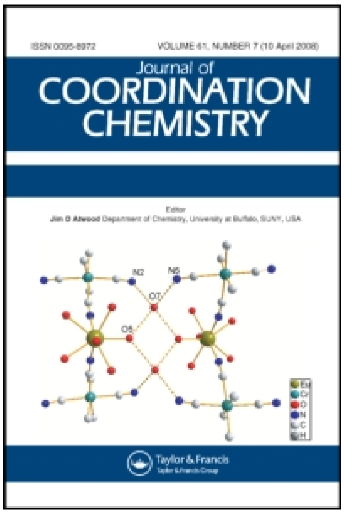

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Syntheses and characterization of lead(II) complexes, Pb(dmphen)X_2 and dmphen=2,9-dimethyl-1,10-phenanthroline), and crystal structure of [Pb(dmphen)$(NO_3)_2$]*_n*, a new polymeric compound with holodirected geometry

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SYNTHESES AND CHARACTERIZATION OF LEAD(II) COMPLEXES, Pb(DMPHEN)X_2 ($X = NO_3^-$, CLO_4^- AND CH_3COO^-; DMPHEN = 2,9-DIMETHYL-1,10-PHENANTHROLINE), AND CRYSTAL STRUCTURE OF $[Pb(DMPHEN)(NO_3)_2]_n$, A NEW POLYMERIC COMPOUND WITH HOLODIRECTED GEOMETRY

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New lead(II) complexes, Pb(dmphen)X_2 ($X = NO_3^-$, ClO_4^- and CH_3COO^-; dmphen = 2,9-dimethyl-1,10-phenanthroline), have been synthesized and characterized by CHN elemental analysis, IR, ^1H, ^{13}C and ^{207}Pb NMR spectroscopy. The structure of $[Pb(dmphen)(NO_3)_2]_n$ was confirmed by X-ray crystallography. The single-crystal X-ray data of this compound show that the complex is polymeric and the Pb atom has an unsymmetrical eight-coordinate geometry, coordinated by two nitrogen atoms of dmphen and six oxygen atoms of the nitrate group. Two oxygen atoms of the nitrate are chelated and one of them is linked to two different lead atoms. The arrangement of the dmphen and nitrate groups does not exhibit any coordination gap around the Pb(II) ion and the coordination around the lead atoms is holodirected.

Keywords: Lead(II) complexes; Crystal structure; Lone pair

INTRODUCTION

The toxic effects of lead(II) have been indicated historically by the Greeks, Romans and Arabs. Lead interferes with the metabolism and action of essential metals such as Ca, Fe and Zn [1–3]. The only oxidation state important in biological systems is Pb(II) [4]. Research on the coordination chemistry of lead(II) complexes has progressed very rapidly over the past two decades [5–8]. An issue frequently discussed in considering the coordination and stereoactivity of lead(II) complexes is that of the "stereochemical activity" of valence-shell electron lone pairs. The possible stereochemical activity of the lone pair in divalent lead compounds has been discussed by Shimoni-Livny *et al.* based

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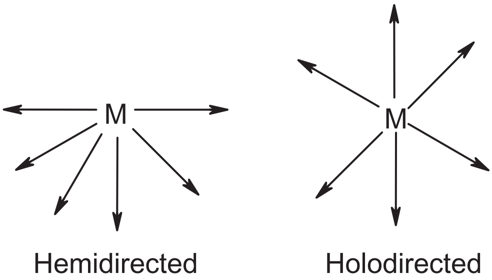
on a thorough review of crystal data available in the Cambridge Structural Database (CSD) and through the use of *ab initio* calculations [9]. They classify lead coordination as holodirected, which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand.



Hemidirected bonds are present in all Pb(II) compounds with coordination numbers 2–5, are fairly common in Pb(II) compounds with coordination numbers 6, 7 and 8, and do not exist in lead complexes with higher coordination numbers. To design sequestering agents capable of removing Pb(II) selectively from biological systems, it is important to consider the factors that affect the stereoactivity of the lone pair of electrons [9,10]. The lone pair in most lead(II) complexes is active, and structures with an inactive lone pair are rarely observed. Interligand repulsion is an important factor. All reported lead(II) complexes with 1,10-phenanthroline [6,11–13] have hemidirected geometry. We present herein a study of 2,9-dimethyl-1,10-phenanthroline (dmphen) with Pb(II) leading to a holodirected geometry.

EXPERIMENTAL

Physical Measurements

IR spectra were recorded as Nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 instrument and are uncorrected. The ^{207}Pb solution NMR spectra were recorded on a Bruker DRX-500 Avance spectrometer at 104.6 MHz using a 5-mm broad-band probe. Lead chemical shifts are reported (ppm) downfield from tetramethyllead using $PbPh_4$ ($\delta_{Pb} = -178.0$ ppm, saturated in $CDCl_3$) as an external standard at 0.01 M and 25°C. Each lead spectrum was acquired in 3–10 h.

Preparation of [Pb(dmphen)(NO_3)$_2$] (1)

2,9-Dimethyl-1,10-phenanthroline (0.208 g, 1 mmol) was placed in one arm of a branched tube and lead(II) nitrate (0.33 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60°C, while the other was at ambient temperature. After 10 days, yellow crystals deposited in the cooler arm were filtered off, washed with acetone and ether and air dried (0.27 g; yield 50%), m.p. > 320°C. Anal. Calcd. for $C_{14}H_{12}N_4O_6Pb$(%): C, 31.16; H, 2.22; N, 10.38. Found: C, 31.50; H, 2.15; N, 10.43. IR (cm^{-1}) selected bands: 716(m), 856(m), 1022(s), 1259(vs), 1371(vs), 1424(vs), 1583(w), 3040(w). ^1H NMR (DMSO; δ): 2.85 (s, 6H, CH_3–phen), 7.50–7.70 (d, 2H), 7.80–8.00 (s, 2H), 8.30–9.50 (d, 2H). $^{13}C\{^1H\}$ NMR (DMSO; δ): 25.00 ($^{13}CH_3$–phen), 123.71, 125.62, 126.84, 136.74, 158.44, 177.66. ^{207}Pb NMR (DMSO; δ) 450.03 ppm.

Preparation of [Pb(dmphen)(ClO_4)$_2$] (2) and [Pb(dmphen)(CH_3COO)$_2$] (3)

Complexes **2** and **3** were prepared by an analogous method to that used for the synthesis of the [Pb(dmphen)(NO_3)$_2$] **1** complex.

Complex 2 Reactant materials: dmphen, lead(II) acetate, sodium perchlorate (1 : 1 : 2). Yellow crystals; m.p. > 320°C; yield 0.442 g, 60%. Anal. Calcd. for $C_{14}H_{12}N_2O_8Cl_2Pb$(%): C, 22.76; H, 1.62; N, 3.79. Found: C, 22.41; H, 1.63; N, 3.90. IR (cm^{-1}) selected bands: 718(m), 854(m), 1015(s), 1100(vs), 1420(s), 1579(w), 3035(w). ^1H NMR (DMSO; δ): 2.80 (s, 6H), 7.65–7.80 (d, 2H), 7.95–8.10 (s, 2H), 9.20–9.40 (d, 2H). $^{13}C\{^1H\}$ NMR (DMSO; δ): 25.04 ($^{13}CH_3$–phen), 123.75, 125.60, 126.80, 136.70, 158.46, 177.70. ^{207}Pb NMR (DMSO; δ) 463.80 ppm.

Complex 3 Reactant materials: dmphen, lead(II) acetate (1 : 1). Yellow crystals; m.p. > 320°C; yield: 0.267 g, 50%. Anal. Calcd. for $C_{18}H_{18}N_2O_4Pb$(%): C, 40.44; H, 3.37; N, 5.24. Found: C, 40.44; H, 3.30; N, 5.11. IR (cm^{-1}) selected bands: 720(m), 855(m), 1017(s), 1270(s), 1404(vs), 1534(vs), 2970(w), 3037(w). ^1H NMR (DMSO; δ): 1.70 (s, 6H), 2.80 (s, 6H), 7.60–7.80 (d, 2H), 7.90–8.10 (s, 2H), 9.25–9.40 (d, 2H). $^{13}C\{^1H\}$ NMR (DMSO; δ): 25.04 ($^{13}CH_3$–phen), 27.30 ($^{13}CH_3$–COO), 123.75, 125.60, 126.80, 136.70, 158.46, 177.70, 178.58 (CH_3–^{13}COO). ^{207}Pb NMR (DMSO; δ) 410.50 ppm.

Crystallography

Crystallographic measurements were made at 293(2) K using a Siemens R3m/V diffractometer. Intensity data were collected within the range $3.57 \leq \theta \leq 30.06°$ using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 2337 unique reflections were measured, from which 2020 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of the hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. With goodness-of-fit on $F^2 = 1.069$: $R = 0.0468$ and $R_w = 0.1185$. The final difference density map showed a maximum peak and hole of 2.234 and -1.514 e Å^3, respectively. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the Sadabs programs were applied. All structural calculations were carried out with a PDP–11/23 + computer using the SDP-PLUS program package [14,15].

Crystal data and structure refinement are given in Table I, and selected bond lengths and angles in Table II. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figs. 1 and 2.

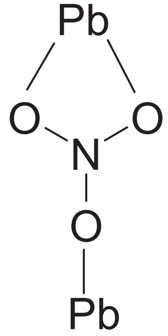
DISCUSSION

Synthesis

The reaction between 2,9-dimethyl-1,10-phenanthroline (dmphen) and lead(II) acetate, nitrate or perchlorate provided crystalline material analyzed as [Pb(dmphen)X_2] ($X = CH_3COO^-$, NO_3^- and ClO_4^-). The IR spectrum of [Pb(dmphen)$(CH_3COO)_2$] shows ν(COO) at *ca* 1407 and 1539 cm^{-1} and the [Pb(dmphen)$(NO_3)_3$] complex shows $\nu(NO_3)$ at *ca* 1371 cm^{-1}. The IR spectrum of Pb(dmphen)$(ClO_4)_2$ shows $\nu(ClO_4)$ at *ca* 1100 cm^{-1}.

Crystal Structure of [Pb(dmphen)$(NO_3)_2$]

The crystal structure of this compound consists of polymeric units of [Pb(dmphen) $(NO_3)_2$]. Each lead atom is chelated by the nitrogens of 2,9-dimethyl-1,10-phenanthroline with Pb–N distances of 2.462 Å, and the nitrate anions with Pb–O distances of 2.597 and 2.822 Å and also oxygen atoms of adjacent nitrate ligands with Pb–O distances of 3.103 Å. The coordination number in this complex is eight (two from the dmphen ligand, six from the nitrate ligands). Interaction of lead(II) with oxygen atoms of adjacent molecules produces polymer units in the solid state. The nitrate anion could be bidentate or bridged. Indeed, two oxygen atoms of this anion are chelated and one of them is linked to two different lead atoms.



The bond lengths of the three N–O bonds and also the three bond angles for the nitrate anions in this complex are different: N(2)–O(1) = 1.225, N(2)–O(2) = 1.2234, N(2)–O(3) = 1.189 Å; O(1)–N(2)–O(3) = 122.7, O(3)–N(2)–O(2) = 121.7, O(1)–N(2)–O(2) = 115.7°. Nitrate anions forming bridges between two lead atoms, producing the polymeric structure, are distorted, causing the varieties of bond lengths and angles of the nitrate anions in this complex.

Determination of the structure of this material by X-ray crystallography (Table I) showed the complex in the solid state (Fig. 1) to be polymeric with similarities to the

TABLE I Crystal data and structure refinement for $[Pb(dmphen)(NO_3)_2]_n$

Empirical formula	$C_{14}H_{12}N_4O_6Pb$
Formula weight	539.47
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	
a (Å)	16.769(3)
b (Å)	11.411(2)
c (Å)	8.7730(18)
α (°)	90.00
β (°)	108.03(3)
γ (°)	90.00
Volume ($Å^3$)	1596.3(6)
Z	4
Density (calculated) ($Mg\,m^{-3}$)	2.245
Absorption coefficient (mm^{-1})	10.610
$F(000)$	1016
Crystal size (mm^3)	$0.50 \times 0.30 \times 0.30$
θ range for data collection	3.57–30.06
Index ranges	$0 \leq h \leq 23$, $0 \leq k \leq 16$, $-12 \leq l \leq 11$
Reflections collected	2406
Independent reflections	2337 [$R(\text{int}) = 0.0236$]
Completeness to $\theta = 30.060$	96.4%
Absorption correction	Semiempirical, Ψ-scans
Max. and min. transmission	0.029 and 0.005
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2337/0/114
Goodness-of-fit on F^2	1.069
Final R indices for 2020 reflections [$I > 2\sigma(I)$]	$R1 = 0.0468$, $wR2 = 0.1185$
R indices (all data)	$R1 = 0.0538$, $wR2 = 0.1240$
Largest diff. peak, hole ($e\,Å^{-3}$)	2.234, −1.514

TABLE II Selected bond lengths (Å) and angles (°) for $[Pb(dmphen)(NO_3)_2]_n$

Pb(1)–N(1)$^{\#1}$	2.462(5)	N(1)$^{\#1}$–Pb(1)–N(1)	67.9(3)
Pb(1)–N(1)	2.462(5)	N(1)$^{\#1}$–Pb(1)–O(1)	70.5(2)
Pb(1)–O(1)	2.597(9)	N(1)–Pb(1)–O(1)	88.7(3)
Pb(1)–O(1)$^{\#1}$	2.597(9)	N(1)$^{\#1}$–Pb(1)–O(1)$^{\#1}$	88.7(3)
Pb(1)–O(2)	2.822(9)	N(1)–Pb(1)–O(1)$^{\#1}$	70.5(2)
Pb(1)–O(2)$^{\#1}$	2.822(9)	O(1)–Pb(1)–O(1)$^{\#1}$	155.1(5)
Pb(1)$\cdots$O(2)$^{\#2}$	3.103(9)	N(2)–O(1)–Pb(1)	104.4(7)
Pb(1)$\cdots$O(2)$^{\#3}$	3.103(9)	C(2)–N(1)–Pb(1)	123.9(6)
O(1)–N(2)	1.225(12)	C(6)–N(1)–Pb(1)	116.8(4)
O(2)–N(2)	1.234(14)	O(1)–N(2)–O(3)	122.7(14)
O(3)–N(2)	1.189(15)	O(2)–N(2)–O(3)	121.7(13)
		O(2)–N(2)–O(1)	115.7(10)

$^{\#1}-x+1, y, -z+1/2$; $^{\#2}-x+1, -y, -z$; $^{\#3}x, -y, z+1/2$.

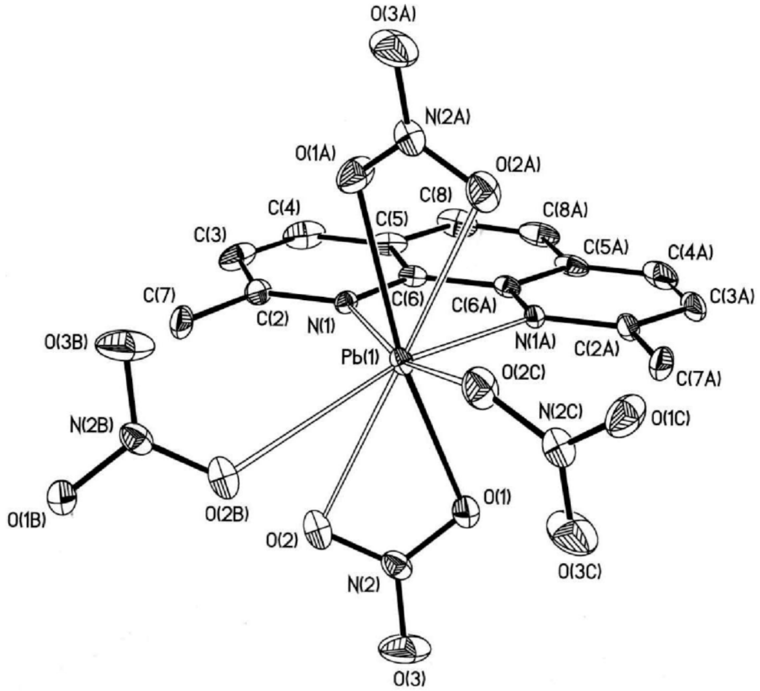


FIGURE 1 ORTEP diagram of [Pb(dmphen)$(NO_3)_2$]$_n$.

polymeric structures of [Pb(phen)$(NO_3)_2$]$_n$ and [Pb(phen)$(ClO_4)_2$]$_n$ and the dimeric structure of [Pb(phen)$(O_2CCH_3)_2$]$_2$ [16].

The arrangement of 2,9-dimethyl-1,10-phenanthroline and the nitrate anions does not suggest any gap or hole in the coordination geometry around the metal ion, so a holodirected geometry is observed. In this holodirected geometry, the lone pair can be stereochemically active or inactive. The mean Pb–O distance with a holodirected homoleptic stereochemistry is 2.53 Å [9]. Here we observe three different Pb–O distances, 2.597, 2.822 and 3.103 Å. In agreement with Brown [17] and Wang *et al.* [18], such a specific pattern of differences in bond lengths in holodirected homoleptic complexes can be attributed to repulsions involving the stereochemically active lone pair of electrons. Thus, the lone pair can be considered stereochemically active, but interligand repulsions prevent a gap. Hence, the geometry of the nearest coordination environment of every lead atom is only caused by the geometrical constraints of the coordinated 2,9-dimethyl-1,10-phenanthroline ligand and the nitrate anions. The stereochemically active lone pair of electrons have not influenced the geometry.

The striking difference between [Pb(dmphen)$(NO_3)_2$] and [Pb(phen)$(NO_3)_2$]$_n$, [Pb(phen)$(ClO_4)_2$]$_n$ and [Pb(phen)$(O_2CCH_3)_2$] is that the former complex is holodirected, whereas the latter three are hemidirected. The similarity of [Pb(dmphen) $(NO_3)_2$] to [Pb(phen)$(NO_3)_2$]$_n$, [Pb(phen)$(ClO_4)_2$]$_n$ and [Pb(phen)$(O_2CCH_3)_2$] lies in the π–π stacking [19,20] interactions (charge-transfer arrays) between the parallel aromatic rings belonging to adjacent chains in all four compounds, as shown in Fig. 2.

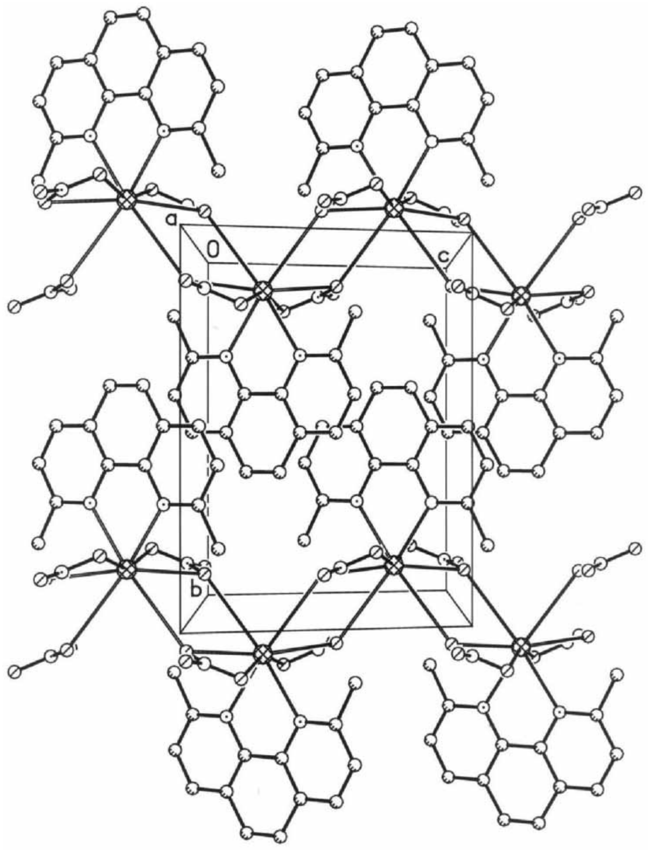


FIGURE 2 The unit cell and showing π–π stacking interaction in $[Pb(dmphen)(NO_3)_2]_n$.

Acknowledgment

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Supplementary Material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 208611 for $[Pb(dmphen)(NO_3)_2]$.

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