# The Interaction of Lead(II) with Oxa-aza Macrocycles: The X-Ray Crystal Structures of Lead(II) Complexes of an $\mathrm{N}_{3} \mathrm{O}_{3}$ Schiff-base Macrocycle and of the Corresponding Saturated Macrocycle $\dagger$ 

Alan Bashall, Mary McPartlin, and Brian P. Murphy*<br>Department of Applied Chemistry and Life Sciences, The Polytechnic of North London, Holloway Road, London N7 8DB<br>David E. Fenton * and Simon J. Kitchen<br>Department of Chemistry, The University, Sheffield S3 7HF<br>Peter A. Tasker<br>ICI Colours and Fine Chemicals, Hexagon House, Blackley, Manchester M9 3DA

The complexes $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, (1) $\cdot \mathrm{H}_{2} \mathrm{O}$, and $\left[\mathrm{PbL}^{2}\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O},(2) \cdot \mathrm{H}_{2} \mathrm{O}$, where $\mathrm{L}^{1}$ and $\mathrm{L}^{2}$ are corresponding di-imino- and diamino-macrocycles containing an $\mathrm{N}_{3} \mathrm{O}_{3}$ donor set, have been synthesized and characterised. $X$-Ray structural analyses of the anhydrous form of (1) and (2) have revealed significantly different co-ordination environments for the lead(11) ion in the complexes. In (1), $L^{1}$ utilises all six possible donors in a ten-co-ordinate complex, with no apparent stereochemical activity of the lone pair on lead(II). Crystals of (1) were monoclinic, space group $P 2_{1} / n$ (alternative no. 14) with $a=30.245(6), b=10.271(2), c=16.246(3) \AA, \beta=95.05(3)^{\circ}$, and $Z=8.2872$ Independent reflections above background were measured and the structure refined to $R=0.0648$. In contrast, $L^{2}$ employs only the three nitrogen donor atoms of the macrocycle in a six-co-ordinate complex, apparently with a stereochemically active lone pair. Crystals of (2) were triclinic, space group $P \overline{1}$ (no. 2) with $a=15.117(3), b=9.658(2), c=9.182(2) \AA, \alpha=76.24(2)$, $\beta=105.03(3), \gamma=92.19(3)^{\circ}$, and $Z=2.3214$ Independent reflections above background were measured and the structure refined to $R=0.0508$.

Structural studies of alkali, alkaline-earth, and transitionmetal complexes of macrocycles have been extensively reported; ${ }^{1}$ but, in contrast, those of the main group elements are less common. For lead(II) these are limited to mononuclear complexes derived from saturated polyaza macrocycles, ${ }^{2,3}$ imine Schiff-base macrocycles, ${ }^{4-7}$ an oxazolidinecontaining macrocycle, ${ }^{8}$ polyoxa- ${ }^{9}$ and oxa-aza-coronands ${ }^{10}$ and cryptands, ${ }^{11}$ and also to homo ${ }^{12}$ and hetero-dinuclear ${ }^{13}$ complexes derived from Schiff bases.

In a programme designed to synthesize a wide range of oxaaza macrocycles for the study of metal-ion recognition, we have previously developed an expedient synthetic route to ligands of this type. ${ }^{14}$ In this approach, template cyclocondensation of $1, n$-diamines with heterocyclic dicarbonyls, in the presence of lead(II) salts, leads to the precursor macrocyclic Schiff-base complexes of lead(II), and crucially, these may be reductively demetallated in situ to give the corresponding metal-free diamino macrocycle. This novel approach to macrocyclic synthesis therefore overcomes the usual limitations of the more traditional template routes where the metal tends to be 'locked' into the macrocycle with demetallation often resulting in decomposition. ${ }^{15}$ In this paper we report the syntheses and $X$-ray structure analysis of the lead(II) complexes of a precursor di-imino-macrocycle ( $\mathrm{L}^{1}$ ) and the corresponding diaminomacrocycle ( $\mathrm{L}^{2}$ ), which show marked differences in coordination behaviour.

## Experimental

Spectra and Other Procedures.-Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer as KBr discs, ${ }^{1} \mathrm{H}$ n.m.r. spectra using a Bruker WM250 instrument (see structures $L^{1}$ and $L^{2}$ for proton assignments). Mass spectra [fast atom bombardment (f.a.b.) source] were recorded

using a Kratos MS80 spectrometer, the samples being prepared as 3-nitrobenzyl alcohol matrices. Microanalyses were determined by the University of Sheffield Microanalytical service. A Philips PW1100 four-circle diffractometer was used for $X$-ray data collection with Mo- $K_{\alpha}$ radiation from a graphite-crystal monochromator. Computing was carried out on a Digital Equipment Corporation VAX 8260.

The lead(II) complex $\left[\mathrm{PbL}^{1}\left(\mathrm{ClO}_{4}\right)_{2}\right]$ and the free macrocycle $L^{2}$ were prepared by the methods reported earlier, ${ }^{14,16}$

Syntheses and Characterisation.- $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, (1) $\cdot \mathrm{H}_{2} \mathrm{O}$. The salt $\left[\mathrm{PbL}^{1}\right]\left[\mathrm{ClO}_{4}\right]_{2}(1 \mathrm{mmol})$ was dissolved in hot EtOH-MeCN ( $25 \mathrm{~cm}^{3}$ ) and excess of $\mathrm{NaNO}_{3}$ in water ( 5 $\mathrm{cm}^{3}$ ) was added. The solution was filtered hot and then allowed to cool. The yellow crystals of $(\mathbf{1}) \cdot \mathrm{H}_{2} \mathrm{O}$ were filtered off, washed with EtOH and then $\mathrm{Et}_{2} \mathrm{O}$, and dried in vacuo. I.r. ( KBr disc): $1620 \mathrm{w}[v(\mathrm{C}=\mathrm{N})], 1575\{v[\mathrm{C}=\mathrm{N}(\mathrm{py})]\}, 1435,1385,1322$, and $1298 \mathrm{~cm}^{-1}\left[\mathrm{v}\left(\mathrm{NO}_{3}\right)\right] .{ }^{1} \mathrm{H}$ N.m.r. $\left[\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right]: \delta 9.87(2 \mathrm{H}$, s,

[^0]$\left.\mathrm{H}^{3}\right), 8.72\left(1 \mathrm{H}, \mathrm{t}, \mathrm{H}^{1}\right), 8.44\left(2 \mathrm{H}, \mathrm{d}, \mathrm{H}^{2}\right), 7.78\left(2 \mathrm{H}, \mathrm{d}, \mathrm{H}^{4}\right), 7.48(2 \mathrm{H}$, $\left.\mathrm{t}, \mathrm{H}^{6}\right), 7.29\left(2 \mathrm{H}, \mathrm{d}, \mathrm{H}^{7}\right), 7.19\left(2 \mathrm{H}, \mathrm{t}, \mathrm{H}^{5}\right), 4.37\left(4 \mathrm{H}, \mathrm{br}, \mathrm{H}^{8}\right)$, and $3.92\left(4 \mathrm{H}, \mathrm{br}, \mathrm{H}^{9}\right)$. M.s. (f.a.b. positive ion): $\mathrm{m} / \mathrm{z} 657$ $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)\right]^{+}$and $595\left[\mathrm{PbL}^{1}\right]^{2+}$. Bulk-sample microanalysis: (Found: C, 37.7; H, 3.1; N, 9.4. Calc. for $\mathrm{C}_{23} \mathrm{H}_{23} \mathrm{~N}_{5} \mathrm{O}_{10} \mathrm{~Pb}$ : C, $37.50 ; \mathrm{H}, 3.15 ; \mathrm{N}, 9.50 \%$ ). Although the best agreement with the bulk-sample microanalytical data is given by the monohydrate (1) $\cdot \mathrm{H}_{2} \mathrm{O}$, no water of hydration was located in the $X$-ray crystal structure (see below).
$\left[\mathrm{PbL}^{2}\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O},(2) \cdot \mathrm{H}_{2} \mathrm{O}$. The salt $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}(1 \mathrm{mmol})$ was added to a refluxing solution of the ligand $\mathrm{L}^{2}(1 \mathrm{mmol})$ in $\mathrm{MeOH}\left(30 \mathrm{~cm}^{3}\right)$. A yellow precipitate developed and MeCN was added dropwise to the refluxing solution until the precipitate had dissolved. The yellow solution was filtered hot and then allowed to cool. The resulting yellow crystals of compound (2) were filtered off, washed with MeOH then $\mathrm{Et}_{2} \mathrm{O}$, and dried in vacuo. I.r ( KBr disc): $3245[\mathrm{v}(\mathrm{NH})], 1580$ $\{v[\mathrm{C}=\mathrm{N}(\mathrm{py})]\}, 1435,1385$, and $1290 \mathrm{~cm}^{-1}\left[v\left(\mathrm{NO}_{3}\right)\right] .{ }^{1} \mathrm{H}$ N.m.r. $\left[\left(\mathrm{CD}_{3}\right)_{2} \mathrm{SO}\right]: \delta 7.79\left(1 \mathrm{H}, \mathrm{t}, \mathrm{H}^{1}\right), 7.40\left(2 \mathrm{H}, \mathrm{d}, \mathrm{H}^{2}\right), 6.9-$ $6.6\left(8 \mathrm{H}, \mathrm{m}, \mathrm{H}^{4-7}\right), 5.48(2 \mathrm{H}, \mathrm{s}, \mathrm{NH}), 4.42\left(4 \mathrm{H}, \mathrm{br}, \mathrm{H}^{3}\right), 4.13(4$ $\mathrm{H}, \mathrm{br}, \mathrm{H}^{8}$ ), and $3.89\left(4 \mathrm{H}\right.$, br, $\left.\mathrm{H}^{9}\right)$. M.s. (f.a.b. positive ion): $m / z$ $661\left[\mathrm{PbL}^{2}\left(\mathrm{NO}_{3}\right)\right]^{+}$and $598\left[\mathrm{~Pb}\left(\mathrm{~L}^{2}-\mathrm{H}\right)\right]^{3+}$. Bulk sample microanalysis: (Found: C, 37.2; H, 3.4; N, 9.3. Calc. for $\mathrm{C}_{23} \mathrm{H}_{27} \mathrm{~N}_{5} \mathrm{O}_{10} \mathrm{~Pb}: \mathrm{C}, 37.30 ; \mathrm{H}, 3.65 ; \mathrm{N}, 9.45 \%$ ). No water of hydration was located in the $X$-ray crystal structure (see below).

X-Ray Structural Analyses.-Crystal data. (1), $\mathrm{C}_{23} \mathrm{H}_{21-}$ $\mathrm{N}_{5} \mathrm{O}_{9} \mathrm{~Pb}, M=718.64$, monoclinic, space group $P 2_{1} / n$ (alternative no. 14), $a=30.245(6), b=10.271(2), c=16.246$ (3) $\AA$, $\beta=95.05(3)^{\circ}, Z=8, U=5025.07 \AA^{3}, D_{\mathrm{c}}=1.899 \mathrm{~g} \mathrm{~cm}^{-3}$, $F(000)=2784, \mu\left(\mathrm{Mo}-K_{\alpha}\right)=67.30 \mathrm{~cm}^{-1}$.
(2), $\mathrm{C}_{23} \mathrm{H}_{25} \mathrm{~N}_{5} \mathrm{O}_{9} \mathrm{~Pb}, M=722.68$, triclinic space group $P \overline{1}$ (no. 2), $a=15.117(3), b=9.658(2), c=9.182(2) \AA, \alpha=$ 76.24(2), $\beta=105.03(3), \gamma=92.19(3)^{\circ}, Z=2, U=1257.16$ $\AA^{3}, D_{\mathrm{c}}=1.909 \mathrm{~g} \mathrm{~cm}^{3}, F(000)=704,\left(\mathrm{Mo}-K_{\alpha}\right)=67.28 \mathrm{~cm}^{-1}$.

Data collection. Data were collected in the $\theta$ range $3-25^{\circ}$ by the method described previously, ${ }^{17}$ with a constant scan speed of $0.05^{\circ} \mathrm{s}^{-1}$ and an $\omega$-scan width of $0.90^{\circ}$ for both crystals, which were of dimensions $0.26 \times 0.13 \times 0.08$ for (1) and $0.20 \times 0.20 \times 0.18 \mathrm{~mm}$ for (2). Three reference reflections were measured every 5 h in each case and showed no significant changes in intensities. The data were corrected for Lorentz and polarisation factors and equivalent reflections were merged to give a total of 2872 [(1)] and 3214 [(2)] unique data with $I>3 \sigma(I)$.

Structure solution and refinement. ${ }^{18}$ For each structure the position of the lead atom was determined from a Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. After several cycles of refinement with isotropic thermal parameters, the hydrogen atoms (apart from those bonded to nitrogen donors) were included at calculated positions (C-H $1.08 \AA$ ). For each structure common isotropic thermal parameters were assigned to the aromatic and aliphatic hydrogen atoms and the free variables refined to final values of 0.079 and 0.113 respectively for (1) and 0.080 and $0.082 \AA^{2}$ for (2). A Fourier-difference synthesis using data with $(\sin \theta) / \lambda<0.35$ revealed suitable maxima for the hydrogen atoms of the secondary amine donors in (2) and these were included in the structure-factor calculations with isotropic thermal parameters of $0.08 \AA^{2}$ but were not refined. Absorption corrections were applied to the data for both structures at this stage. ${ }^{19}$ In the final cycles of fullmatrix refinement the lead [(1) and (2)] and the nitrogen and oxygen atoms [(2) only] were assigned anisotropic thermal parameters. Neutral scattering factors, corrected for the real and imaginary components of anomalous dispersion, were used throughout. ${ }^{20}$ Individual weights of $1 / \sigma^{2}(I)$ were assigned to each reflection and refinement converged at $R 0.0648$ and $R^{\prime}$
0.0648 for (1) and $R 0.0508$ and $R^{\prime} 0.0501$ for (2), where $R^{\prime}=$ $\Sigma\left|\left|F_{\mathrm{o}}\right|-\left|F_{\mathrm{c}} \| w^{\frac{1}{2}} / \Sigma\right| F_{\mathrm{o}}\right| w^{\frac{1}{2}}$.

Due to the poor diffraction by the only crystals of compound (1) which could be obtained there was considerable shortage of data. Refinement of (1) was difficult as there was an approximate translational relationship of $0.25,0,0.25$ between many of the corresponding atoms in the two independent molecules and best results were obtained by refinement of the parameters of the two independent molecules in separate blocks. This poor diffraction by the crystals is reflected in the relatively high estimated standard deviations (e.s.d.s) of the bond lengths and angles of the structure of (1). The gross features of complex (1) are well established however and provide a useful comparison to those of (2) and are therefore reported. Selected final atomic co-ordinates of (1) and (2) are listed in Table 1, selected bond lengths and angles in Tables 2 and 3 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H -atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

## Results and Discussion

The complex $\left[\mathrm{PbL}^{1}\right]\left[\mathrm{ClO}_{4}\right]_{2}$ was prepared by a template cyclo-condensation of pyridine-2,6-dicarbaldehyde and 1,5-bis( $2^{\prime}$-aminophenoxy)-3-oxapentane in aqueous ethanol, ${ }^{16}$ and $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O}$, (1) $\cdot \mathrm{H}_{2} \mathrm{O}$, was prepared from the per-chlorato-complex by anion exchange using sodium nitrate. The presence of an imine stretch at $1620 \mathrm{~cm}^{-1}$ and the absence of bands corresponding to free carbonyl or free amine, together



Figure 1. The structure of $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)_{2}\right]$ : (a) showing donor interactions and (b) 'side-on' view showing macrocycle conformation

Table 1. Fractional atomic co-ordinates

| Atom | $x$ | $y$ | $x$ | Atom | $x$ | $y$ | $z$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Complex (1) |  |  |  |  |  |  |  |
| $\mathrm{Pb}(1)$ | -0.225 82(4) | $0.14639(14)$ | 0.034 79(8) | $\mathrm{Pb}(2)$ | 0.036 43(4) | $0.12889(15)$ | $0.26917(8)$ |
| N (2a) | $-0.3026(10)$ | 0.0023 (30) | 0.0261 (18) | $\mathrm{N}(2 \mathrm{x})$ | $-0.0408(9)$ | $-0.0050(27)$ | 0.2701 (17) |
| $\mathrm{N}(2 \mathrm{~b})$ | -0.171 8(7) | 0.1751 (24) | -0.083 7(14) | $\mathrm{N}(2 \mathrm{y})$ | 0.0875 (9) | 0.143 6(32) | $0.1438(16)$ |
| N(1c) | -0.239 6(9) | -0.0019(26) | -0.088 2(16) | N(1z) | $0.0189(8)$ | -0.027 2(25) | $0.1503(15)$ |
| O(1a) | -0.281 6(8) | 0.118 2(26) | 0.168 0(15) | $\mathrm{O}(1 \mathrm{x})$ | -0.016 0(7) | 0.139 6(26) | 0.404 4(13) |
| $\mathrm{O}(1 \mathrm{~b})$ | -0.147 8(9) | $0.2902(25)$ | 0.057 4(17) | $\mathrm{O}(1 \mathrm{y})$ | 0.118 4(8) | 0.264 7(26) | 0.2815 (17) |
| O (1c) | -0.200 5(9) | 0.265 2(26) | 0.190 8(17) | $\mathrm{O}(1 \mathrm{z})$ | 0.068 4(8) | 0.263 4(24) | $0.4200(15)$ |
| $\mathrm{O}(3 \mathrm{a})$ | -0.209 1(10) | -0.090 3(31) | 0.113 1(18) | $\mathrm{O}(3 \mathrm{x})$ | 0.049 3(9) | $-0.1195(30)$ | 0.342 8(16) |
| $\mathrm{O}(3 \mathrm{~b})$ | -0.151 4(10) | -0.011 4(31) | 0.067 5(20) | $\mathrm{O}(3 \mathrm{y})$ | $0.1079(9)$ | -0.042 2(30) | 0.2907 (18) |
| $\mathrm{O}(3 \mathrm{c})$ | $-0.1460(10)$ | -0.193 9(31) | 0.127 8(19) | $\mathrm{O}(3 \mathrm{z})$ | $0.1094(9)$ | -0.2261(30) | $0.3579(19)$ |
| $\mathrm{N}(3 \mathrm{a})$ | -0.169 6(10) | -0.097 0(33) | 0.1014 (18) | $\mathrm{N}(3 \mathrm{x})$ | 0.0901 (10) | -0.123 0(34) | 0.326 9(17) |
| $\mathrm{O}(4 \mathrm{a})$ | -0.263 7(13) | 0.397 7(44) | 0.037 6(26) | $\mathrm{O}(4 \mathrm{x})$ | -0.014 4(10) | 0.270 8(32) | 0.167 7(19) |
| $\mathrm{O}(4 \mathrm{~b})$ | -0.265 5(10) | 0.2915 (33) | -0.077 4(19) | $\mathrm{O}(4 \mathrm{y})$ | 0.011 5(13) | 0.3914 (41) | 0.266 4(24) |
| $\mathrm{O}(4 \mathrm{c})$ | -0.290 6(11) | 0.489 8(35) | $-0.0761(20)$ | $\mathrm{O}(4 \mathrm{z})$ | -0.0279(10) | 0.4831 (33) | 0.173 6(20) |
| $\mathrm{N}(4 \mathrm{a})$ | -0.273 9(11) | 0.3912 (37) | -0.0410 (23) | $\mathrm{N}(4 \mathrm{x})$ | -0.010 2(11) | 0.384 4(39) | 0.198 6(21) |
| C(1c) | -0.254 4(11) | -0.179 1(32) | -0.220 4(21) | C(1z) | $-0.0011(10)$ | -0.214 8(33) | 0.029 5(21) |
| C(2a) | -0.2811(11) | -0.183 8(33) | -0.154 6(21) | C(2x) | -0.023 6(15) | -0.205 9(46) | $0.0897(28)$ |
| C(3a) | -0.274 9(10) | -0.093 5(34) | -0.089 1(20) | C(3x) | $-0.0190(11)$ | -0.106 9(38) | $0.1565(22)$ |
| C(4a) | -0.305 4(11) | $-0.0857(33)$ | -0.028 9(19) | $\mathrm{C}(4 \mathrm{x})$ | -0.044 0(11) | -0.092 0(35) | 0.2145 (20) |
| C(5a) | -0.334 7(12) | 0.0217 (36) | 0.085 6(23) | $\mathrm{C}(5 \mathrm{x})$ | -0.072 8(12) | 0.0281 (35) | 0.329 0(22) |
| C(9a) | -0.3787(12) | -0.021 2(37) | 0.0658 (24) | C(9x) | -0.113 4(11) | -0.027 2(36) | 0.324 4(22) |
| C(10a) | -0.4103(16) | $-0.0001(45)$ | $0.1147(29)$ | C(10x) | -0.144 0(13) | 0.007 2(40) | 0.384 3(25) |
| C(11a) | $-0.4007(13)$ | 0.0657 739) | 0.189 7(24) | C(11x) | -0.132 6(13) | 0.077 2(38) | 0.4506 (25) |
| $\mathrm{C}(12 \mathrm{a})$ | $-0.3565(10)$ | 0.112 1(32) | 0.2110 (20) | C(12x) | -0.089 3(11) | 0.1331 (40) | 0.453 9(21) |
| C(6a) | $-0.3260(13)$ | 0.092 6(37) | 0.155 3(23) | C(6x) | -0.058 2(12) | 0.1025 (37) | $0.3965(23)$ |
| C(7a) | -0.268 6(14) | $0.1964(45)$ | 0.246 6(26) | C(7x) | $0.0014(12)$ | 0.2121 (38) | 0.4808 (22) |
| $\mathrm{C}(8 \mathrm{a})$ | -0.221 4(18) | 0.208 6(60) | 0.270 4(34) | $\mathrm{C}(8 \mathrm{x})$ | 0.052 5(12) | 0.196 5(40) | 0.489 2(23) |
| $\mathrm{C}(2 \mathrm{~b})$ | -0.221 2(10) | -0.084 4(33) | -0.220 4(20) | C(2y) | 0.035 7(10) | -0.126 5(37) | 0.022 4(19) |
| $\mathrm{C}(3 \mathrm{~b})$ | -0.213 8(11) | $-0.0031(34)$ | $-0.1523(21)$ | C(3y) | 0.045 4(12) | -0.035 8(39) | $0.0862(24)$ |
| $\mathrm{C}(4 \mathrm{~b})$ | -0.177 8(12) | 0.0919 (35) | -0.144 5(23) | C(4y) | 0.0810 (10) | $0.0587(31)$ | 0.0828 (19) |
| $\mathrm{C}(5 \mathrm{~b})$ | -0.137 4(12) | 0.264 8(36) | $-0.0820(22)$ | C(5y) | 0.122 0(12) | 0.233 2(36) | 0.140 7(22) |
| C(9b) | -0.1177(12) | 0.304 2(37) | $-0.1557(24)$ | C(9y) | 0.140 1(11) | 0.2630 0(35) | $0.0647(22)$ |
| C(10b) | -0.084 4(13) | 0.399 7(41) | $-0.1506(25)$ | C(10y) | 0.174 2(12) | 0.359 3(44) | 0.070 8(25) |
| C(11b) | -0.073 1(13) | 0.452 0(39) | $-0.0705(23)$ | C(11y) | 0.188 3(13) | 0.419 0(42) | 0.1315 (25) |
| $\mathrm{C}(12 \mathrm{~b})$ | -0.094 3(11) | 0.425 5(36) | -0.005 6(22) | C(12y) | 0.1710 (13) | 0.395 7(43) | $0.2118(25)$ |
| C(6b) | -0.126 3(11) | 0.326 6(34) | -0.010 8(22) | C(6y) | $0.1377(12)$ | 0.3027 (37) | $0.2108(22)$ |
| C (7b) | -0.135 9(14) | 0.347 0(46) | $0.1328(25)$ | C(7y) | $0.1331(11)$ | 0.3279 (35) | $0.3581(21)$ |
| $\mathrm{C}(8 \mathrm{~b})$ | $-0.1535(14)$ | 0.274 3(45) | 0.2009 (29) | C(8y) | $0.1167(13)$ | $0.2460(40)$ | 0.4221 (25) |
| Complex (2) |  |  |  |  |  |  |  |
| Pb | 0.243 72(3) | 0.186 92(5) | $0.39176(6)$ | C(9a) | 0.0223 (8) | -0.117 8(11) | 0.2039 (12) |
| $\mathrm{O}(1 \mathrm{a})$ | 0.037 6(5) | 0.235 2(8) | 0.2670 (9) | C(10a) | -0.059 7(8) | -0.165 8(11) | 0.248 4(12) |
| $\mathrm{O}(1 \mathrm{~b})$ | 0.316 4(6) | 0.4257 (8) | 0.539 4(9) | C(11a) | -0.106 3(8) | $-0.0805(11)$ | 0.293 7(12) |
| $\mathrm{O}(1 \mathrm{c})$ | 0.123 6(6) | 0.434 4(8) | 0.4390 (10) | C(12a) | $-0.0777(8)$ | 0.057 8(11) | 0.306 5(12) |
| $\mathrm{N}(2 \mathrm{a})$ | 0.1354 (6) | 0.072 2(9) | 0.1750 (10) | C(6a) | 0.0005 (7) | 0.104 5(10) | 0.263 7(11) |
| $\mathrm{N}(2 \mathrm{~b})$ | $0.4115(6)$ | 0.289 5(8) | 0.418 8(10) | C(7a) | -0.012 8(8) | 0.334 6(11) | 0.318 3(13) |
| N(1c) | $0.3262(6)$ | 0.1031 (8) | 0.2280 (9) | $\mathrm{C}(8 \mathrm{a})$ | $0.0408(8)$ | 0.4641 (11) | 0.3219 (12) |
| $\mathrm{O}(3 \mathrm{a})$ | 0.247 3(6) | 0.4047 (8) | 0.183 5(9) | C(2b) | $0.4478(8)$ | 0.147 5(10) | $0.1003(12)$ |
| $\mathrm{O}(3 \mathrm{~b})$ | 0.149 3(6) | 0.370 4(9) | $-0.0190(10)$ | C(3b) | 0.4111 (7) | 0.155 5(10) | 0.218 9(11) |
| $\mathrm{O}(3 \mathrm{c})$ | 0.2181 (7) | 0.5578 8(9) | $-0.0383(10)$ | C(4b) | 0.466 6(7) | 0.206 6(10) | 0.358 5(11) |
| N(3) | 0.2046 (7) | 0.442 4(10) | $0.0467(11)$ | C(5b) | 0.458 8(7) | 0.321 9(10) | 0.5631 (11) |
| $\mathrm{O}(4 \mathrm{a})$ | 0.245 4(6) | -0.098 3(9) | $0.5081(10)$ | C(9b) | $0.5469(8)$ | 0.287 0(11) | 0.643 8(12) |
| $\mathrm{O}(4 \mathrm{~b})$ | 0.355 9(6) | 0.010 6(8) | $0.6297(10)$ | C(10b) | $0.5869(9)$ | 0.329 2(11) | 0.782 9(13) |
| $\mathrm{O}(4 \mathrm{c})$ | $0.3229(6)$ | -0.202 4(9) | 0.738 6(10) | C(11b) | 0.5340 (9) | 0.4041 (11) | 0.839 0(13) |
| N(4) | $0.3084(6)$ | -0.099 4(9) | $0.6270(10)$ | C(12b) | 0.4437 (8) | 0.4361 (11) | 0.764 7(12) |
| C(1c) | $0.3977(8)$ | 0.085 8(11) | $-0.0163(12)$ | C(6b) | 0.404 4(8) | 0.397 2(10) | $0.6257(11)$ |
| C(2a) | $0.3155(8)$ | 0.0278 (10) | -0.005 2(12) | C(7b) | 0.2610 (9) | 0.512 9(12) | 0.5847 (13) |
| C(3a) | $0.2802(7)$ | $0.0387(10)$ | 0.115 2(11) | C(8b) | 0.173 3(8) | 0.560 4(11) | 0.448 6(12) |
| C(4a) | 0.1907 (7) | $-0.0247(10)$ | $0.1314(11)$ | H(n2a) | 0.12110 | 0.16130 | 0.08700 |
| C(5a) | 0.0530 (7) | 0.017 5(10) | $0.2120(11)$ | H(n2b) | 0.36820 | 0.37580 | 0.31960 |

with the ${ }^{1} \mathrm{H}$ n.m.r. spectrum showed that the discrete nature of the Schiff-base complex had been retained. The f.a.b. mass spectrum (positive-ion mode) showed a parent peak corresponding to $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)\right]^{+}$. Reductive demetallation of $\left[\mathrm{PbL}^{1}\right]\left[\mathrm{ClO}_{4}\right]_{2}$ using $\mathrm{NaBH}_{4}$ gave the free macrocycle $\mathrm{L}^{2},{ }^{14}$ which on reaction with $\mathrm{Pb}\left(\mathrm{NO}_{3}\right)_{2}$ gave the complex $\left[\mathrm{PbL}^{2}\left(\mathrm{NO}_{3}\right)_{2}\right] \cdot \mathrm{H}_{2} \mathrm{O},(2) \cdot \mathrm{H}_{2} \mathrm{O}$, as yellow crystals. The presence
of a secondary amine stretch at $3245 \mathrm{~cm}^{-1}$ and the absence of any band corresponding to an imino stretch, and the ${ }^{1} \mathrm{H}$ n.m.r. spectrum, indicated that the discrete nature of the complex was retained. The f.a.b. mass spectrum (positive-ion mode) showed a parent peak attributable to $\left[\mathrm{PbL}^{2}\left(\mathrm{NO}_{3}\right)\right]^{+}$.

The availability of crystals of both the precursor complex (1) and its reduced form (2) gave an opportunity to compare the

Table 2. Selected bond lengths ( $\AA$ )
Complex (1)

| $\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 2.75(3) | $\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 2.71(3) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 2.648 (22) | $\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 2.67(3) |
| $\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 2.52(3) | $\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 2.529(24) |
| $\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 2.874(24) | $\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 2.822(21) |
| $\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{~b})$ | 2.78(3) | $\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{y})$ | 2.835(25) |
| $\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{c})$ | 2.86(3) | $\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{z})$ | 2.903(25) |
| $\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{a})$ | 2.77(3) | $\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{x})$ | 2.83(3) |
| $\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{~b})$ | 2.79(3) | $\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{y})$ | 2.79(3) |
| $\mathrm{Pb}(1)-\mathrm{O}(4 \mathrm{a})$ | 2.83(4) | $\mathrm{Pb}(2)-\mathrm{O}(4 \mathrm{x})$ | 2.60(3) |
| $\mathrm{Pb}(1)-\mathrm{O}(4 \mathrm{~b})$ | 2.57(3) | $\mathrm{Pb}(2)-\mathrm{O}(4 \mathrm{y})$ | 2.80(4) |
| Complex (2) |  |  |  |
| $\mathrm{Pb}-\mathrm{N}(2 \mathrm{a})$ | 2.663(9) | $\mathrm{N}(2 \mathrm{a})-\mathrm{C}(4 \mathrm{a})$ | $1.465(15)$ |
| $\mathrm{Pb}-\mathrm{N}(2 \mathrm{~b})$ | 2.661(9) | $\mathrm{N}(2 \mathrm{a})-\mathrm{C}(5 \mathrm{a})$ | $1.424(14)$ |
| $\mathrm{Pb}-\mathrm{N}(1 \mathrm{c})$ | 2.470 (10) | $\mathrm{N}(2 \mathrm{~b})-\mathrm{C}(4 \mathrm{~b})$ | $1.463(16)$ |
| $\mathrm{Pb}-\mathrm{O}(3 \mathrm{a})$ | 2.493(7) | $\mathrm{N}(2 \mathrm{~b})-\mathrm{C}(5 \mathrm{~b})$ | $1.433(13)$ |
| $\mathrm{Pb}-\mathrm{O}(4 \mathrm{a})$ | 2.706(8) | $\mathrm{N}(1 \mathrm{c})-\mathrm{C}(3 \mathrm{a})$ | $1.358(13)$ |
| $\mathrm{Pb}-\mathrm{O}(4 \mathrm{~b})$ | 2.661(7) | $\mathrm{N}(1 \mathrm{c})-\mathrm{C}(3 \mathrm{~b})$ | 1.376(14) |
| $\mathrm{Pb} \cdot . . \mathrm{O}(1 \mathrm{a})$ | 3.04 | $\mathrm{O}(3 \mathrm{a})-\mathrm{N}(3)$ | 1.227(11) |
| $\mathrm{Pb} \cdot . . \mathrm{O}(1 \mathrm{~b})$ | 2.98 | $\mathrm{O}(3 \mathrm{~b})-\mathrm{N}(3)$ | 1.199(13) |
| $\mathrm{Pb} \cdot . . \mathrm{O}(1 \mathrm{c})$ | 3.23 | $\mathrm{O}(3 \mathrm{c})-\mathrm{N}(3)$ | 1.244(12) |
| $\mathrm{H}(\mathrm{n} 2 \mathrm{a}) \cdots \mathrm{O}(3 \mathrm{~b})$ | 2.10 | $\mathrm{O}(4 \mathrm{a})-\mathrm{N}(4)$ | 1.247(12) |
| $\mathrm{H}(\mathrm{n} 2 \mathrm{~b}) \cdots \mathrm{O}(3 \mathrm{a})$ | 1.92 | $\mathrm{O}(4 \mathrm{~b})-\mathrm{N}(4)$ | 1.261(12) |
| $\mathrm{N}(2 \mathrm{a})-\mathrm{H}(\mathrm{n} 2 \mathrm{a})$ | 1.017(7) | $\mathrm{O}(4 \mathrm{c})-\mathrm{N}(4)$ | $1.225(11)$ |
| $\mathrm{N}(2 \mathrm{~b})-\mathrm{H}(\mathrm{n} 2 \mathrm{~b})$ | 1.151(7) | C(3a)-C(4a) | 1.492(15) |
| $\mathrm{O}(1 \mathrm{a})-\mathrm{C}(6 \mathrm{a})$ | $1.365(13)$ | C(5a)-C(6a) | $1.413(17)$ |
| $\mathrm{O}(1 \mathrm{a})-\mathrm{C}(7 \mathrm{a})$ | $1.475(16)$ | C(7a)-C(8a) | 1.467(16) |
| $\mathrm{O}(1 \mathrm{~b})-\mathrm{C}(6 \mathrm{~b})$ | 1.360(13) | C(3b)-C(4b) | 1.517(14) |
| $\mathrm{O}(1 \mathrm{~b})-\mathrm{C}(7 \mathrm{~b})$ | 1.409(17) | C(5b)-C(6b) | $1.423(17)$ |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{C}(8 \mathrm{a})$ | 1.409(13) | $\mathrm{C}(7 \mathrm{~b})-\mathrm{C}(8 \mathrm{~b})$ | 1.563(15) |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{C}(8 \mathrm{~b})$ | $1.415(14)$ |  |  |

co-ordination environments of the lead(II) ions, and the structures of the complexes are shown in Figures 1 and 2 respectively. The most striking difference in the two is that in the precursor complex (1) all six potential donors of $\mathrm{L}^{1}$ may be regarded as co-ordinated to the lead(II) ion, whereas the reduced ligand $\mathrm{L}^{2}$ gives rise to a complex in which the only macrocyclic donors strongly bound to the metal are the three nitrogen atoms.
In the structure of $\left[\mathrm{PbL}^{1}\left(\mathrm{NO}_{3}\right)_{2}\right]$ (1) the central lead ion exhibits ten-co-ordination with an equatorial $\mathrm{N}_{3} \mathrm{O}_{3}$ set of macrocyclic donor atoms plus two bidentate nitrate ions in axial positions. The co-ordination sphere geometry in the two independent molecules of $(1)$ is distorted hexagonal bipyramidal with bidentate nitrates occupying the two axial sites. The six macrocyclic donor atoms are not coplanar in either molecule, the mean maximum deviation from the least-squares $\mathrm{N}_{3} \mathrm{O}_{3}$ planes being $0.244 \AA$.

In contrast, the co-ordination polyhedron of compound (2) may be envisaged as derived from that of (1) by loss of the three equatorial donor oxygen atoms, and as such would be classed as 'hypho' hexagonal bipyramidal. One of the axial nitrate ligands is monodentate and at $2.493(7) \AA$ the $\mathrm{Pb}-\mathrm{O}(3 \mathrm{a})$ bond length of this nitrate is short when compared with the lengths for the bidentate nitrate [mean $\mathrm{Pb}-\mathrm{O} 2.683(8) \AA$ ]. This short bond facilitates strong hydrogen bonding with the secondary amines of $\mathrm{L}^{2}[\mathrm{O}(3 \mathrm{a}) \cdots \mathrm{H}-\mathrm{N}(2 \mathrm{~b}) 1.92 ; \mathrm{O}(3 \mathrm{~b}) \cdots \mathrm{H}-\mathrm{N}(2 \mathrm{a}) 2.10 \AA]$. All $\mathrm{Pb}-\mathrm{O}$ (nitrate) distances are significantly shorter than those found in lead nitrate $(2.805 \AA) .{ }^{21}$

It is interesting that in both structures the length of the $\mathrm{Pb}-\mathrm{N}($ pyridyl) bond [2.52(3) $\AA$ mean for (1) and $2.470(10) \AA$ for (2)] is shorter than the other $\mathrm{Pb}-\mathrm{N}$ distances [means 2.69(4) for (1) and $2.662(9) \AA$ for (2)]. This appears to be emerging as a common feature of the co-ordination of this pyridyl fragment in related macrocyclic complexes of lead ${ }^{22}$ and other metal ions. ${ }^{23}$ These differences are not directly attributable to differences in



Figure 2. The structure of $\left[\mathrm{PbL}^{2}\left(\mathrm{NO}_{3}\right)_{2}\right]$ : (a) showing donor interactions and (b) 'side-on' view showing macrocycle conformation
hybridisation of the nitrogen atoms, as in (1), for example, all the N -donors are using $s p^{2}$ hybrid orbitals.

The main difference in the structures is that in (2) the three oxygens of the macrocycle were located at distances of $\mathrm{O}(1 \mathrm{a})$ 3.04, $\mathrm{O}(1 \mathrm{~b}) 2.98$, and $\mathrm{O}(2 \mathrm{c}) 3.23 \AA$ from the lead [cf. $\mathrm{Pb}-\mathrm{O}$ means of 2.848(23), 2.807(23), and 2.881(24) in (1)] and appear to have very little covalent character. Although these $\mathrm{Pb} \cdots \mathrm{O}$ distances are long their orientation towards the lead may indicate some weak electrostatic interaction with the metal. In a study of an analogue of (1), where the macrocyclic phenylene units are substituted by ethylene units, the mean $\mathrm{Pb}-\mathrm{O}$ (macrocycle) distances were found to be $3.061 \AA$. All the $\mathrm{Pb}-\mathrm{O}-$ (macrocycle) distances in (2) are significantly longer than the sum of the van der Waals radius of $O$ and the ionic radius of ten-co-ordinate $\mathrm{Pb}^{\text {II }}(2.80 \AA) .{ }^{24}$

In addition to differences in $\mathrm{Pb}-\mathrm{O}$ distances, the two phenylene groups of the macrocyclic in compound (2) are tilted towards each other with a dihedral angle of $118.12^{\circ}$ between their mean planes, giving rise to a 'saddle' conformation for the macrocycle. The six macrocyclic heteroatoms are approximately coplanar [deviations: $\mathrm{N}(2 \mathrm{a}) 0.11, \mathrm{~N}(1 \mathrm{c})-0.09, \mathrm{~N}(2 \mathrm{~b})-0.05$, $\mathrm{O}(1 \mathrm{~b}) 0.16, \mathrm{O}(1 \mathrm{c})-0.14$, and $\mathrm{O}(1 \mathrm{a})-0.01 \AA]$ and the lead atom lies $0.646 \AA$ above this plane towards the bidentate nitrate.

Although distortions of the above nature might well implicate the existence of a stereochemically active lone pair on the lead(II) in (2), there is, paradoxically, no evidence for a stereochemical role for the lone pair in the structure of (1). It may be that a stronger ligand field exerted by the comparatively electron-rich, planar macrocycle $L^{1}$ confines the lone pair to the

Table 3. Selected interbond angles ( ${ }^{\circ}$ )
Complex (1)

| $\mathrm{N}(2 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 126.5(8) | $\mathrm{N}(2 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 126.2(9) | $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 82.8(9) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 78.7(8) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{N}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 63.4(8) | $\mathrm{N}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 63.9(8) | $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 108.4(8) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 114.2(8) |
| $\mathrm{N}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 63.9(8) | $\mathrm{N}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 63.2(9) | $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{~b})$ | 67.8(8) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{y})$ | 68.7(8) |
| $\mathrm{O}(1 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 55.6(8) | $\mathrm{O}(1 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 58.2(8) | $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{c})$ | 86.0(8) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{z})$ | 89.8(7) |
| $\mathrm{O}(1 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 177.8(7) | $\mathrm{O}(1 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 174.4(8) | $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{a})$ | 44.8(9) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{x})$ | 45.7(8) |
| $\mathrm{O}(1 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 118.0(8) | $\mathrm{O}(1 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 121.7(7) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 80.0(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 99(1) |
| $\mathrm{O}(1 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 175.4(8) | $\mathrm{O}(1 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 175.5(8) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 80.4(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 101(1) |
| $\mathrm{O}(1 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 57.8(7) | $\mathrm{O}(1 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 57.7(8) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 78.4(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 122(1) |
| $\mathrm{O}(1 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 120.4(8) | $\mathrm{O}(1 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 119.3(8) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 97.5(8) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 79(1) |
| $\mathrm{O}(1 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 120.1(7) | $\mathrm{O}(1 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 118.2(7) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{y})$ | 103.5(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{~b})$ | 82(1) |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 115.8(8) | $\mathrm{O}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 117.3(7) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{z})$ | 113.7(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{c})$ | 71(1) |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 117.6(7) | $\mathrm{O}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 116.5(8) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{x})$ | 145.6(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{a})$ | 148(1) |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 167.3(8) | $\mathrm{O}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 167.8(8) | $\mathrm{O}(4 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{y})$ | 147.4(9) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{~b})$ | 148(1) |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 60.3(7) | $\mathrm{O}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 59.5(7) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 104.9(9) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 86.3(9) |
| $\mathrm{O}(1 \mathrm{c})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{~b})$ | 59.8(7) | $\mathrm{O}(1 \mathrm{z})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{y})$ | 58.8(6) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 96(1) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 72.5(8) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 70.7(9) | $\mathrm{O}(3 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{x})$ | 68.1(8) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 124(1) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 76(1) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 109.4(8) | $\mathrm{O}(3 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 107.8(9) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 78.9(9) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 108.9(8) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{N}(1 \mathrm{c})$ | 81.0(9) | $\mathrm{O}(3 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{N}(1 \mathrm{z})$ | 76.3(8) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{y})$ | 76.1(9) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{~b})$ | 97.1(9) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{a})$ | 70.2(8) | $\mathrm{O}(3 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{x})$ | 76.8(7) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{z})$ | 68(1) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{c})$ | 117.0(9) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{~b})$ | 106.7(8) | $\mathrm{O}(3 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{y})$ | 109.0(7) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{x})$ | 154.4(9) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{a})$ | 153(1) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}(1)-\mathrm{O}(1 \mathrm{c})$ | 86.8(8) | $\mathrm{O}(3 \mathrm{x})-\mathrm{Pb}(2)-\mathrm{O}(1 \mathrm{z})$ | 92.8(7) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(3 \mathrm{y})$ | 145(1) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(3 \mathrm{~b})$ | 142.4(9) |
| $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{a})$ | 111.2(9) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 x)$ | 109.8(9) | $\mathrm{O}(4 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{O}(4 \mathrm{x})$ | 46(1) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{O}(4 \mathrm{a})$ | 47(1) |
| $\mathrm{O}(3 \mathrm{~b})-\mathrm{Pb}(1)-\mathrm{N}(2 \mathrm{~b})$ | 70.4(8) | $\mathrm{O}(3 \mathrm{y})-\mathrm{Pb}(2)-\mathrm{N}(2 \mathrm{y})$ | 68.7(9) |  |  |  |  |
| Complex (2) |  |  |  |  |  |  |  |
| $\mathrm{N}(2 \mathrm{~b})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{a})$ | 131.5(3) | $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{~b})$ | 68.2(2) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}-\mathrm{N}(1 \mathrm{c})$ | 79.4(3) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}-\mathrm{N}(1 \mathrm{c})$ | 85.8(3) |
| $\mathrm{N}(1 \mathrm{c})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{a})$ | 66.4(3) | $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}-\mathrm{N}(1 \mathrm{c})$ | 76.9(3) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}-\mathrm{O}(3 \mathrm{a})$ | 153.7(3) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}-\mathrm{O}(3 \mathrm{a})$ | 140.6(3) |
| $\mathrm{N}(1 \mathrm{c})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{~b})$ | 67.4(3) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{a})$ | 72.2(2) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{a})$ | 117.2(3) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}-\mathrm{O}(4 \mathrm{a})$ | 47.1(3) |
| $\mathrm{O}(3 \mathrm{a})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{a})$ | 87.9(3) | $\mathrm{O}(4 \mathrm{a})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{~b})$ | 112.4(3) | $\mathrm{O}(4 \mathrm{~b})-\mathrm{Pb}-\mathrm{N}(2 \mathrm{~b})$ | 72.5(2) |  |  |

inner core of the lead(II) in an unhybridised $s$ orbital. The significant discrepancies in the structures of the complexes must be attributable not only to lone-pair effects but also to differences in the conformational constraints of $L^{1}$ and $L^{2}$. Clearly, the requirement for near-tetrahedral arrangements about the $s p^{3}$-hybridised nitrogens of $L^{2}$, as opposed to the trigonal requirements for $s p^{2}$ hybridisation of the corresponding nitrogens of $L^{1}$, is achieved at the expense of co-ordination of the relatively weakly basic phenoxy-ether oxygens. The situation is akin to that of a 'bucket with handle,' where the 'handle' moves at nitrogen 'hinges' and the lead sits in the $\mathrm{N}_{3}$ chelating 'bucket.' Whether the handle remains over the bucket [as in (1)] or falls to one side [as in (2)], is governed by the stereochemical requirements of the hinge nitrogens.

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