DALTON
FULL PAPER

# Macrocyclic ligand design. Interaction of selected transition and post-transition metal ions with a new $N_2O_2$-donor macrocycle incorporating a pyridylmethyl pendant arm

Ian M. Atkinson,[a] Jy D. Chartres,[a] Grover W. Everett,[b] Xue-Kui Ji,[c] Leonard F. Lindoy,*[c] Owen A. Matthews,[a] George V. Meehan,[a] Brian W. Skelton,[d] Gang Wei[c] and Allan H. White[d]

[a] *School of Biomedical and Molecular Science, James Cook University, Townsville, Qld. 4811, Australia*
[b] *Chemistry Department, University of Kansas, Lawrence, Kansas 66045, USA*
[c] *School of Chemistry, The University of Sydney, N.S.W. 2006, Australia*
[d] *Department of Chemistry, The University of Western Australia, Nedlands, W.A. 6907, Australia*

***Received 17th November 1999, Accepted 3rd February 2000***
***Published on the Web 9th March 2000***

A pyridylmethyl derivative of a 14-membered, $N_2O_2$-donor macrocycle (L) and its complexes with cobalt(II), copper(II), zinc(II), silver(I), cadmium(II) and lead(II) have been prepared. Thermodynamic stabilities of the 1 : 1 (metal : ligand) complexes in 95% methanol ($I = 0.1$ mol dm$^{-3}$, $NEt_4ClO_4$; 25 °C) and crystal structures of the 1 : 1 complexes of copper(II), silver(I) and lead(II) with L were determined. The structure of the copper complex shows the presence of a cation of type $[CuL(NO_3)]^+$; it has a distorted octahedral geometry in which one co-ordination site is occupied by a unidentate nitrate ligand. In contrast, the cationic silver complex is of type $[AgL]^+$ with the two pyridine ring nitrogen atoms of L dominating the co-ordination environment, which may be regarded as essentially two-co-ordinate. On the other hand, the lead complex, $[PbL(NO_3)(ClO_4)]$, is eight-co-ordinate and incorporates bidentate nitrate and unidentate perchlorate ligands. A competitive mixed-metal transport experiment across a bulk chloroform membrane incorporating L as ionophore was performed. The aqueous source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I), and lead(II) as their nitrate salts. Under the influence of a back proton gradient, silver and copper were preferentially transported to the aqueous receiving phase.

## Introduction

Previous work in our laboratories has been concerned with the elucidation of structure/function relationships between mixed-donor macrocycles and their co-ordination preferences towards a range of transition and post-transition metal ions.[1] As part of these investigations we also reported the co-ordination behaviour of pendant arm derivatives of mixed-donor macrocycles (in which the pendant arms incorporate additional donor groups) with metals of the above type.[2,3] As pointed out previously,[4,5] aspects of the metal-ion chemistry of these species tend to resemble those of both macrocyclic and open-chain compounds.

In the present study we report the synthesis of a new 2-pyridylmethyl pendant arm macrocycle L together with the results of an investigation of its interaction with cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II).

A molecular model (Corey–Pauling–Koltun, CPK) of L indicated that the four macrocyclic ring donors will experience difficulty in aligning themselves in a square fashion towards a centrally bound metal ion. This arises because of the partial rigidity of the macrocyclic backbone coupled with the necessity of yielding a 5,5,6,6 chelate ring pattern on binding a metal ion in the $N_2O_2$-donor cavity of the macrocyclic ring. Thus it was anticipated that L may favour an unsymmetrical co-ordination arrangement. Indeed, macrocyclic systems incorporating appended 2-pyridylmethyl arms have been documented to exhibit a wide variety of interesting, and often novel, heavy metal co-ordination behaviour.[6]

## Experimental

### Physical methods

$^1H$ NMR spectra were recorded in $CDCl_3$ using a Bruker AM200 or AM-300 spectrometer, HRMS on Kraytos M25RFA or Bruker BioApex 47e 1CR mass spectrometers and low resolution (ES) spectra on a Finnigan LCQ-8 spectrometer. Cyclic voltammetry was performed using a BAS-100B electrochemical system in conjunction with a glassy carbon working electrode in dry acetonitrile (supporting electrolyte was 0.1 mol dm$^{-3}$ tetrabutylammonium perchlorate); scans at a number of scan rates were performed. All melting points are uncorrected. The ESR spectrum was obtained on a powdered sample at ambient temperature using a Bruker EMX ESR spectrometer at 9.475 GHz (X-band).

Potentiometric titrations were carried out in a water-jacketed titration vessel and a water-jacketed calomel reference electrode, connected by a salt bridge. A Philips glass electrode (GA-110) was used for all pH measurements. Tetraethylammonium perchlorate (0.1 mol dm$^{-3}$) was used as the background electrolyte. Methanol-saturated nitrogen was bubbled through the solution in the measuring cell; tetraethylammonium hydroxide solution (0.1 mol dm$^{-3}$) was introduced into the cell using a Metrohm Dosimat 655 automatic titrator. A Corning model 130 Research pH meter was employed for the pH determinations. The data were processed using a local version of MINIQUAD[7] with selected data also being processed with SUPERQUAD;[8] both programs yielded near identical log $K$ values in each case. All quoted log $K$ values represent the

DOI: 10.1039/a909102e

mean of data from at least three (and up to six) titrations performed at different metal to ligand ratios. Errors represent the average deviation from the mean obtained for between three and six separate experimental determinations (rounded to one significant figure). All measurements were fully automated under personal computer control. Titrations were performed at 25.0 ± 0.05 °C at constant ionic strength ($I = 0.1$ mol dm$^{-3}$, $NEt_4ClO_4$) in 95% methanol solution under purified nitrogen. Analytical grade methanol was fractionated and distilled over magnesium before use.

## Membrane transport

The transport experiments employed a 'concentric cell' in which the aqueous source phase (10 cm$^3$) and receiving phase (30 cm$^3$) were separated by a chloroform phase (50 cm$^3$). Details of the cell design have been reported elsewhere.[9] For each experiment both aqueous phases and the chloroform phase were stirred separately at 10 rpm; the cell was enclosed by a water jacket and thermostatted at 25 °C. The aqueous source phase was buffered ($CH_3CO_2H$–$CH_3CO_2Na$) at pH 4.9 (±0.1) and contained an equimolar mixture of the metal ions (see Results and discussion section), each at a concentration of $\approx 1 \times 10^{-3}$ mol dm$^{-3}$. The chloroform phase contained L ($1 \times 10^{-3}$ mol dm$^{-3}$), as well as hexadecanoic acid ($4 \times 10^{-3}$ mol dm$^{-3}$). The receiving phase was buffered ($HCO_2H$–NaOH) at pH 3.0 (±0.1). All transport runs were terminated after 24 hours and atomic absorption spectroscopy was used to determine the amount of metal ion transported over this period. The transport results are quoted as the average values obtained from duplicate runs (errors ±10%). Transport rates ($J$ values) are in mol h$^{-1}$ and represent mean values measured over 24 h. A 'control' experiment containing only hexadecanoic acid in the chloroform membrane phase confirmed that no metal ion transport took place in the absence of the macrocyclic ionophore.

## Structure determinations: $L{\cdot}M(X/Y)_m{\cdot}nH_2O$

Full spheres of area-detector/CCD diffractometer data were measured (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) yielding $N_{t(otal)}$ reflections, merging after 'empirical' absorption correction to $N$ unique (Bruker proprietary software: SMART, SAINT, SADABS, XPREP), $N_o$ with $F > 4\sigma(F)$ being used in the full-matrix least squares refinement, non-hydrogen atom thermal parameter forms being anisotropic and $(x,y,z,U_{iso})_H$ included at constrained estimates. Conventional residuals $R$, $R_w$ (statistical weights) on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed, within the XTAL 3.4 program system.[10] Pertinent results are given in Fig. 2(a)–2(c) and Tables 2 and 3 and below, individual variations in procedure being noted.

**Crystal/refinement data.** $L{\cdot}Cu(NO_3)_2{\cdot}{\approx}3H_2O \equiv C_{35}H_{47}CuN_5O_{11}$. $M = 777.3$, $T$ *ca.* 295 K, orthorhombic, space group *Pbcn* ($D_{2h}^{14}$, no. 60), $a = 20.641(9)$, $b = 14.447(7)$, $c = 24.91(1)$ Å, $V = 7429$ Å$^3$, $D_c$ $(Z = 8) = 1.39_0$ g cm$^{-3}$, $\mu_{Mo} = 6.4$ cm$^{-1}$, specimen $0.55 \times 0.10 \times 0.80$ mm, $T_{min,max} = 0.88$, 0.93, $2\theta_{max} = 50°$, $N = 6457$, $N_o = 2813$, $R = 0.070$, $R_w = 0.066$.

*Individual features.* A unique data set was measured with a single counter/'four-circle' instrument, on an independent reciprocal lattice component of a twinned crystal, 58 overlapping reflections being refined with a separate scale factor. Nitrate 2 was modelled as disordered with component populations $x = 0.619(3)$, $1 - x$ (minor component thermal parameters isotropic); even so, 'thermal motion' for this and the lattice water molecules was very high. Redetermination of the structure on recrystallized material did not improve the precision of the determination. The 'observed' criterion for $N_o$ was $I > 3\sigma(I)$.

$L{\cdot}Pb(NO_3)(ClO_4) \equiv [PbL(O_2NO)(OClO_3)] \equiv C_{35}H_{41}ClN_4O_9Pb$. $M = 904.4$, $T$ *ca.* 300 K, orthorhombic, space group *Pccn* ($D_{2h}^{10}$, no. 56), $a = 26.494(2)$, $b = 12.4426(8)$, $c = 22.046(1)$ Å, $V = 7267$ Å$^3$, $D_c$ $(Z = 8) = 1.65_3$ cm$^{-3}$, $\mu_{Mo} = 47$ cm$^{-1}$, specimen $0.40 \times 0.40 \times 0.10$ mm, $T_{min,max} = 0.33$, 0.56, $2\theta_{max} = 58°$, $N_t = 84511$, $N = 9438$ ($R_{int} = 0.028$), $N_o = 5639$, $R = 0.033$, $R_w = 0.040$.

*Individual variations.* The perchlorate was modelled as rotationally disordered about the (co-ordinated) O(11)–Cl vector, O(12–14) being distributed over two sets of sites, occupancies refining to $x = 0.65(1)$, $1 - x$ (minor component thermal parameters isotropic).

$L{\cdot}AgNO_3 \equiv [AgL]NO_3 \equiv C_{35}H_{41}AgN_4O_5$. $M = 705.6$, $T$ *ca.* 153 K, monoclinic, space group $P2_1/c$ ($C_{2h}^5$, no. 14), $a = 18.303(2)$, $b = 11.177(1)$, $c = 15.940(2)$ Å, $\beta = 90.221(2)°$, $V = 3261$ Å$^3$, $D_c$ $(Z = 4) = 1.43_7$ cm$^{-3}$, $\mu_{Mo} = 6.7$ cm$^{-1}$, specimen $0.25 \times 0.09 \times 0.025$ mm, '$T$'$_{min,max} = 0.65$, 0.88, $2\theta_{max} = 58°$, $N_t = 36819$, $N = 8120$ ($R_{int} = 0.035$), $N_o = 4869$, $R = 0.049$, $R_w = 0.046$.

*Individual variations.* The two *tert*-butyl groups were modelled as rotationally disordered, site occupancies of C($n$32–4, $n'$32–4) refining to 0.59(2), 0.78(1) and complements; the nitrate also was modelled as two components (with O(01) common), of equal occupancy (isotropic thermal parameter forms).

CCDC reference number 186/1839.

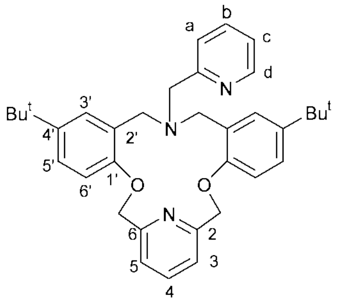
See http://www.rsc.org/suppdata/dt/a9/a909102e/ for crystallographic files in .cif format.

## Syntheses

The synthesis and characterization of 2,6-bis[(2-formyl-4-*tert*-butylphenoxy)methyl]pyridine **1** has been described previously.[11]

**14,22-Di-*tert*-butyl-2,10-dioxa-18,25-diazatetracyclo[18.4.1$^{4,8}$.0$^{11,16}$]pentaicosa-4,6,8(25),11,13,15,20,22,24-nonaene 2.** Ammonium acetate (7.0 g, 90.0 mmol), molecular sieves (4 Å, 10 g) and sodium cyanotrihydridoborate (1.7 g, 25.7 mmol) were added to a suspension of dialdehyde **1** (2.0 g, 4.4 mmol) in dry methanol (165 cm$^3$). The resultant mixture was stirred at room temperature overnight, filtered through filter-aid Celite 521 and washed thoroughly with absolute ethanol ($4 \times 15$ cm$^3$). The filtrate was taken to dryness on a rotary evaporator to give a white powder which was partitioned between dichloromethane (170 cm$^3$) and sodium hydroxide solution (40 cm$^{-3}$, 2 mol dm$^{-3}$). The separated organic phase was dried over anhydrous sodium sulfate and the volume reduced to 3 cm$^3$. This solution was loaded onto a column ($2.5 \times 5$ cm) of neutral alumina which was eluted with 4:1 dichloromethane–methanol. The eluate was taken to dryness to yield compound **2** as a white solid (1.7 g, 87%) which was dried in a vacuum, mp 128–130 °C (decomp.) [Found M$^+$, *m*/*z* 444.2770 (EI). $C_{29}H_{36}N_2O_2$ requires 444.2777]. $^1H$ NMR ($CDCl_3$): $\delta$ 1.28 [s, $(CH_3)_3$, 18 H], 3.85 (s, $CH_2N$, 4 H), 5.15 (s, $CH_2O$, 4 H), 6.79 (d, $J = 9$, H-6′, 2 H), 7.18 [d, $J = 8$, H-3(5), 2 H], 7.21 (dd, $J = 3$, 9, H-5′, 2 H), 7.30 (d, $J = 3$, H-3′, 2 H) and 7.67 (t, $J = 8$ Hz, H-4, 1 H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 31.5, 34.0, 51.7, 69.6, 111.2, 120.9, 125.0, 128.6, 136.8, 143.3, 154.9 and 156.6. The product was further characterized as its hydrochloride salt. This was obtained by bubbling hydrogen chloride through a dichloromethane solution of **1**. The solvent was removed and the residue recrystallized from diethyl ether–dichloromethane to yield colourless needles, mp 273–275 °C (decomp.) (Found: C, 68.4; H, 7.7; N, 5.6. Calc. for $C_{29}H_{36}N_2O_2{\cdot}HCl{\cdot}1.5H_2O$: C, 68.55; H, 7.94; N, 5.51%). $^1H$ NMR ($CDCl_3$): $\delta$ 1.28 (s, $(CH_3)_3$, 18 H), 4.13 (s, $CH_2N$, 4 H), 5.21 (s, $CH_2O$, 4 H), 6.81 (d, $J = 9$, H-6′, 2 H), 7.24 (d, $J = 8$, H-3(5), 2 H), 7.28 (dd, $J = 3$, 9, H-5′, 2 H), 7.40 (d, $J = 3$, H-3′, 2 H) and 7.73 (t, $J = 8$ Hz, H-4, 1 H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 31.5, 34.0, 51.8, 69.6, 111.2, 120.9, 124.8, 128.5, 136.8, 143.3, 154.9 and 156.5.

**14,22-Di-*tert*-butyl-18-(2-pyridylmethyl)-2,10-dioxa-18,25-diazatetracyclo[18.4.1$^{4,8}$.0.0$^{11,16}$]pentaicosa-4,6,8(25),11,13,15,20,22,24-nonaene L.** The product **2** from above (0.46 g, 1.03 mmol), 2-picolyl (2-pyridylmethyl) chloride hydrochloride (0.22 g, 1.31 mmol), caesium carbonate (1.7 g, 5.2 mmol) and toluene (15 cm$^3$) were stirred at 100 °C for 24 hours. The toluene was evaporated and the solid mixture thoroughly extracted with dichloromethane (3 × 50 cm$^3$). The combined dichloromethane solutions were then evaporated to yield the crude pendant arm macrocycle as a white solid which was recrystallized from diethyl ether–light petroleum (bp 60–65 °C) (0.45 g, 83%), mp 148–150 °C [Found: M$^+$, *m*/*z* 535.3208 (EI). $C_{35}H_{41}N_3O_2$ requires 535.3199] (Found: C, 78.3; H, 7.6; N, 7.7. Calc. for $C_{35}H_{41}N_3O_2$: C, 78.47; H, 7.71; N, 7.84%). $^1$H NMR (CDCl$_3$): $\delta$ 1.24 (s, (CH$_3$)$_3$, 18 H), 3.83 (s, NC$_5$H$_4$CH$_2$N, 2 H), 3.94 (s, CH$_2$N, 4 H), 5.21 (s, CH$_2$O, 4 H), 6.88 (d, $J$ = 9, H-6′, 2 H), 7.12 (dd, $J$ = 3, 9, H-5′), 7.14 (Hc), 7.17 (d, $J$ = 8, H-3(5), 2 H), 7.42 (d, $J$ = 3, H-3′, 2 H), 7.59 (t, $J$ = 8, H-4, 1 H), 7.71 (dt, $J$ = 2, 8, Hb, 1 H), 7.97 (d, $J$ = 8, Ha, 1 H) and 8.53 (d, $J$ = 4 Hz, Hd, 1 H). $^{13}$C NMR (CDCl$_3$): $\delta$ 31.4, 34.0, 52.6, 59.6, 72.3, 113.8, 121.6, 121.9, 122.7, 123.9, 127.7, 128.9, 136.1, 136.7, 143.8, 148.8, 155.0, 156.7 and 161.3.



**[CoL(NO$_3$)]NO$_3$·0.5CH$_2$Cl$_2$.** Cobalt(II) nitrate hexahydrate (0.19 g, 0.65 mmol) in water (3 cm$^3$) was added to a solution of L (0.10 g, 0.187 mmol) in dichloromethane (2 cm$^3$). The mixture was shaken vigorously for 20 minutes. The organic phase was separated, dried over molecular sieves and filtered. Diffusion of ether vapour into the filtrate over two days produced a pink microcrystalline product (29 mg). This was collected, washed with ether and dried over $P_4O_{10}$ in a vacuum (Found: C, 55.9; H, 5.6; N, 9.1. Calc. for $C_{35}H_{41}CoN_5O_8\cdot0.5CH_2Cl_2$: C, 56.02; H, 5.56; N, 9.20%).

**[CuL(NO$_3$)]NO$_3$·CH$_2$Cl$_2$.** Copper(II) nitrate trihydrate (0.15 g, 0.62 mmol) in water (3 cm$^3$) was added to a solution of L (0.10 g, 0.187 mmol) in dichloromethane (2 cm$^3$) and hexane (3 cm$^3$). The mixture was shaken vigorously for 20 minutes. The organic phase was separated, dried over molecular sieves and filtered. Diffusion of ether vapour into the filtrate over 1 hour produced blue crystals (27 mg). These were collected, washed with ether and dried over $P_4O_{10}$ in a vacuum [Found: CuL$^{2+}$, *m*/*z* 299.2306 (ES). $C_{35}H_{41}N_3O_2Cu/2$ requires 299.2292] (Found: C, 53.4; H, 5.3; N, 8.5. Calc. for $C_{36}H_{43}Cl_2CuN_5O_8$: C, 53.50; H, 5.36; N, 8.67%).

**[ZnL(NO$_3$)]NO$_3$·0.25CH$_2$Cl$_2$.** Using a similar procedure to that described for [CoL(NO$_3$)]NO$_3$, zinc(II) nitrate tetrahydrate (0.17 g, 0.65 mmol) produced the product as colourless crystals (32 mg) [Found: ZnL$^{2+}$, *m*/*z* 299.6256 (ES). $C_{35}H_{41}N_3O_2Zn/2$ requires 299.6241] (Found: C, 56.8; H, 5.8; N, 9.4. Calc. for $C_{35}H_{41}N_5O_8Zn\cdot0.25CH_2Cl_2$: C, 56.73; H, 5.60; N, 9.38%). The $^1$H NMR in CDCl$_3$ confirmed the presence of dichloromethane.

**[CdLCl]Cl·0.33CH$_2$Cl$_2$.** Using a similar procedure to that described for [CoL(NO$_3$)$_2$], cadmium chloride hemipentahydrate (0.20 g, 0.88 mmol) produced the product as a white powder (30 mg) (Found: C, 56.7; H, 5.4; N, 5.6. Calc. for $C_{35}H_{41}CdCl_2N_3O_2\cdot0.33CH_2Cl_2$: C, 56.79; H, 5.62; N, 5.62%). The $^1$H NMR in CDCl$_3$ confirmed the presence of dichloromethane.

**[AgL]NO$_3$.** Using a similar procedure to that described for [CoL(NO$_3$)$_2$], silver(I) nitrate (0.11 g, 0.64 mmol) yielded the product as colourless crystals (70 mg) [Found: AgL$^+$, *m*/*z* 644.2209 (ES). $C_{35}H_{41}AgN_3O_2$ requires 644.2245] (Found: C, 59.5; H, 6.2; N, 7.6. Calc. for $C_{35}H_{41}AgN_4O_5$: C, 59.58; H, 5.86; N, 7.94%).

**[PbL(NO$_3$)]NO$_3$.** Lead(II) nitrate (0.06 g, 0.18 mmol) was added to a stirred solution of L (0.05 g, 0.09 mmol) in absolute ethanol (25 cm$^3$). The mixture was warmed at ≈50 °C and stirred for 20 minutes. The solution was allowed to stand overnight and colourless crystals (13 mg) formed which were collected and dried over $P_4O_{10}$ in a vacuum (Found: C, 48.5; H, 5.2; N, 8.0. Calc. for $C_{35}H_{41}N_5O_8Pb$: C, 48.49; H, 4.77; N, 8.08%).

**[PbL(NO$_3$)(ClO$_4$)].** Lead(II) nitrate (0.12 g, 0.36 mmol) was added to a stirred solution of L (0.10 g, 0.187 mmol) in dry methanol (25 cm$^3$). The mixture was warmed at ≈50 °C and stirred for 20 minutes. Lithium perchlorate trihydrate (0.5 g) was then added to the solution which was warmed and stirred for 20 minutes. On standing the solution overnight, colourless crystals of product (30 mg) formed. These were washed with absolute ethanol and dried over $P_4O_{10}$ in a vacuum (Found: C, 46.8; H, 4.5; N, 6.0. Calc. for $C_{35}H_{41}ClN_4O_9Pb$: C, 46.48; H, 4.57; N, 6.19%).

**CAUTION**: perchlorate-containing complexes are potentially explosive and appropriate precautions should be in place for their preparation, handling and storage.

## Results and discussion

### Ligand synthesis

The stepwise synthesis (Scheme 1) of the pendant-arm ligand L from the previously reported dialdehyde **1** involved initial (novel) formation of the intermediate macrocyclic product **2** *via* reductive amination. The procedure involved stirring a mixture of a large excess of ammonium acetate, sodium cyanotrihydridoborate (6 equivalents), dialdehyde **1** and 4 Å molecular sieves overnight.[12] Sodium cyanotrihydridoborate was employed because it is known to reduce imines selectively in the presence of aldehydes.[13] The major product was the required macrocycle **2** which was isolated as a white solid in 87% yield. The proposed mechanism for the formation of this product involves a reductive amination of a single aldehyde group to yield an intermediate primary aminoaldehyde. This is capable of intramolecular cyclization/condensation to give a cyclic imine which is then reduced to yield **2**. The formation of 5- and 6-membered heterocycles from dialdehydes using related reductive amination conditions has been reported previously.[12,14] Alkylation of **2** with 2-chloromethylpyridine in toluene using caesium carbonate as the base gave L in 83% yield.

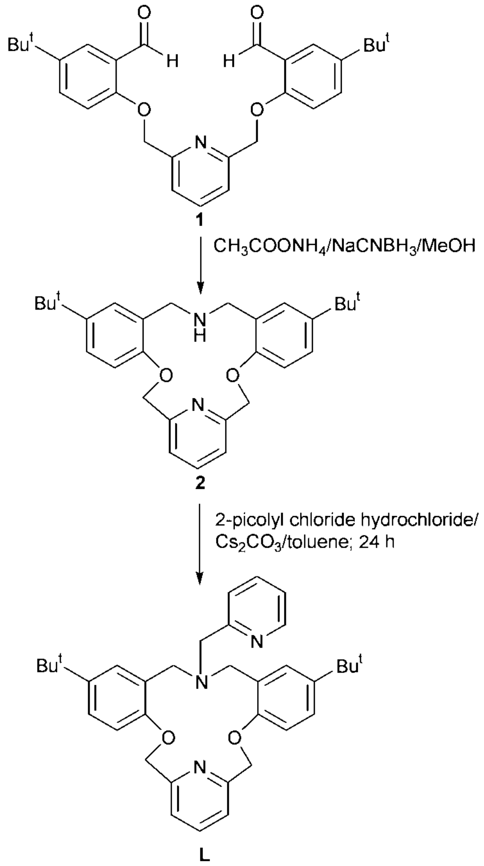
### Isolation and characterization of metal complexes

In an attempt to obtain crystalline products suitable for X-ray diffraction studies, cobalt(II), copper(II), zinc(II), silver(I) and lead(II) complexes of L, showing 1 : 1 (metal : ligand) stoichiometries, were synthesized (Table 1). For each complex except those of lead, the resulting dinitrato (dichloro in the case of cadmium) product was isolated after a two phase synthetic procedure in which a dichloromethane or dichloromethane–hexane solution of L was shaken with an aqueous solution of the required metal salt (in excess). Metal ion extraction into the organic phase was observed in each case and the required metal nitrate (or in the case of cadmium, chloride) complex

**Table 1** Conductance and stability constant data for the complexes

| Complex | Colour | $\Lambda^a$ | $\log K_{ML}{}^b$ |
|---|---|---|---|
| $[CoL(NO_3)]NO_3 \cdot 0.5CH_2Cl_2$ | Pink | 85 | —$^c$ |
| $[CuL(NO_3)]NO_3 \cdot CH_2Cl_2$ | Blue | 158 | >14 |
| $[ZnL(NO_3)]NO_3 \cdot 0.25CH_2Cl_2$ | White | 102 | 7.7(1) |
| $[CdLCl]Cl \cdot 0.33CH_2Cl_2$ | White | 90 | —$^c$ |
| $[AgL]NO_3$ | White | 72 | >14 |
| $[PbL(NO_3)]NO_3$ | White | 97 | 6.7(2) |
| $[PbL(NO_3)(ClO_4)]$ | White | 97 | |

$^a$ Conductance (S cm$^2$ mol$^{-1}$) at 20 °C in methanol; expected range for a 1 : 1 electrolyte in methanol is 80–115 S cm$^2$ mol$^{-1}$ while that for a 2 : 1 electrolyte is 160–220 S cm$^2$ mol$^{-1}$, see ref. 18. $^b$ In 95% MeOH; $I = 0.1$ mol dm$^{-3}$, $NEt_4ClO_4$ at 25 °C; each value is the mean of at least three (and up to six) determinations at different metal : ligand ratios rounded to the first decimal place; log protonation constants for L of 9.96 and 2.66 were determined potentiometrically under identical conditions to those used to obtain the metal stability constants. $^c$ Precipitation, slow approach to equilibrium or competing hydrolysis inhibited log $K$ determination in this case.



**Scheme 1**

crystallized on diffusion of ether vapour into the separated organic layers; the latter had been dried previously over molecular sieves. This two phase procedure was adopted in order to circumvent precipitation of L as its protonated nitrate or chloride salts. These were found to form readily (together with metal hydrolysis), leading to contaminated products, if protic (or non-dry aprotic) solvents were employed for the synthesis. However, the above procedure was found to be unnecessary for obtaining pure complexes of lead; $[PbL(NO_3)]NO_3$ and $[PbL(NO_3)(ClO_4)]$ were successfully isolated uncontaminated directly from ethanol and methanol solutions, respectively.

The complexes isolated are listed in Table 1. Several attempts at obtaining a complex of nickel nitrate using both two-phase and direct conditions were unsuccessful; in all cases the corresponding colourless salt, $L \cdot HNO_3 \cdot nH_2O$, was obtained as the major product. This was also the situation with cadmium nitrate, although use of cadmium chloride did lead to isolation of the corresponding dichloro, solvated species, $[CdLCl]Cl \cdot 0.33CH_2Cl_2$, when the two phase ($CH_2Cl_2$–water) procedure was employed.

With respect to the above, it is pertinent that previous attempts to isolate a pure nickel(II) complex of a related (dibenzo-substituted) $N_2O_2$-donor macrocycle incorporating a *N*-pendant pyridylmethyl group by the addition of this ligand to a methanol solution of nickel(II) nitrate in the presence of a slight excess of lithium perchlorate were not successful; co-crystallization of the desired nickel complex together with a colourless, water soluble, crystalline solid (which appeared to be the corresponding hydroperchlorate and/or hydronitrate salt of the ligand) occurred.[3] Competing precipitation of protonated ligand salts has also been documented previously during the attempted preparation of metal complexes of other related mixed donor macrocycles in ethanol when the ligand systems incorporated less than three secondary amines.[15]

The infrared spectra of the respective complexes confirmed the presence of nitrate[16] and, for $[PbL(NO_3)(ClO_4)]$, also perchlorate ion.[16,17] The latter mixed anion complex shows a strong $\nu(ClO_4^-)$ absorption at approximately 1110 cm$^{-1}$ (major peak) that appears split; this absorption is absent in the spectrum of $[PbL(NO_3)]NO_3$. The unsymmetrical nature of the $ClO_4^-$ peak suggests co-ordination of this anion, consistent with the solid state structure of this complex (see later).

The conductance values in methanol (Table 1) indicate that all the complexes isolated except $[CuL(NO_3)]NO_3$ are 1 : 1 electrolytes in this solvent, with values that fall within (or marginally below in the case of $[AgL]NO_3$) the expected range of 80–115 S cm$^3$ mol$^{-1}$ for an electrolyte of this type.[18] Such behaviour is thus in accord with single anion co-ordination occurring in solution for the cobalt, zinc, cadmium and lead complexes, while the silver species has its (single) nitrate group essentially ionized. The value for the copper complex approaches that for a 2 : 1 electrolyte (expected range: 160–220 S cm$^3$ mol$^{-1}$) indicating part ionization of the second nitrate group in this case.

The X-ray data for $[AgL]NO_3$ show that the nitrate group remains unco-ordinated in the solid state (see later). In contrast, even though the crystal structure of $[PbL(NO_3)(ClO_4)]$ shows that both anions are co-ordinated in the solid state, the conductance value for this complex once again approximates that of a 1 : 1 electrolyte and hence one or other of these anions is displaced under the conditions employed for the measurement.

The magnetic moment (4.36 $\mu_B$, 22 °C) of the pink cobalt complex confirms its high-spin nature; the solid state visible spectrum shows a broad (composite) band with maxima at 481 (sh), 517 and 549 nm, consistent with the presence of a distorted octahedral co-ordination geometry.[19] The magnetic moment of the copper complex ($\mu = 2.07$ $\mu_B$, 22 °C) falls in the normal range for a copper(II) species with $S = \frac{1}{2}$. The ESR spectrum (X-band) of a powdered sample of this complex yielded $g_{\parallel} = 2.162$ and $g_{\perp} = 2.101$. The solid state electronic spectrum shows a broad envelope of bands in the region 550–850 nm; the latter is typical of many copper complexes of mixed donor ligands.[20] However, the featureless nature of this spectrum results in it being of little value for the assignment of the corresponding co-ordination geometry. A cyclic voltammogram of the copper complex recorded in dry acetonitrile at a scan rate of 200 mV s$^{-1}$ with tetrabutylammonium perchlorate as supporting electrolyte (0.1 mol dm$^{-3}$) yielded two non-reversible reduction waves, presumably reflecting sequential Cu$^{II}$–Cu$^{I}$ and Cu$^{I}$–Cu$^{0}$ redox steps.

## Stability constants

The protonation constants for L were obtained by potentiometric (pH) titration in 95% methanol ($I = 0.1$ mol dm$^{-3}$; $NEt_4ClO_4$). As in previous studies, this solvent system was

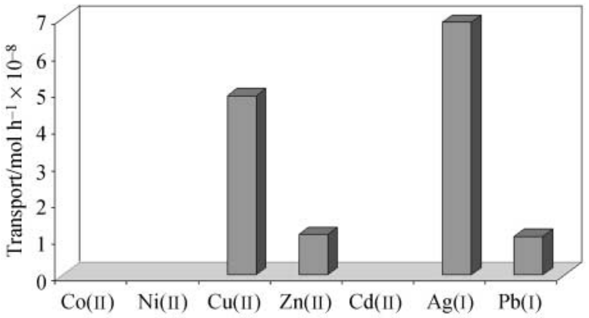


**Fig. 1** Comparative metal transport rates for a competitive metal-ion experiment employing L as ionophore. Aqueous source phase: 10 cm$^3$, containing seven metal ions, each initial concentration 0.01 mol dm$^{-3}$ in buffer solution ($CH_3CO_2H$–$CH_3CO_2Na$) at pH 4.9. Chloroform (membrane) phase: 50 cm$^3$ containing L ($10^{-3}$ mol dm$^{-3}$) and hexadecanoic acid ($4 \times 10^{-3}$ mol dm$^{-3}$). Aqueous receiving phase: 30 cm$^3$ buffer solution ($HCO_2H$–$HCO_2Na$) at pH 3.0; all three phases stirred for 24 hours at 25 °C.

employed by us since its use helps to overcome the generally low solubility of ligands of the present type (and/or their metal complexes) in water.[1] The complex stability constants were also determined potentiometrically under similar conditions (Table 1). Where solubilities/hydrolysis interference permitted, log $K$ values corresponding to the formation of 1 : 1 (metal : ligand) species were obtained. From the limited data obtained, it is clear that L is an excellent ligand towards both copper(II) and silver(I), the stabilities of the complexes of these cations being at least 6–7 orders of magnitude greater than the corresponding values for lead(II) and zinc(II). Nevertheless, relative to the corresponding log $K_{ML}$ values obtained for related mixed-donor macrocyclic systems (containing pyridylmethyl arms and determined previously in our laboratory),[3] the magnitude of each of the present log $K_{ML}$ values suggest that, at a minimum, all three nitrogens of the donor set of L contribute to metal ion binding in solution.

## Bulk membrane transport

Competitive mixed metal transport experiments (water/chloroform/water) have been undertaken, with the chloroform membrane phase containing L as the ionophore. The aqueous source phase contained equimolar concentrations of the nitrate salts of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II), with individual metal ion concentrations of $10^{-2}$ mol dm$^{-3}$. As mentioned in the Experimental section, transport was performed against a back gradient of protons, with hexadecanoic acid also being present in the organic phase. The major role of the latter is to aid the transport process by providing a lipophilic counter ion in the organic phase (after proton loss to the aqueous source phase) for charge neutralization of the metal cation being transported; in this manner the need for uptake of lipophobic nitrate anions into the organic phase may be avoided. Under the conditions employed, selectivity towards transport of silver(I) and copper(II) was observed, with silver(I) being favoured over copper(II) (Fig. 1). Minor amounts of zinc and lead were also present in the receiving phase at the conclusion of the experiment. While not necessarily dictated by theory,[21] the silver(I) and copper(II) complexes of L are nevertheless the ones that were shown to yield particularly stable complexes in the thermodynamic studies presented above.

## Crystal structures

Hot saturated solutions of copper(II) nitrate trihydrate in water and L in chloroform were mixed and left to stand in a test tube. Blue-green crystals of $[CuL(NO_3)]NO_3\cdot{\approx}3H_2O$, suitable for X-ray diffraction, formed on the wall of the tube in the aqueous phase over several hours. Suitable crystals of $[AgL(NO_3)]$ were obtained by diffusion of ether vapour into a solution of the complex in dichloromethane. Crystals of $[PbL(NO_3)(ClO_4)]$ were obtained directly from methanol solution.

Ligand L may be considered an array wherein one half may be related to the other, either by *2* or *m* (but not *i*) symmetry; its disposition about the metal atom M in the three complexes mentioned above is examined in the light of those possibilities, and the prospect that the maximum five-($N_{2+1}O_2$)-co-ordination offered by it ($N_2O_2$ with maximum 2-symmetry, $N_{(2+1)}O_2$ *m*) may or may not be achieved.

The crystal structures of the present complexes confirm that the pendant pyridyl group of L co-ordinates to the respective metals in each case. Previous structural studies by us[3] and others[22] have also demonstrated related pyridylmethyl arm co-ordination in a range of heavy metal complexes of macrocyclic ligand derivatives.

The copper(II) complex, $Cu(NO_3)_2$ : L (1 : 1), with additional residues unassociated with the copper atom and modelled as *ca.* $3H_2O$, is best described as $[CuL(ONO_2)]NO_3\cdot{\approx}3H_2O$, the unco-ordinated nitrate anion being disordered. Within the cation, $[L(O_2N_{2+1})Cu(ONO_2)]$, with a putatively six-co-ordinate metal atom, we find the common (here, highly-) distorted six-co-ordinate array about the metal with four donor atoms, the nitrogen atoms of the ligand plus the unidentate nitrate oxygen, comprising a putative 'square plane' about the metal. Cu–N,O ranges between 1.966(6) (N(01)) and 2.090(6) Å (N(0)), with the two oxygen atoms O(2,2′) of L lying in quasi-*trans* positions (O(2)–Cu–O(2′) 151.6(2)°, Cu–O(2,2′) 2.315(6), 2.300(5) Å), and bonding less strongly than the nitrate oxygen. The ligand L adopts quite a reasonable approximation to *m* symmetry, at least in respect of the macrocycle itself with associated phenyl rings, as evidenced in the torsion angles of Table 3 and Fig. 2(a); the *tert*-butyl groups are not disordered, and broadly conform to the general overall symmetry also. It is noted that the torsion angles in the macrocycle in the bonds to either side of each $C_6$ aromatic ring are of similar magnitude and sign so that N(0) and C(3) are disposed to either side. 'Macroscopically', the structure comprises columns of cations along *b*, interspersed by (less-ordered) columns of anions and solvent molecules.

The cations of the silver(I) and lead(II) adducts, even though of different valence states, resemble each other more closely than they do the copper(II) adduct, perhaps in consequence of the size of the large, albeit electronically different, metal atoms encompassed by ligand L. The dispositions of the macrocycles about the central metal atom are similar in both adducts [Fig. 2(b),(c)], and different to that found in the copper(II) complex, the putative *m* symmetry found in the latter having been lost (Table 3). This is most readily evident in the C(11)–C(16)–O(2)–C(3) torsion, now almost *trans* in all of these strings, approaching 180°, rather than 90° as in the copper complex, and the similar signs of the N(0)–C(1)–C(11)–C(16) torsion. The overall result is that, *cf.* the copper adduct, the macrocycle pyridine component now lies more nearly parallel to the macrocycle 'plane' (rather than quasi-normal as in the copper(II) adduct) and that the two $C_6$ aromatic rings differ in their orientation *vis-à-vis* the macrocycle plane, that of the primed ring being quasi-parallel (as in both strings of the copper(II) adduct), but that of the unprimed string quasi-normal. The two *tert*-butyl substituents of the lead adduct are not disordered, but both of the silver adduct are.

In the silver complex the metal atom rests within the cavity offered by the macrocycle, resting upon the $N_2O_2$ array above that plane, with a further approach by the pendant pyridine nitrogen; the latter and the other pyridine ring nitrogen atom dominate the co-ordination environment, which may be regarded as essentially two-co-ordinate (Ag–N, 2.160(3), 2.179(4) Å; N(01)–Ag–N(31) 153.5(1)°), *cf.* the $[Ag(py)_2]^+$ array in which Ag–N are 2.15(1), 2.16(1) Å with N–Ag–N 173.7(4)°.[23] Despite the latter approach, a large unfilled void remains in the co-ordination sphere, with no close approaches by anions or $\eta^n$-aromatic components.

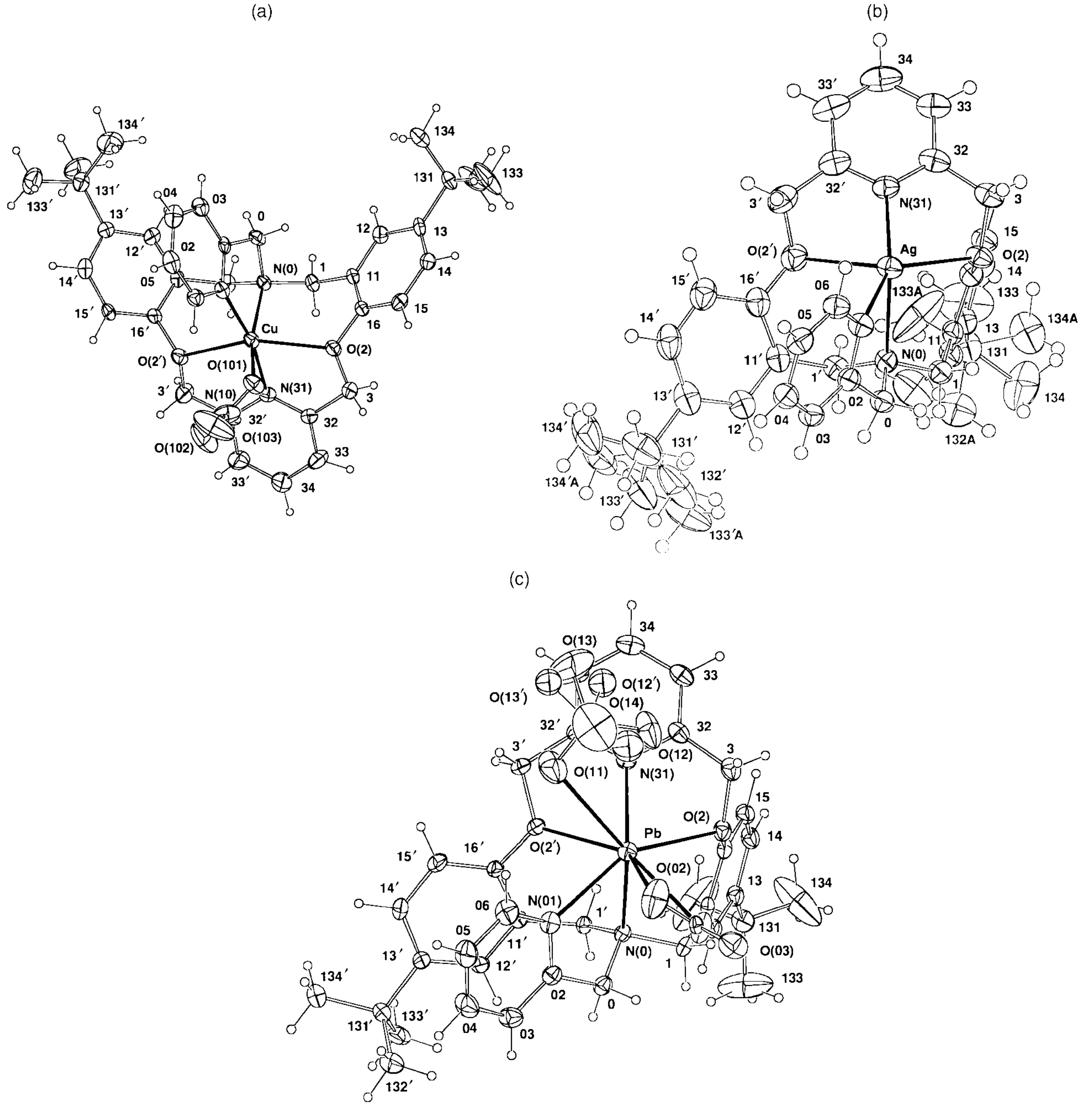


**Fig. 2** (a) Projection of the $[CuL(ONO_2)]^+$ cation. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å in this and the subsequent figures (non-H atoms 50% in the low temperature silver(I) adduct). Projection is through the $[(L\text{-}N_3)\text{-}Cu(ONO_2)]$ array, with the long Cu–O(11,11′) distances horizontal in the page. (b), (c) Projections of the $[AgL]^+$ and $[PbL(O_2NO)(OClO_3)]$ arrays, disposed so as to display the similarity in macrocycle conformations.

Such is not the case with the lead complex. Although the approach of the lead atom to the ligand is essentially similar to that of the silver(I) complex, the electronic imperatives of the latter are not present and lead–donor atom interactions are longer, as befits a larger metal atom, the M···L donor distances ranging from 2.449(4) to 2.807(3) Å; the lead–nitrogen distances are only marginally shorter than the lead–oxygen. Again, the nature of the metal–ligand approach is such that a large void remains in the co-ordination sphere, but here it is filled by approaches from anions of both types, the perchlorate as an *O*-unidentate, modelled as rotationally disordered about that Cl–O bond, and the nitrate as an unsymmetrical bidentate, the lead atom lying 0.65(1) Å out of its plane. It is an apparent curiosity of nitrogen-base lead(II) salt complexes that a disproportionate array of the relatively small number structurally characterized have been of adducts containing mixed anions, both of which may co-ordinate; for example, $L_2PbXY$, L = phen, $X = NO_3$, Y = SCN,[24] L = bpy, $X = ClO_4$, Y = acetate or chloride[25] (phen = 1,10-phenanthroline; bpy = 2,2′-bipyridyl), or not, for example, $[Pb(tet\text{-}b)Cl][ClO_4]\cdot MeOH$, $[(tet\text{-}b)Pb(OClO_2\text{-}O)_2Pb(tet\text{-}b)][ClO_4]Cl\cdot H_2O$[26] (tet-b = (5*R**,14*R**)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), suggesting a widespread ambivalence in respect of anion competitiveness as ligands.

## Concluding remarks

The pendant arm ligand L yields a series of 1 : 1 (metal : macrocycle) transition and post-transition metal complexes. The evidence presented confirms that the pyridylmethyl arm of L participates in co-ordination in each of the complexes for which structural data were obtained, with each of these complexes exhibiting a different co-ordination geometry. Competitive transport across a bulk chloroform membrane using L as the ionophore resulted in the preferential transfer of copper(II) and silver(I) from the aqueous source phase to the aqueous receiving phase.

**Table 2** Metal atom environments, $LM(X/Y)_m{\cdot}nH_2O$; *r* is the metal–ligand distance (Å), other entries being the angles (degrees) subtended at the metal by the relevant ligand atoms at the head of the row and column.

(a) $[CuL(ONO_2)]^+$

| Atom | *r* | O(2) | O(2′) | N(31) | N(01) | O(101) |
|---|---|---|---|---|---|---|
| N(0) | 2.090(6) | 87.5(2) | 91.5(2) | 98.6(3) | 83.0(3) | 162.6(2) |
| O(2) | 2.315(6) |  | 151.6(2) | 75.4(2) | 116.6(2) | 81.3(2) |
| O(2′) | 2.300(5) |  |  | 76.8(2) | 91.4(2) | 104.7(2) |
| N(31) | 2.024(6) |  |  |  | 168.1(3) | 91.4(3) |
| N(01) | 1.966(6) |  |  |  |  | 90.1(3) |
| O(101) | 2.002(6) |  |  |  |  |  |

(b) $[PbL(O_2NO)(OClO_3)]$

| Atom | *r* | N(01) | O(2) | O(2′) | N(31) | O(11) | O(01) | O(02) |
|---|---|---|---|---|---|---|---|---|
| N(0) | 2.557(4) | 69.2(1) | 74.6(1) | 72.0(1) | 96.7(1) | 140.8(1) | 78.3(1) | 110.8(1) |
| N(01) | 2.449(4) |  | 143.4(1) | 74.8(1) | 129.9(1) | 84.8(1) | 86.5(1) | 72.9(1) |
| O(2) | 2.807(3) |  |  | 98.9(1) | 58.7(1) | 128.8(1) | 81.3(1) | 117.1(1) |
| O(2′) | 2.767(3) |  |  |  | 55.2(1) | 73.3(1) | 148.9(1) | 143.5(1) |
| N(31) | 2.718(4) |  |  |  |  | 77.7(1) | 139.3(1) | 150.3(1) |
| O(11) | 2.902(5) |  |  |  |  |  | 130.3(1) | 87.3(1) |
| O(01) | 2.597(4) |  |  |  |  |  |  | 43.6(1) |
| O(02) | 2.895(6) |  |  |  |  |  |  |  |

(c) $[AgL]NO_3$

| Atom | *r* | N(01) | O(2) | O(2′) | N(31) |
|---|---|---|---|---|---|
| N(0) | 2.457(3) | 78.6(1) | 79.22(9) | 76.5(1) | 118.1(1) |
| N(01) | 2.160(3) |  | 137.9(1) | 102.6(1) | 153.5(1) |
| O(2) | 2.621(3) |  |  | 106.22(9) | 68.2(1) |
| O(2′) | 2.745(3) |  |  |  | 65.2(1) |
| N(31) | 2.179(4) |  |  |  |  |

**Table 3** Macrocycle conformation data

|  | Cu | Ag | Pb |
|---|---|---|---|
| (a) Torsion angles (degrees); the two values in each entry are for unprimed/primed ligand sections respectively |  |  |  |
| C(1′)–N(0)–C(1)–C(11) | 173.7(6), −174.1(6) | 61.0(4), 179.9(3) | 46.9(5), 171.8(4) |
| C(0)–N(0)–C(1)–C(11) | 54.8(9), −54.8(8) | −177.5(3), 59.6(4) | 165.3(4), 55.6(5) |
| M–N(0)–C(1)–C(11) | −64.9(7), 61.9(7) | −67.3(4), −53.8(4) | −83.1(4), −63.5(4) |
| N(0)–C(1)–C(11)–C(16) | −63.4(10), −72.7(9) | 74.9(5), 77.3(5) | 73.3(5), 76.4(5) |
| C(1)–C(11)–C(16)–O(2) | 8(12), 4.6(11) | 1.4(6), 0.7(6) | 3.6(6), −7.8(6) |
| C(11)–C(16)–O(2)–M | −43.5(9), 48.2(9) | −56.5(4), −65.5(4) | −45.8(5), −54.1(5) |
| C(11)–C(16)–O(2)–C(3) | 95.5(9), −84.3(9) | −170.1(4), −167.0(4) | −170.7(4), 146.6(4) |
| C(16)–O(2)–C(3)–C(32) | −135.8(8), 143.7(8) | 71.0(4), 169.3(4) | 72.2(5), −154.3(4) |
| M–O(2)–C(3)–C(32) | 6.2(9), 10.7(9) | −53.3(3), 60.2(3) | −64.5(4), −45.3(4) |
| O(2)–C(3)–C(32)–N(31) | 5.0(12), −16.7(12) | 38.3(5), −46.8(5) | 34.9(6), −12.8(6) |
| C(3)–C(32)–N(31)–M | −16.2(11), 14.7(11) | 8.9(4), −8.4(5) | 18.9(5), −26.4(5) |
| C(3)–C(32)–N(31)–C(32′) | 178.9(8), 180.0(9) | −172.7(4), 173.2(4) | 176.7(4), 177.3(4) |
| C(1)–N(0)–C(0)–C(02) | −150.3(6), 91.9(7) | 151.2(3), −88.1(4) | 161.6(4), −80.8(5) |
| M–N(0)–C(0)–C(02) | −26.5(7) | 34.1(4) | 46.7(4) |
| N(0)–C(0)–C(02)–N(01) | 27.1(9) | −46.7(5) | −36.7(6) |
| (b) Metal atom deviations from aromatic planes, $\delta$/Å |  |  |  |
| $C_5N(0n)$ | 0.23(1) | 0.777(6) | 0.014(8) |
| $C_6(1n,1n')$ | 1.49(1), 1.87(1) | 1.613(8), 2.358(7) | 1.374(0), 2.031(9) |
| $C_5N(3n')$ | 0.43(1) | 0.239(7) | 0.939(9) |
| (c) Interplanar dihedral angles (degrees) |  |  |  |
| $C_5N(0n)/C_6(1n,1n')$ | 60.0(3), 63.0(3) | 28.0(1), 36.0(2) | 36.8(2), 31.2(2) |
| $C_5N(0n)/C_5N(3n')$ | 87.4(3) | 71.3(2) | 57.4(2) |
| $C_5N(3n')/C_6(1n,1n')$ | 33.0(3), 80.3(3) | 87.9(2), 36.6(2) | 86.4(2), 42.3(2) |
| $C_6(1n)/C_6(1n')$ | 62.2(3) | 61.4(2) | 67.9(2) |

## Acknowledgements

We thank the Australian Research Council for support and acknowledge A. J. Leong, A. Nezhadali and Gh. Rounaghi for experimental assistance.

## References

1 M. Ahearn, J. Kim, A. J. Leong, L. F. Lindoy, O. A. Matthews and G. V. Meehan, *J. Chem. Soc., Dalton Trans.*, 1996, 3591 and references therein.

2 K. R. Adam, C. Clarkson, A. J. Leong, L. F. Lindoy, M. McPartlin, H. R. Powell and S. V. Smith, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2791.

3 K. R. Adam, L. F. Lindoy, B. W. Skelton, S. V. Smith and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3361.

4 T. A. Kaden, *Top. Curr. Chem.*, 1984, **121**, 157; P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297; G. W. Gokel, *Chem. Soc. Rev.*, 1992, **21**, 39.

5 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989.

6 See, for example: D. E. Fenton and G. Rossi, *Inorg. Chim. Acta*, 1985, **98**, L29; K. V. Damu, M. S. Shaikjee, J. P. Michael, A. S. Howard and R. D. Hancock, *Inorg. Chem.*, 1986, **25**, 3879; L. Christiansen, D. N. Hendrickson, H. Toftlund, S. R. Wilson and C.-L. Xie, *Inorg. Chem.*, 1986, **25**, 2813; E. Kimura, *Pure Appl. Chem.*, 1986, **58**, 1461; G. Bombieri, A. Polo, F. Benetollo, M. L. Tobe, M. Humanes and C. Chatterjee, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 1866; N. W. Alcock, K. P. Balakrishnan, A. Berry, P. Moore and C. J. Reader, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 1089; H. Tsukube, K. Yamashita, T. Iwachido and M. Zenki, *Tetrahedron Lett.*, 1988, **29**, 569; E. Kimura, T. Koike, H. Nada and Y. Iitaka, *Inorg. Chem.*, 1988, **27**, 1036; K. P. Balakrishnan, H. A. A. Omar, P. Moore, N. W. Alcock and G. A. Pike, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 2965; S. Chirayil, V. Hegde, Y. Jahng and R. P. Thummel, *Inorg. Chem.*, 1991, **30**, 2821; H. Tsukube, T. Yoden, T. Iwachido and M. Zenki, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1069; S. C. Rawle, P. Moore and N. W. Alcock, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 684; H. Tsukube, T. Hamada, T. Tanaka and J. Uenishi, *Inorg. Chim. Acta*, 1993, **214**, 1; H. Tsukube, J. Uenishi, H. Higaki, K. Kikkawa, T. Tanaka, S. Wakabayashi and S. Oae, *J. Org. Chem.*, 1993, **58**, 4389; W. S. Szulbinski, P. R. Warburton, D. H. Busch and N. W. Alcock, *Inorg. Chem.*, 1993, **32**, 297; G. D. Fallon, G. A. McLachlan, B. Moubaraki, K. S. Murray, L. O'Brien and L. Spiccia, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2765; M. Koikawa, K. B. Jensen, H. Matsushima, T. Tokii and H. Toftlund, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1085; S. J. Brudenell, L. Spiccia, D. C. R. Hockless and E. R. T. Tiekink, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1475; X. Zhang, D. Zhang, D. H. Busch and R. van Eldik, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2751; J. Costa, R. Delgardo, M. G. B. Drew and V. Felix, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 4331.

7 P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

8 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 1195.

9 P. S. K. Chia, L. F. Lindoy, G. W. Walker and G. W. Everett, *Pure Appl. Chem.*, 1993, **65**, 521.

10 S. R. Hall, G. S. D. King and J. M. Stewart (Editors), *The Xtal 3.4 User's Manual*, University of Western Australia, Lamb, Perth, 1995.

11 I. M. Atkinson, A. R. Carroll, R. J. A. Janssen, L. F. Lindoy, O. A. Matthews and G. V. Meehan, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 295.

12 R. F. Borch, M. D. Bernstein and H. D. Durst, *J. Am. Chem. Soc.*, 1971, **93**, 2897.

13 C. F. Lane, *Synthesis*, 1975, 135.

14 G. W. Gribble, *J. Org. Chem.*, 1972, **37**, 1833; A. S. Kende, T. J. Bentley, R. A. Mader and D. Ridge, *J. Am. Chem. Soc.*, 1974, **96**, 4332.

15 K. R. Adam, M. Antolovich, D. S. Baldwin, L. G. Brigden, P. A. Duckworth, L. F. Lindoy, A. Bashall, M. McPartlin and P. A. Tasker, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1869.

16 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.

17 B. I. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

18 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

19 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Fifth Edition, Wiley, New York, 1988.

20 K. R. Adam, M. Antolovich, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, M. McPartlin and P. A. Tasker, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1013.

21 B. G. Cox and H. Schneider, *Coordination and Transport Properties of Macrocyclic Compounds in Solution*, Elsevier, Amsterdam, 1992; J. P. Behr, M. Kirch and J. M. Lehn, *J. Am. Chem. Soc.*, 1985, **107**, 241; R. M. Izatt, R. L. Bruening, M. L. Bruening, G. C. Lindh and J. J. Christensen, *Anal. Chem.*, 1989, **61**, 1140.

22 K. Wieghardt, E. Schöffmann, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 4877; N. W. Alcock, K. P. Balakrishnan and P. Moore, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 1743; D. Funkemeier and R. Mattes, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 1313; S.-G. Kang, S.-J. Kim and J. H. Jeong, *Polyhedron*, 1998, **17**, 3227; C. Bazzicalupi, A. Bencini, A. Bianchi, V. Fedi, V. Fusi, C. Giorgi, P. Paoletti, L. Tei and B. Valtancoli, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1101.

23 J. C. Dyason, P. C. Healy, L. M. Engelhardt and A. H. White, *Aust. J. Chem.*, 1985, **38**, 1325.

24 L. M. Engelhardt, J. M. Patrick and A. H. White, *Aust. J. Chem.*, 1989, **42**, 335.

25 L. M. Engelhardt, J. M. Harrowfield, H. Miyamae, J. M. Patrick, B. W. Skelton, A. A. Soudi and A. H. White, *Aust. J. Chem.*, 1996, **49**, 1111.

26 J. M. Harrowfield, H. Miyamae, B. W. Skelton, A. A. Soudi and A. H. White, *Aust. J. Chem.*, 1996, **49**, 1067.

*Paper a909102e*