

2,9-Dimethyl-1,10-phenanthroline as Ligand in the Holo- and Hemidirected 1:1 and 1:2 Lead(II) Complexes

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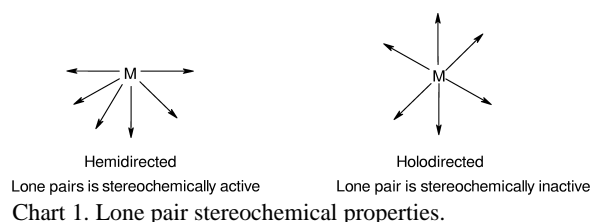
1:1 and 1:2 lead(II) complexes with 2,9-dimethyl-1,10-phenanthroline (Dmphen), $\{[\text{Pb}(\text{Dmphen})(\text{NO}_3)_n]$ and $[\text{Pb}(\text{Dmphen})_2(\text{ClO}_4)_2]$ have been synthesized and characterized by CHN elemental analysis, IR, ^1H NMR, ^{13}C NMR and ^{207}Pb NMR spectroscopy. The structure of these complexes was confirmed by X-ray crystallography. The single crystal X-ray data of $[\text{Pb}(\text{Dmphen})(\text{NO}_3)_n]$ show the complex to be polymeric and the Pb atom to have an unsymmetrical eight-coordinate geometry, the coordination being holodirected, whereas the $[\text{Pb}(\text{Dmphen})_2(\text{ClO}_4)_2]$ complex is monomeric and the Pb atom has an unsymmetrical eight-coordinate geometry with the coordination hemidirected.

Key words: Lead(II) Complexes, Crystal Structure, Lone Pair of Electrons, 2,9-Dimethyl-1,10-phenanthroline

Introduction

Research on the coordination chemistry of lead(II) complexes has progressed very rapidly over the last two decades [1 – 6]. According to its electronic configuration, $[\text{Xe}]4f^{14}5d^{10}6s^2$, and size, Pb(II) exhibits variable coordination numbers and geometries, on which the role of the lone pair of electrons has a great influence. The possible stereo-chemical activity of the lone pair in divalent lead compounds has recently been discussed by Shimoni-Livny *et al.* based on a thorough review of crystal data available in the Cambridge Structural Database (CSD) and through the use of ab-initio calculations [7]. They classify lead coordination as holodirected which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of the 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 (Chart 1).

The latter, present in all Pb(II) compounds with coordination number 2 to 5, is also quite common in Pb(II) compounds with coordination numbers 6, 7 and 8, but does not exist in lead complexes with higher coordination numbers, where holodirected geometry is the rule. To design sequestering agents ca-



pable of removing Pb(II) selectively from biological systems, it is important to consider the factors that affect the stereo-activity of the lone pair of electrons [8 – 9]. The lone pair in most lead(II) complexes is active, and structures with inactive lone pairs were rarely observed [7]. As previously reported, the inter-ligand repulsion is an important factor. All lead(II) complexes with 1,10-phenanthroline ligand [6, 10 – 12] have hemidirected geometry. We present herein a study of the 2,9-dimethyl-1,10-phenanthroline ligand in Pb(II) complexes.

Experimental Section

Physical property 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 Electro-

| | | | |
|---|---|--|--|
| Empirical formula | C ₁₄ H ₁₂ N ₄ O ₆ Pb | C ₂₈ H ₂₄ Cl ₂ N ₄ O ₈ Pb | Table 1. Crystal data and structure refinement for [Pb(dmphen)(NO ₃) ₂] and [Pb(dmphen) ₂](ClO ₄) ₂ . |
| Formula weight | 539.47 | 822.60 | |
| Temperature [K] | 293(2) | 120(2) | |
| Wavelength [Å] | 0.71073 | 0.71073 | |
| Crystal system | monoclinic | orthorhombic | |
| Space group | <i>C2/c</i> | <i>Pbcn</i> | |
| Unit cell dimensions [Å] | <i>a</i> = 16.769(3) <i>b</i> = 11.411(2) <i>c</i> = 8.7730(18) β = 108.03(3)° | <i>a</i> = 17.0289(8) <i>b</i> = 9.8987(5) <i>c</i> = 16.9290(8) | |
| Volume [Å ³] | 1596.3 (6) | 2853.6(2) | |
| <i>Z</i> | 4 | 4 | |
| Density (calculated) [g/cm ³] | 2.245 | 1.915 | |
| Absorption coefficient [mm ⁻¹] | 10.610 | 6.158 | |
| <i>F</i> (000) | 1016 | 1600 | |
| Crystal size [mm ³] | 0.50 × 0.30 × 0.30 | 0.35 × 0.25 × 0.10 | |
| Theta range for data collection [°] | 3.57 to 30.06 | 2.38 to 30.03 | |
| Index ranges | 0 ≤ <i>h</i> ≤ 23, 0 ≤ <i>k</i> ≤ 16, −12 ≤ <i>l</i> ≤ 11 | −23 ≤ <i>h</i> ≤ 23, −13 ≤ <i>k</i> ≤ 13, −23 ≤ <i>l</i> ≤ 23 | |
| Reflections collected | 2406 | 34167 | |
| Independent reflections | 2337 [<i>R</i> (int) = 0.0236] | 4151 [<i>R</i> (int) = 0.0475] | |
| Completeness to theta [%] | 96.4 | 99.4 | |
| Absorption correction | Semi-empirical, Ψ -scans | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.029 and 0.005 | 0.358 and 0.169 | |
| Refinement method | Full-matrix least-squares on <i>F</i> ² | Full-matrix least-squares on <i>F</i> ² | |
| Data / restraints / parameters | 2337/0/114 | 4151/0/197 | |
| Goodness-of-fit on <i>F</i> ² | 1.069 | 0.983 | |
| Final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)] | indices for 2020 ref1 <i>R</i> 1 = 0.0468, <i>wR</i> 2 = 0.1185 | indices for 2744 ref1 <i>R</i> 1 = 0.0338, <i>wR</i> 2 = 0.0826 | |
| <i>R</i> Indices (all data) | <i>R</i> 1 = 0.0538, <i>wR</i> 2 = 0.1240 | <i>R</i> 1 = 0.0506, <i>wR</i> 2 = 0.0872 | |
| Largest diff. Peak, hole [e.Å ⁻³] | 2.234, −1.514 | 5.490, −1.276 | |

thermal 9100 apparatus and are uncorrected. The ²⁰⁷Pb solution NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 104.6 MHz using a 5-mm broadband probe. Lead chemical shifts are reported (ppm) downfield from tetramethyllead using PbPh₄ ($\delta_{\text{Pb}} = -178.0$ ppm, saturated in CDCl₃) as an external standard in 0.01 M and in 25 °C. Each lead spectrum was acquired in 3–10 h.

Preparation of [Pb(dmphen)(NO₃)₂]

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, were deposited in the cooler arm which were filtered off, washed with acetone and ether and air dried (0.27 g yield 50%), m.p. > 320 °C. C₁₄H₁₂N₄O₆Pb: calcd. 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), 7.50–7.70 (d, 2H), 7.80–8.00 (s, 2H), 8.30–9.50 (d, 2H). ¹³C-{¹H} NMR (DMSO) δ = 25.00

Table 2. Selected bond lengths [Å] and angles [°] for the [Pb(dmphen)(NO₃)₂].

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

^{#1} *x* + 1, *y*, −*z* + 1/2; ^{#2} *x* + 1, −*y*, −*z*; ^{#3} *x*, −*y*, *z* + 1/2.

(CH₃), 123.71, 125.62, 126.84, 136.74, 158.44, 177.66. ²⁰⁷Pb NMR (DMSO) δ = 450.03 ppm.

Preparation of [Pb(dmphen)₂(ClO₄)₂]

2,9-Dimethyl-1,10-phenanthroline (0.416 g, 2 mmol) was placed in one arm of a branched tube and lead(II) acetate (0.36 g, 1 mmol) and sodium perchlorate (0.246 g, 2 mmol) in the other. Methanol was carefully added to fill both

Table 3. Selected bond lengths [Å] and angles [°] for the [Pb(dmphen)₂](ClO₄)₂.

| | | | |
|---------------------|------------|---------------------|------------|
| Pb(1)-N(2)#1 | 2.547(3) | Pb(1)-N(2) | 2.547(3) |
| Pb(1)-N(1) | 2.554(3) | Pb(1)-N(1)#1 | 2.554(3) |
| Pb(1)-O(1)#1 | 2.867(3) | Pb(1)-O(1) | 2.867(3) |
| Pb(1)···O(2)#1 | 3.325(3) | Pb(1)···O(2) | 3.325(3) |
| N(2)#1-Pb(1)-N(2) | 73.43(13) | N(2)-Pb(1)-N(1) | 65.41(10) |
| N(1)-Pb(1)-N(2)#1 | 81.39(9) | N(1)#1-Pb(1)-N(2) | 81.39(9) |
| N(2)#1-Pb(1)-N(1)#1 | 65.41(10) | N(1)-Pb(1)-N(1)#1 | 138.67(15) |
| N(2)-Pb(1)-O(1)#1 | 151.47(9) | N(2)#1-Pb(1)-O(1)#1 | 84.50(9) |
| N(1)-Pb(1)-O(1)#1 | 94.03(9) | N(1)#1-Pb(1)-O(1)#1 | 105.92(9) |
| N(2)-Pb(1)-O(1) | 84.50(9) | N(2)#1-Pb(1)-O(1) | 151.47(9) |
| N(1)-Pb(1)-O(1) | 105.92(9) | N(1)#1-Pb(1)-O(1) | 94.03(9) |
| O(1)#1-Pb(1)-O(1) | 121.56(12) | N(2)-Pb(1)-O(2)#1 | 144.90(8) |
| N(2)#1-Pb(1)-O(2)#1 | 81.89(9) | N(1)-Pb(1)-O(2)#1 | 135.34(9) |
| N(1)#1-Pb(1)-O(2)#1 | 65.59(9) | O(1)#1-Pb(1)-O(2)#1 | 43.26(7) |
| O(1)-Pb(1)-O(2)#1 | 108.42(8) | N(2)-Pb(1)-O(2) | 81.89(9) |
| N(2)#1-Pb(1)-O(2) | 144.90(8) | N(1)-Pb(1)-O(2) | 65.59(9) |
| N(1)#1-Pb(1)-O(2) | 135.34(9) | O(1)#1-Pb(1)-O(2) | 108.42(8) |
| O(1)-Pb(1)-O(2) | 43.26(7) | O(2)#1-Pb(1)-O(2) | 130.05(8) |

#1 $x+1, y, -z+1/2$; #2 $x+1, -y, -z$; #3 $x, -y, z+1/2$.

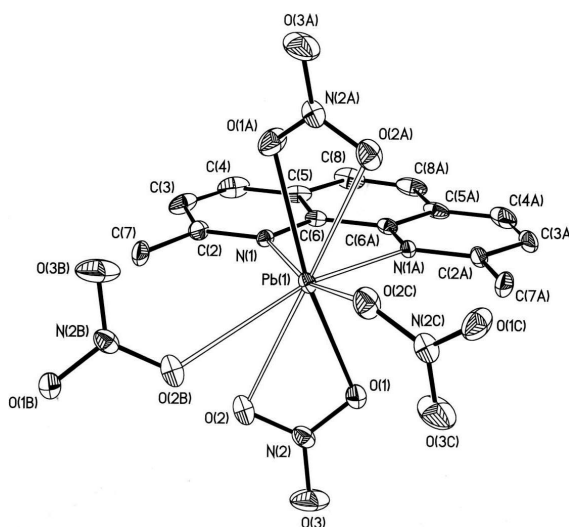
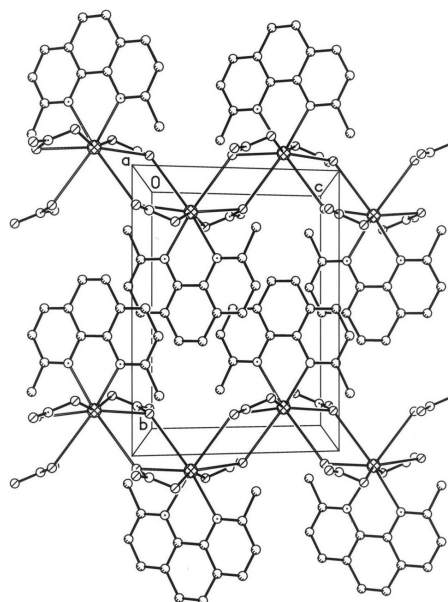
arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60 °C, while the other was at ambient temperature. After 5 d, Yellow crystals, (m. p. > 320 °C) had deposited in the cooler arm. Yield: 0.369 g, 45%. C₂₈H₂₄N₄O₈Cl₂Pb: calcd. C 40.82, H 2.91, N 6.80; found C 41.20, H 2.70, N 6.60. IR (cm⁻¹) selected bands: 720(m), 850(m), 1100(vs), 1425(s), 1580(w), 3030(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). ¹³C-{¹H} NMR (DMSO) δ = 25.04 (CH₃), 123.75, 125.60, 126.80, 136.70, 158.46, 177.70. ²⁰⁷Pb NMR (DMSO) δ = -390.50 ppm.

Crystallography

Intensity data measurements were carried out using a Siemens R3m/V diffractometer. Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 . There is a high positive residual density of 5.490 e.Å⁻³ near the Pb1 center in the [Pb(dmphen)₂](ClO₄)₂ due to considerable absorption effects which could not be completely corrected.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic displacement parameter. 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 [13–14].

Crystal data and structure refinement are given in Table 1. Selected bond lengths and angles are given in Tables 2 and 3. Anisotropic displacement parameters, observed and calcu-

Fig. 1. ORTEP diagram of the monomeric unit [Pb(dmphen)-(NO₃)₂] and its environment.Fig. 2. The unit cell of [Pb(dmphen)(NO₃)₂]_n.

lated structure factors, full lists of bond distances, bond angles and torsion angles. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figures 1–4.

Results and Discussion

Synthesis

Reaction between dmphen ligand and lead(II) nitrate or lead(II) perchlorate provided crystalline

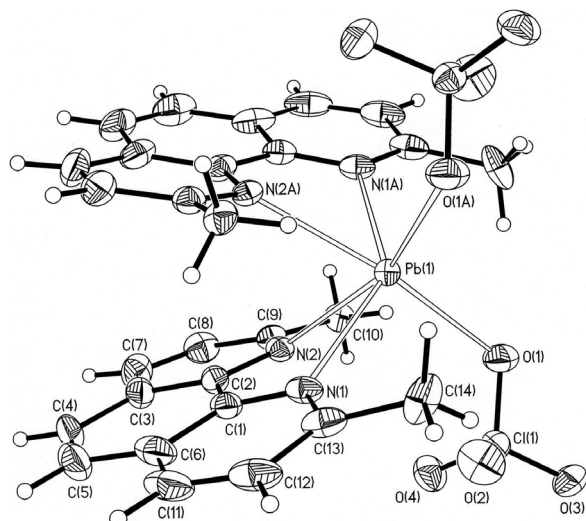


Fig. 3. ORTEP diagram of the $[\text{Pb}(\text{dmphen})_2(\text{ClO}_4)_2]$ molecule.

material analyzing as $[\text{Pb}(\text{dmphen})(\text{NO}_3)_2]$ and $[\text{Pb}(\text{dmphen})_2(\text{ClO}_4)_2]$, respectively. The IR spectrum of $[\text{Pb}(\text{dmphen})(\text{NO}_3)_2]$ shows $\nu(\text{NO}_3)$ at ca. 1371 cm^{-1} . The IR spectrum of $[\text{Pb}(\text{dmphen})_2(\text{ClO}_4)_2]$ has $\nu(\text{ClO}_4)$ at 1100 cm^{-1} .

Crystal structure of $[\text{Pb}(\text{dmphen})(\text{NO}_3)_2]$

The crystal structure of this compound consists of polymers of the units $[\text{Pb}(\text{dmphen})(\text{NO}_3)_2]$. Each lead atom is chelated by the nitrogen atoms of 2,9-dimethyl-1,10-phenanthroline with a Pb–N distance of 2.462 \AA and by the nitrate anions with Pb–O distances of 2.597 and 2.822 and also oxygen atoms of adjacent nitrate ligands with a Pb–O distances of 3.103 \AA . The coordination number in this complex is eight (Chart 2).

The three N–O bonds and also the three bond angles for the nitrate anion in the $[\text{Pb}(\text{dmphen})(\text{NO}_3)_2]$ complex are different, $[\text{N}(2)\text{--O}(1) = 1.225$, $\text{N}(2)\text{--O}(2) = 1.234$, $\text{N}(2)\text{--O}(3) = 1.189\text{ \AA}$, $\text{O}(1)\text{--N}(2)\text{--O}(3) = 122.7^\circ$, $\text{O}(2)\text{--N}(2)\text{--O}(3) = 121.7^\circ$ and $\text{O}(1)\text{--N}(2)\text{--O}(2) = 115.7^\circ]$, showing that the nitrate anion is distorted.

The structure (Table 1) has various similarities to the polymeric structures of $[\text{Pb}(\text{phen})(\text{NO}_3)_2]_n$,

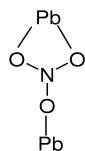


Chart 2.

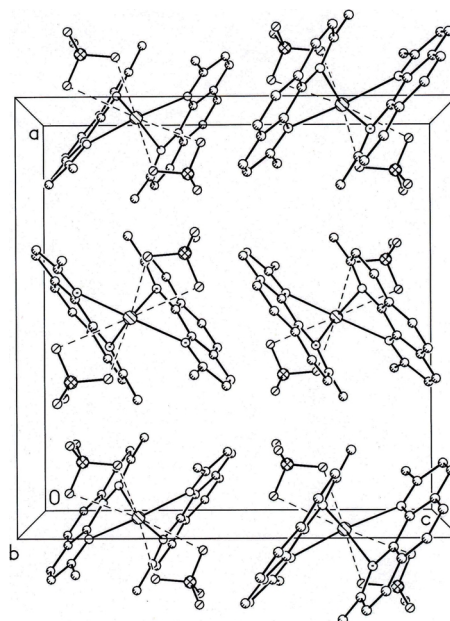


Fig. 4. The unit cell showing π - π stacking interactions in $[\text{Pb}(\text{dmphen})_2(\text{ClO}_4)_2]$.

$[\text{Pb}(\text{phen})(\text{ClO}_4)_2]_n$ and the dimeric structure of $[\text{Pb}(\text{phen})(\text{O}_2\text{CCH}_3)_2]_2$ [6].

The arrangement of the 2,9-dimethyl-1,10-phenanthroline ligand 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. The striking difference between $[\text{Pb}(\text{dmphen})(\text{NO}_3)_2]$ and $[\text{Pb}(\text{phen})(\text{NO}_3)_2]_n$, $[\text{Pb}(\text{phen})(\text{ClO}_4)_2]_n$ and $[\text{Pb}(\text{phen})(\text{O}_2\text{CCH}_3)_2]$ is that the structure of this complex is holodirected, whereas the structures in the $[\text{Pb}(\text{phen})(\text{NO}_3)_2]_n$, $[\text{Pb}(\text{phen})(\text{ClO}_4)_2]_n$ and $[\text{Pb}(\text{phen})(\text{O}_2\text{CCH}_3)_2]$ complexes are hemidirected. Possibly the presence of two methyl groups in the 2 and 9 positions of the dmphen ligand causes intra-ligand repulsions and results in the holodirected geometry.

Crystal structure of $[\text{Pb}(\text{dmphen})_2(\text{ClO}_4)_2]$

The crystal structure of this compound consists of monomeric units $[\text{Pb}(\text{dmphen})_2(\text{ClO}_4)_2]$. Each lead atom is chelated by the nitrogen atoms of the dmphen ligands with Pb–N distances of 2.547 , 2.547 , 2.554 and 2.554 \AA , and also by oxygen atoms of the perchlorate anions with Pb–O distances of 2.867 and 2.867 . The coordination number in this complex is six. There are weak interactions of the lead(II) atoms with other oxy-

gen atoms of perchlorate anions. In fact each Pb atom in this structure along with six normal bonds forms two “weak” Pb···O bonds, the distances being 3.325 and 3.325 Å. (Table 3). The presence of a lone pair at the lead atom is apparently the reason that the weak interactions can not become shorter. The arrangement of the dmphen ligands and the perchlorate anions suggests a gap or hole in the coordination geometry around the metal ion, the [O(1)-Pb-O(1A)] angle is 121.56°. The geometry of the nearest coordination environment occupied by the lone pair of electrons in a hybrid orbital on the metal atom. Such an environment leaves space for bonding of oxygen atoms of the perchlorate anions (Fig. 4).

Thus, the coordination geometry in [Pb(dmphen)₂-(ClO₄)₂] is hemidirected and for the [Pb(dmphen)-(NO₃)₂] complex it is holodirected. It is becoming increasingly clear, however, that it is not necessarily true that one of the effects of the lone pair activity in Pb(II) compounds is to cause a void in the coordination geometry; in fact this geometry can take various forms [15]. Some authors [16] have suggested that in the holodirected Pb(II) complexes a specific pattern of differences in the bond lengths has to be attributed to repulsion involving a stereo-chemically active lone pair [17]. In the [Pb(dmphen)(NO₃)₂] complex, the bond lengths of the coordination sphere are very different (2.597–3.103 Å).

In the reported complexes here, there is some minor or major π - π stacking [18–19] interaction between the parallel aromatic rings of adjacent chains as shown in Figs 4 and 5. The mean molecular planes are close to parallel and separated by a distance of ~ 3.5 Å, close to that of the planes in graphite.

Parallel arrays of the planes of the aromatic moieties indicate that the interactions in [Pb(dmphen)₂(ClO₄)₂] are of the “ π -stacking” type, rather than “edge-to-face” or “vertex-to-face” types [20–23]. Projection of the structure perpendicular to the ring plane shows the overall form of “slipped” stacking [20–24], which is at least qualitatively understandable in terms of

optimizing approaches between atoms of opposite charges [25]. In [Pb(dmphen)(NO₃)₂]_n these interactions are “edge-to-face”.

A simple model to describe the nature of π - π interactions has been developed by Hunter *et al.* [25]. This model predicts that face-to-face π -stacked interactions will be disfavored due to the dominance of π - π repulsion. However, in offset π -stacked, and edge-on or T-shaped geometries, favourable π - σ attractions dominate. The polarization of aromatic systems, through the introduction of heteroatoms, electron-withdrawing or electron-donating groups, alters the nature of any π - π interactions. It has been shown [26–27] that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups. Hence, it can be expected that within [Pb(dmphen)₂(ClO₄)₂] the electron-poor pyridyl rings will interact with phenyl groups and within [Pb(dmphen)(NO₃)₂]_n the edge-to-face model must be favored (Fig. 5).

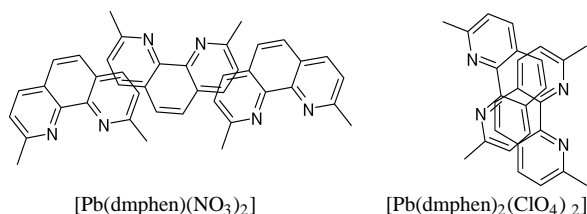


Fig. 5. Projection of nearest neighbor π - π stacking in Pb(II) complexes containing the dmphen ligand.

Supplementary material: Complete lists of bond lengths and angles, co-ordinates and displacement parameters have been deposited at 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)(NO₃)₂] and 227395 for [Pb(dmphen)₂(ClO₄)₂].

Acknowledgements

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