Ji Li* and Ming-Zhi Miao

The crystal structure of aqua{*N,N,N',N'*-tetrakis[(1*H*-benzimidazol- κ *N*³)methyl]cyclohexane-1,2-diamine}lead(II) diacetate–methanol (1/2), $C_{44}H_{54}N_{10}O_7Pb$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.16 × 0.12 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.7 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX2, φ and ω
$\theta_{\max}$, completeness:	56.6°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7966, 7966,
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 7079
$N(\text{param})_{\text{refined}}$:	566
Programs:	Bruker [1], SHELX [2–4], Diamond [5], Olex2 [6]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Pb1	0.50164(3)	0.75760(2)	0.74428(2)	0.04121(13)
C1	0.6977(7)	0.9397(6)	0.6758(5)	0.0436(19)
H1	0.7436	0.8861	0.6683	0.052*
C2	0.7253(9)	1.0225(7)	0.6264(6)	0.062(2)
H2A	0.6773	1.0745	0.6293	0.074*
H2B	0.6999	0.9842	0.5637	0.074*
C3	0.8627(9)	1.0862(8)	0.6656(7)	0.070(3)
H3A	0.9110	1.0355	0.6591	0.084*
H3B	0.8749	1.1390	0.6331	0.084*
C4	0.9047(10)	1.1453(8)	0.7639(7)	0.072(3)
H4A	0.8601	1.1993	0.7702	0.086*
H4B	0.9916	1.1833	0.7889	0.086*
C5	0.8818(8)	1.0631(8)	0.8140(6)	0.057(2)
H5A	0.9081	1.1022	0.8767	0.068*
H5B	0.9320	1.0132	0.8110	0.068*
C6	0.7468(7)	0.9953(6)	0.7780(5)	0.0421(18)
H6	0.6994	1.0476	0.7854	0.050*
C7	0.5352(8)	0.7917(7)	0.5536(5)	0.051(2)
H7A	0.5646	0.8246	0.5145	0.061*
H7B	0.4467	0.7622	0.5229	0.061*
C8	0.5912(7)	0.7009(7)	0.5711(6)	0.048(2)
C9	0.6573(8)	0.5789(7)	0.6327(6)	0.052(2)
C10	0.6924(10)	0.5133(8)	0.6871(7)	0.074(3)
H10	0.6848	0.5241	0.7417	0.088*
C11	0.7394(9)	0.4309(8)	0.6585(8)	0.071(3)
H11	0.7629	0.3848	0.6942	0.085*
C12	0.7520(10)	0.4158(8)	0.5785(9)	0.078(3)
H12	0.7855	0.3602	0.5619	0.094*

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Abstract

$PbC_{44}H_{54}N_{10}O_7$, triclinic, $P\bar{1}$ (no. 2), $a = 12.096(2)$ Å, $b = 12.916(2)$ Å, $c = 16.5904(7)$ Å, $\alpha = 101.163(2)^\circ$, $\beta = 110.634(2)^\circ$, $\gamma = 100.698(2)^\circ$, $V = 2287.0(4)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0604$, $wR_{\text{ref}}(F^2) = 0.1409$, $T = 298(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents and solvents were used as obtained without further purification. The ligand CTB was synthesized

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C13	0.7170(9)	0.4800(7)	0.5213(7)	0.066(3)
H13	0.7247	0.4690	0.4667	0.079*
C14	0.6692(8)	0.5623(7)	0.5518(6)	0.052(2)
C15	0.4836(8)	0.9483(7)	0.6221(6)	0.050(2)
H15A	0.4818	0.9725	0.5699	0.060*
H15B	0.5169	1.0130	0.6733	0.060*
C16	0.3554(8)	0.8945(7)	0.6076(5)	0.049(2)
C17	0.1921(8)	0.7831(7)	0.5960(6)	0.051(2)
C18	0.1053(9)	0.6956(9)	0.5954(7)	0.073(3)
H18	0.1250	0.6313	0.6042	0.088*
C19	−0.0090(9)	0.7063(11)	0.5818(8)	0.087(4)
H19	−0.0679	0.6487	0.5818	0.104*
C20	−0.0389(10)	0.8001(12)	0.5680(8)	0.088(4)
H20	−0.1181	0.8047	0.5584	0.105*
C21	0.0444(10)	0.8873(11)	0.5677(6)	0.076(3)
H21	0.0234	0.9509	0.5582	0.091*
C22	0.1621(8)	0.8770(9)	0.5823(6)	0.058(2)
C23	0.8167(8)	0.8535(7)	0.8471(6)	0.050(2)
H23A	0.8955	0.9031	0.8897	0.060*
H23B	0.8254	0.8230	0.7922	0.060*
C24	0.7811(8)	0.7625(7)	0.8849(6)	0.049(2)
C25	0.6839(10)	0.6344(7)	0.9187(7)	0.060(3)
C26	0.5933(12)	0.5558(9)	0.9257(8)	0.083(3)
H26	0.5099	0.5485	0.8967	0.100*
C27	0.6359(16)	0.4915(12)	0.9775(11)	0.120(5)
H27	0.5796	0.4378	0.9842	0.144*
C28	0.7586(18)	0.5019(13)	1.0206(11)	0.129(6)
H28	0.7820	0.4552	1.0556	0.155*
C29	0.8480(13)	0.5773(11)	1.0148(9)	0.101(4)
H29	0.9311	0.5837	1.0447	0.121*
C30	0.8072(10)	0.6436(8)	0.9614(7)	0.063(3)
C31	0.7242(8)	0.9769(7)	0.9138(5)	0.047(2)
H31A	0.7886	1.0456	0.9386	0.056*
H31B	0.7416	0.9343	0.9566	0.056*
C32	0.6036(8)	0.9996(7)	0.8993(5)	0.047(2)
C33	0.4076(8)	0.9840(7)	0.8525(5)	0.046(2)
C34	0.2828(9)	0.9501(8)	0.8117(6)	0.058(2)
H34	0.2417	0.8827	0.7685	0.070*
C35	0.2193(10)	1.0204(10)	0.8372(7)	0.068(3)
H35	0.1338	0.9994	0.8110	0.082*
C36	0.2802(10)	1.1202(9)	0.9004(7)	0.065(3)
H36	0.2351	1.1669	0.9136	0.078*
C37	0.4036(10)	1.1525(8)	0.9437(6)	0.061(3)
H37	0.4438	1.2186	0.9886	0.073*
C38	0.4691(8)	1.0830(7)	0.9189(6)	0.051(2)
C39	0.0339(12)	0.6633(12)	0.8160(9)	0.120(5)
H39A	0.0625	0.6660	0.7691	0.180*
H39B	−0.0376	0.6899	0.8040	0.180*
H39C	0.0134	0.5888	0.8185	0.180*
C40	0.1337(10)	0.7341(8)	0.9047(6)	0.063(3)
C41	0.2713(19)	0.2104(15)	0.7107(11)	0.156(7)
H41A	0.1883	0.2149	0.6940	0.233*
H41B	0.3227	0.2625	0.7679	0.233*
H41C	0.2741	0.1376	0.7146	0.233*
C42	0.3174(12)	0.2360(12)	0.6399(8)	0.085(4)
C43	0.0862(15)	0.4072(15)	0.6648(13)	0.154(7)

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H43A	0.0836	0.3875	0.7172	0.232*
H43B	0.0594	0.3420	0.6160	0.232*
H43C	0.0329	0.4533	0.6489	0.232*
C44	0.652(2)	0.2835(19)	0.8205(13)	0.217(11)
H44A	0.7213	0.2626	0.8556	0.326*
H44B	0.5899	0.2731	0.8442	0.326*
H44C	0.6768	0.3594	0.8227	0.326*
N1	0.5656(6)	0.8770(5)	0.6377(4)	0.0403(15)
N2	0.7238(6)	0.9153(5)	0.8281(4)	0.0410(15)
N3	0.6086(7)	0.6685(6)	0.6434(5)	0.058(2)
N4	0.6261(6)	0.6406(6)	0.5132(5)	0.0543(19)
H4	0.6223	0.6492	0.4622	0.065*
N5	0.3168(7)	0.7960(6)	0.6127(5)	0.0516(18)
N6	0.2671(7)	0.9475(6)	0.5883(5)	0.0548(19)
H6A	0.2749	1.0123	0.5812	0.066*
N7	0.6698(7)	0.7119(6)	0.8705(5)	0.0511(17)
N8	0.8676(7)	0.7266(6)	0.9390(5)	0.060(2)
H8	0.9458	0.7510	0.9564	0.072*
N9	0.4966(6)	0.9321(5)	0.8415(4)	0.0469(17)
N10	0.5929(6)	1.0917(5)	0.9470(4)	0.0465(17)
H10A	0.6521	1.1455	0.9872	0.056*
O1	0.3451(7)	0.6623(6)	0.8067(6)	0.097(3)
H1A	0.3190	0.5961	0.7824	0.145*
H1B	0.3257	0.6792	0.8491	0.145*
O2	0.1001(6)	0.7763(6)	0.9625(5)	0.076(2)
O3	0.2405(6)	0.7435(5)	0.9145(4)	0.0689(18)
O4	0.3303(8)	0.1593(7)	0.5906(6)	0.094(3)
O5	0.3330(8)	0.3312(6)	0.6334(5)	0.089(2)
O6	0.2079(11)	0.4646(8)	0.6832(9)	0.137(4)
H6B	0.2532	0.4250	0.6962	0.205*
O7	0.6026(19)	0.2172(18)	0.7294(12)	0.245(8)
H7	0.5398	0.2315	0.7003	0.367*

according to the literature methods [7]. The title compound (I) was synthesized by reaction of CTB (0.64 g, 1 mmol) and Pb(CH₃COO)₂ · 3(H₂O) (0.38 g, 1 mmol) in 95% methanol (30 mL) at 333 K for 2 h. The solution was then cooled to room temperature, filtered and evaporated to obtain the product (yield 72%). Crystals of (I) were grown from a methanol solution by slow evaporation at room temperature. **Elemental analysis** calculated: C 50.71, H 5.22, N 13.44%; found: C 50.53, H 5.52, N 13.39%.

Experimental details

Hydrogen atoms bonded to carbon atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.95 Å (aromatic), 0.99 Å (methylene), 0.98 Å (methyl) $U_{iso}(H) = 1.2U_{eq}(\text{aromatic and methylene})$ and $1.5U_{eq}(\text{methyl})$. Hydrogen atoms bonded to nitrogen, O1 and O2 atoms were initially found from the difference maps and refined with the restraints of N—H = 0.88(1) Å,

O—H = 0.82(1) Å. Due to the relatively high thermal factors of methanol solvent, commands DFIX and ISOR were used in the refinement to restrain C—O and their the thermal factors. In the structure refinement, the crystal model was founded to be twinned by the twin law [0.019 0.921 −0.059, 1.019 −0.079 −0.059, −1.019−0.921 −0.941]. In the final result, the best ratio outcome for the major and minor components is 0.748(4):0.252(4).

Comment

As part of our continuing studies on the ligands or metal complexes containing multi-benzimidazole group [8], we have synthesized another ligand *N,N,N',N'*-tetrakis[(1*H*-benzimidazol-2-yl) methyl]cyclohexane-1,2-diamine (CTB). On the other hand, due to the unique lone electron effects with ns^2np^0 configuration of the p-block Pb(II) ion, its metal complexes can provide some special opportunities for the screening of novel photoluminescent materials [9, 10]. Based on this concept, we have synthesized the title compound and reported its crystal structure in this paper.

In (I), its asymmetric unit was composed of each one $[Pb(CTB)(H_2O)]^{2+}$, two acetate anions and two methanol solvent molecules. The Pb(II) ion is coordinated in a distorted monocapped trigonal-prismatic environment by four benzimidazole (bzim) N atoms, two amino N atoms of the ligand CTB and one water molecule. These seven donor atoms occupy a space around the Pb(II) ion and the underneath direction space is occupied by the $6s^2$ lone electron pair, which may induce its special photoluminescence behavior [11]. Around the Pb(II) center, it should be mentioned that the Pb1–N3/N5/O1 bond distances (2.670(7) Å/2.720(7) Å/2.680(7) Å) are apparently longer than the other two Pb1–N_{bzim} distances (2.606(7) Å/2.530(6) Å) which should be ascribed to the lone electron pair steric hindrance. However, these two Pb1–N_{amino} bond distances (2.746(7) Å and 2.772(6) Å) are apparently longer than the mean value (2.641(7) Å) of the five coordination bonds which should be mainly ascribed to the steric effect of ligand CTB. Similar phenomena are observed in some analogs [12–14].

In the crystal packing, the ions and molecules are linked into a three-dimensional network by a combination of extensive N–H...O and O–H...O hydrogen-bondings. In more details, the $[Pb(CTB)(H_2O)]^{2+}$ and O2/O3-containing acetate ions are firstly hydrogen-bonded by intermolecular N8–H8...O2 ($d_{N8...O2} = 2.633(1)$ Å; $1+x, y, z$), N10–H10A...O3 ($d_{N10...O3} = 2.669(2)$ Å; $1+x, 2-y, 2-z$) and O1–H1A...O3 ($d_{O1...O3} = 2.695(1)$ Å) interactions into a one-dimensional chain along the [100] axis. These adjacent [100] chains are further linked into the final three-dimensional network by two N–H...O and three O–H...O hydrogen bonds between $[Pb(CTB)(H_2O)]^{2+}$ cation, O4/O5-containing

acetate and the two methanol molecules. Analysis by Platon [15] indicates that two weak intermolecular $\pi \cdots \pi$ interactions exist between two pairs of symmetry-related imidazole rings (N3/C8/N4/C14/C9 and N9/C32/N10/C38/C33) with centroid-centroid distances of 3.895(6) Å and 3.830(5) Å, respectively.

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