2.92(2)	Pb–O(26a^{I})	2.77(2)
Pb–N(0a)	2.66(2)	Pb–N(0b)	2.67(2)
Pb–O(12a)	2.78(1)	Pb–O(12b)	2.75(1)
Pb–O(22a)	2.65(2)	Pb–O(22b)	2.48(2)
O(1)–Pb–O(26a^{I})	98.3(5)	N(0a)–Pb–O(12a)	61.4(5)
O(1)–Pb–N(0a)	131.8(5)	N(0a)–Pb–O(12b)	130.1(5)
O(1)–Pb–N(0b)	112.2(5)	N(0a)–Pb–O(22a)	61.6(5)
O(1)–Pb–O(12a)	72.0(5)	N(0a)–Pb–O(22b)	70.7(6)
O(1)–Pb–O(12b)	98.1(5)	N(0b)–Pb–O(12a)	135.0(5)
O(1)–Pb–O(22a)	165.5(4)	N(0b)–Pb–O(12b)	60.7(5)
O(1)–Pb–O(22b)	84.7(5)	N(0b)–Pb–O(22a)	67.7(5)
O(26a^{I})–Pb–N(0a)	99.6(5)	N(0b)–Pb–O(22b)	63.9(5)
O(26a^{I})–Pb–N(0b)	124.0(5)	O(12a)–Pb–O(12b)	163.5(5)
O(26a^{I})–Pb–O(12a)	98.2(5)	O(12a)–Pb–O(22a)	119.0(5)
O(26a^{I})–Pb–O(12b)	69.6(5)	O(12a)–Pb–O(22b)	72.2(5)
O(26a^{I})–Pb–O(22a)	71.7(5)	O(12b)–Pb–O(22a)	68.9(5)
O(26a^{I})–Pb–O(22b)	168.7(5)	O(12b)–Pb–O(22b)	121.0(5)
N(0a)–Pb–N(0b)	93.6(5)	O(22a)–Pb–O(22b)	107.2(5)

(*c*) Ligand-hydrogen-bonded contacts (O · · · H <2.5 Å); the angle subtended at the hydrogen is given in parentheses

H(13a) · · · O(24b^{II})	1.8(148)	H(15a) · · · O(26a^{III})	1.9(164)
H(23a) · · · O(14b^{IV})	1.8(163)	H(25a) · · · O(22a^{V})	2.4(144)
H(25a) · · · O(14a^{III})	2.5(125)	H(13b) · · · O(16b^{I})	2.0(160)
H(15b) · · · O(24a^{VI})	1.9(164)	H(23b) · · · O(1^{V})	1.9(152)
H(25b) · · · O(12^{VII})	1.9(168)		

Transformations of the asymmetric unit (x, y, z) are denoted by the following Roman superscripts

I ($x, y, 1 + z$)
II ($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$)
III ($\bar{x}, \bar{y}, \bar{z} - 1$)
IV ($1 - x, \bar{y}, 1 - z$)
V ($x, y, z - 1$)
VI ($1 - x, \bar{y}, \bar{z}$)
VII ($\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$)

ously reported as containing lead incorporated in an N–C–C–O chelate system. In D-penicillinaminatolead-(II) [5] the effective co-ordination number about the lead appears to be lower and the co-ordination more asymmetric, with the tridentate S, N, and O components of the ligand being strongly bound (Pb–S 2.716, Pb–N 2.444, and Pb–O 2.444 Å) on one side of the lead environment, the remainder of the co-ordination sphere being filled by relatively weak bridging interactions and a stereochemically active lone pair. In the macrocyclic derivative [$Pb(SCN)_2(C_{12}H_{26}N_2O_4)$] [6] the lead is eight-co-ordinate, the thiocyanate groups being axial and the oxygen and nitrogen atoms of the ligand symmetrically disposed in the equatorial plane with distances more nearly resembling those found in the present compounds (Pb–O 2.88, 2.79, Pb–N 2.75 Å). These distances are long, presumably a result of the high co-ordination number, and it appears unlikely that the stereochemistry contains a stereochemically active lone pair; the lone pair may well reside in an *s* orbital since it is possible to describe eight-co-ordination by the use of appropriate hybrid combinations of *p* and *d* orbitals only.

In (1), the lead atom is eight-co-ordinate, a pair of normal tridentate purpurate ligands lying opposed to each other in an approximate shallow-pitched two-bladed propeller disposition in an 'equatorial plane' with the two metal–nitrogen bonds [Pb–N(0a,b) 2.83(1), 2.75(1) Å] closely *trans* to each other [N(0a)–Pb–N(0b) 176.2(4)°], with the O(*n*2)–Pb distances being approximately 0.1 Å shorter as usual (range 2.55—2.74 Å). The remaining two sites in the co-ordination sphere are filled by a pair of pseudo-axial oxygen atoms, one from a water molecule [Pb–O(1) 2.52(1) Å] and the other the oxygen atom from one of the ligand sections of a neighbouring centrosymmetrically related molecule [Pb–O(16a)($1 - x, 1 - y, 1 - z$) 2.74(1) Å, O(1)–Pb–O(16a)-($1 - x, 1 - y, 1 - z$) 145.1(5)°] so that a dimer, [$Pb_2L_4(H_2O)_2$], is formed about the cell centre (Figure 2), the equatorial ligands forming parallel wrinkled 'sheets.' The interplanar angle between the two ligand halves in the non-bridging ligand lies much closer to the mean r_{M-O}/θ line of ref. 7 than that of the bridging ligand which is much further distorted (Table 3). Co-ordination *via* the back of ligand 'a,' part 1, through O(16a) involves the latter in a grossly out-of-plane bond to the lead atom; in spite of the interaction of this oxygen with

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[5] H. C. Freeman, G. N. Stevens, and I. F. Taylor, *J.C.S. Chem. Comm.*, 1974, 366.

[6] B. Metz and R. Weiss, *Acta Cryst.*, 1973, **B29**, 1088.

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TABLE 3

Least-squares planes, calculated through the C(n1,n2,n4,n6),N(n3,n5) skeleton of each barbiturate segment of the ligand (n = 1,2) in the form $pX + qY + rZ = s$, where the right-handed orthogonal (Å) frame is defined with X parallel to a, Z in the ac plane. Atom deviations and the estimated standard deviation of the defining atoms are in Å. The angle between the normals to the two barbiturate planes of each ligand is θ°

Compound	(1)				(2)			
Segment (na,b)	1a	1b	2a	2b	1a	1b	1b	2b
10^4p	−3 153	0 186	0 960	3 654	3 706	5 190	3 837	−1 145
10^4q	8 408	9 991	7 682	9 211	6 685	8 510	9 000	8 861
10^4r	4 400	0 376	6 330	1 344	−6 449	−0 801	2 069	4 491
s	5.298	6.292	6.152	9.646	1.641	2.518	5.361	3.595
σ	0.07	0.06	0.05	0.04	0.07	0.04	0.07	0.07
χ^2	111	78	41	32.8	251	71	213	197
C(11)	0.10	0.10	0.07	0.05	0.11	0.04	0.12	0.11
C(12)	−0.04	−0.06	−0.04	−0.03	−0.05	−0.05	−0.07	−0.08
N(13)	−0.05	−0.01	0.00	0.01	−0.03	0.01	−0.02	0.00
C(14)	0.06	0.06	0.02	−0.01	0.05	0.03	0.06	0.05
N(15)	0.01	−0.03	0.01	0.03	0.01	−0.04	−0.01	−0.02
C(16)	−0.09	−0.05	−0.06	−0.05	−0.09	0.00	−0.07	−0.06
N(0)	0.19	0.03	−0.01	−0.06	0.13	0.14	0.15	0.18
O(12)	−0.15	−0.19	−0.12	−0.12	−0.11	−0.10	−0.23	−0.18
O(14)	0.17	0.17	0.01	−0.05	0.20	0.10	0.18	0.19
O(16)	−0.43	−0.28	−0.38	−0.25	−0.37	−0.23	−0.38	−0.23
Pb	−0.49	−0.82	−0.47	−1.20	−0.16	−1.14	−1.23	0.14
0	31.7		34.1		35.6		32.2	

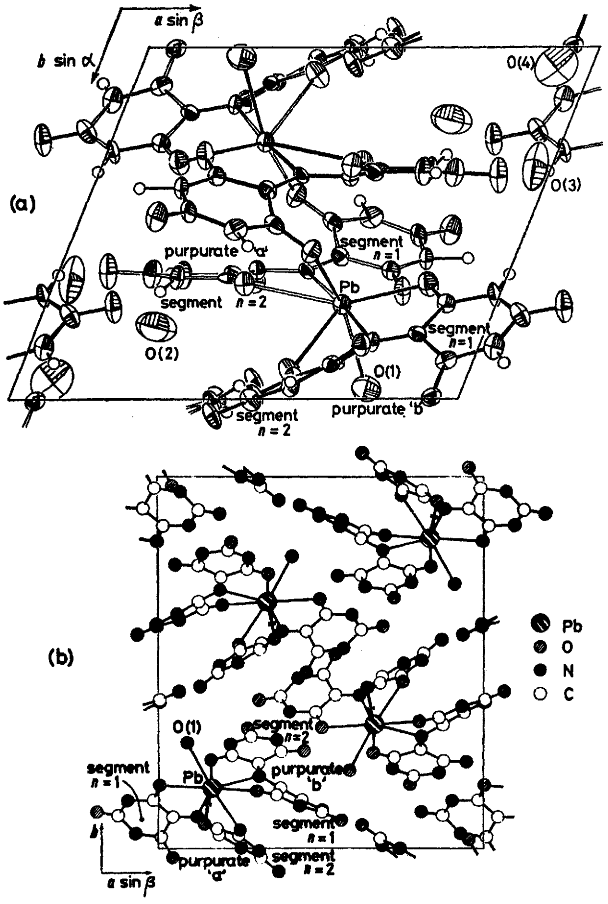

FIGURE 1 Unit-cell contents of (1) (a) and (2) (b) projected along c in each case. 50% thermal ellipsoids are shown for (1), those of the purpurate hydrogen atoms being set arbitrarily at radius 0.1 Å; bonds of the upper purpurates in the cell in (1) are shown as solids for clarity. In (2), polymerization occurs along the projection axis *via* the broken metal–ligand bonds. Labelling of purpurate segments and water molecule oxygen atoms is given. Hydrogen atoms are omitted from (2)

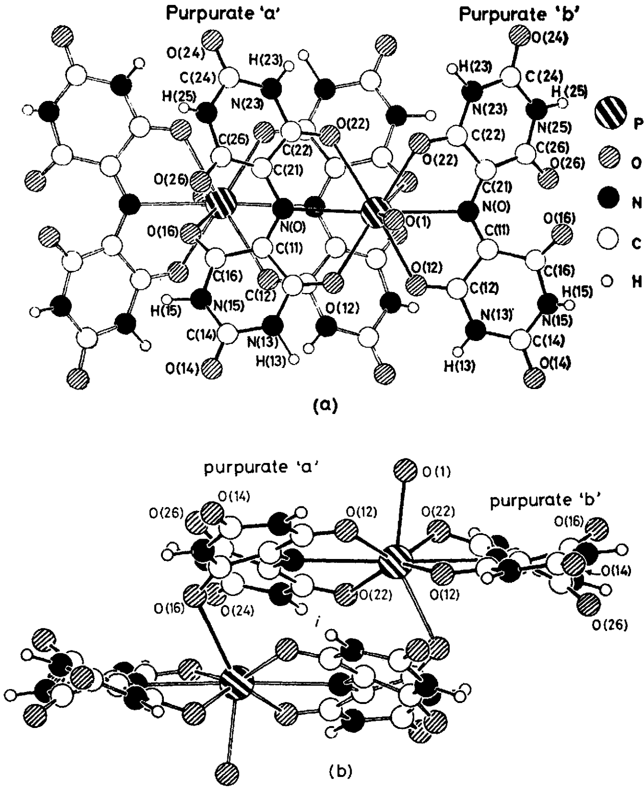

FIGURE 2 Co-ordination about the metal atom in (1), showing the dimer formation by the bridging ligand. Two projections are given. (a) Approximately along the Pb–O(1) axis and normal to the purpurate planes; the purpurate groups of the upper molecule are shown with solid bonds and are given fully labelled. (b) Approximately parallel to the purpurate planes and normal to the Pb–O(1) axis; purpurate ligand and oxygen atoms are labelled

the metal, the O(16) · · · O(26) interaction appears normal.

While the centre of the cell is well filled with the dimer, a considerable cavity remains about the origin, the interligand hydrogen bonding resulting in a cage-like lattice. The origin cavity is occupied by the three remaining water molecules; these have much higher thermal motion than the remainder of the lattice.

In (2), the lead atom is also eight-co-ordinated by a pair of tridentate purpurate ligands with the remaining two co-ordination sites filled again by the only water molecule [Pb–O(1), 2.92(2) Å] and O(26a) from a neighbouring ligand at 2.77(2) Å; as a result, ligands ' a ' act as bridges in the same manner as in (1), but now the relating symmetry element is a simple *c* translation, linking the molecular units into a polymer parallel to *c*. Both bridging and non-bridging ligands in the present derivative deviate rather markedly from the r_{M-O}/θ line of ref. 7. In (2), the pair of non-tridentate co-ordination sites are much more nearly *cis* [O(1)–Pb–O(26a)-(x,y, $1 + z$) 98.3(5)°] as also are the two purpurate nitrogens [N(0a)–Pb–N(0b) 93.6(5)°].[7] The purpurate ligand is chiral; (2) is the only ML_2 complex observed to contain a ligand of each parity within the complex species, and may be regarded as *meso* in that respect; all the other complexes, crystallizing in centrosymmetric space groups, are racemates.

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