

Macrocyclic ligand design. Structure–function relationships involving the interaction of pyridinyl-containing, mixed oxygen–nitrogen donor macrocycles with cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II)

Ronald R. Fenton,^a Robert Gauci,^b Peter C. Junk,^{†b} Leonard F. Lindoy,^{*a} Robert C. Luckay,^a George V. Meehan,^b Jason R. Price,^a Peter Turner^a and Gang Wei^a

^a Centre for Heavy Metals Research, School of Chemistry, The University of Sydney, NSW 2006, Australia. E-mail: lindoy@chem.usyd.edu.au

^b School of Pharmacy and Molecular Sciences, James Cook University, Townsville, Q 4811, Australia

Received 1st February 2002, Accepted 19th March 2002
First published as an Advance Article on the web 24th April 2002

A comparative investigation of the interaction of three dibenzo-substituted, mixed oxygen–nitrogen donor macrocycles with cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) has been carried out. The thermodynamic stabilities of the respective complexes in 95% methanol ($I = 0.1$; Et₄NClO₄, 25 °C) have been determined. All ligands form 1 : 1 (metal : ligand) species with the above metal ions. The results are compared with those obtained previously for related mixed-donor (cyclic) systems. Single crystal structures of six metal complexes of these 20-membered ring ligands have been determined by X-ray diffraction. All of the macrocyclic donor sites participate in binding to the metal ion in the copper(II) and cadmium(II) complexes. The copper complex is six-coordinate, while the cadmium complex is eight-coordinate with the addition of a bidentate nitrate ion. A tri-nuclear complex is formed on complexation with silver(I) in which two silver-containing macrocycles are linked by a bridging two-coordinate silver ion. The metal atoms in each of the cobalt(II), nickel(II) and zinc(II) complexes are six-coordinate, however, they are bound to the macrocycle only at the three secondary amine nitrogen sites. The coordination sphere is completed by two nitrate counterions in the zinc(II) complex, and by a nitrate ion and a methanol molecule in each of the cobalt(II) and nickel(II) complexes.

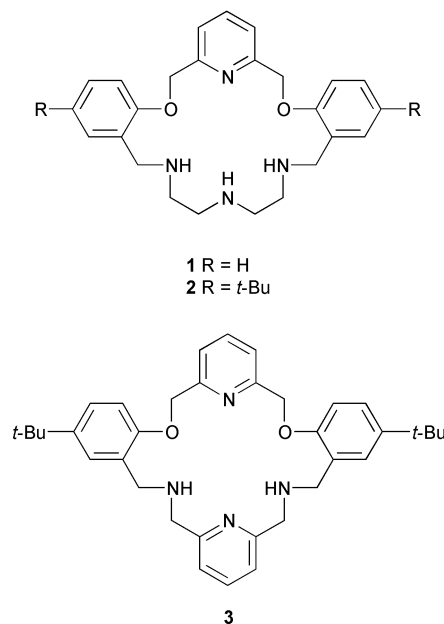
Introduction

For some time now, we¹ and others² have been concerned with investigation of the heavy metal ion chemistry of mixed-donor macrocycles, with the factors influencing metal-ion recognition receiving special attention. Our studies have focused on the complexation behaviour of the industrially important ions, cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) and, for a number of mixed-donor ligand systems, significant metal-ion recognition within this metal-ion series has been achieved. Mixed-donor systems have proved especially suitable for such (solution) investigations since they tend not to exhibit the high thermodynamic and kinetic stabilities that are frequently characteristic of all-nitrogen donor macrocyclic ligand complexes³ (and which can sometimes give rise to difficulties when attempting to measure solution log K values). As part of this ongoing program, we now report the results of a comparative investigation of structure–function relationships underlying metal-ion binding by the pyridinyl-containing, mixed-donor macrocycles **1–3**, incorporating 20-membered backbones, with each of the above metal ions.

Experimental

All commercial reagents and solvents were of analytical (or HPLC) grade where available.

[†] Present address: Chemistry Department, Monash University, Clayton, Vic. 3168, Australia.



Physical measurements

NMR spectra were determined at 298 K on a Bruker AM300 spectrometer; δ_{H} values are relative to Me₄Si at 0 ppm and δ_{C} are relative to CDCl₃ at 77.0 ppm, J values are in Hz. UV-VIS spectra were obtained in methanol on a Cary 5E

Table 1 Crystal structure determination details for complexes $[\text{Zn}(\text{I})(\text{NO}_3)_2]\cdot\text{CH}_3\text{OH}\cdot 0.8\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, $[\text{Co}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot\text{CH}_3\text{OH}$ and $[\text{Ni}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot 0.8\text{CH}_3\text{OH}\cdot 0.2\text{H}_2\text{O}$

	$[\text{Zn}(\text{I})(\text{NO}_3)_2]\cdot\text{CH}_3\text{OH}\cdot 0.8\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	$[\text{Co}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot\text{CH}_3\text{OH}$	$[\text{Ni}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot 0.8\text{CH}_3\text{OH}\cdot 0.2\text{H}_2\text{O}$
Model formula	$\text{C}_{29.20}\text{H}_{42}\text{N}_6\text{O}_{9.80}\text{Zn}$	$\text{C}_{28}\text{H}_{42}\text{CoN}_6\text{O}_{11}$	$\text{C}_{27.80}\text{H}_{41.20}\text{N}_6\text{NiO}_{11}$
Model molecular weight	699.26	697.61	694.18
Crystal system	Tetragonal	Triclinic	Triclinic
Space group	$I\bar{4}$ (no. 82)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
$a/\text{\AA}$	27.980(9)	11.850(3)	11.7459(16)
$b/\text{\AA}$	27.980(9)	13.422(3)	13.4578(18)
$c/\text{\AA}$	8.878(4)	11.066(3)	11.0282(15)
α°		112.555(4)	111.944(2)
β°		86.932(4)	87.059(2)
γ°		101.417(4)	101.493(2)
$V/\text{\AA}^3$	6950(5)	1592.8(7)	1584.0(4)
Z	8	2	2
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.766	0.607	0.681
N	31347	16660	16203
N_{ind}	8146 (R_{merge} 0.0231)	7351 (R_{merge} 0.0223)	7153 (R_{merge} 0.0163)
N_{obs}	7680 [$I > 2\sigma(I)$]	6368 [$I > 2\sigma(I)$]	6584 [$I > 2\sigma(I)$]
Residuals $R1$ (F), $wR2$ (F^2 all data)	0.0378, 0.1027	0.0319, 0.0866	0.0308, 0.0912

spectrophotometer. A Finnigan LCQ-8 spectrometer was employed for low resolution, positive ion ESMS while high resolution mass spectra were obtained on a Kratos M25RFA spectrometer (EI) or a Bruker APEX 47e spectrometer (ES). The ESR spectra were obtained on a powdered sample at ambient temperature using a Bruker EMX ESR spectrometer at 9.28 GHz (X-band). Magnetic susceptibility was measured on a Sherwood Scientific magnetic susceptibility balance (Cambridge Research Laboratories).

The stability constants were determined by potentiometric titration. All reagents were analytical grade, with analytical grade methanol being fractionated and distilled from magnesium/iodine before use. The apparatus consisted of a water-jacketed measuring cell containing a Philips glass electrode (GA-110) and a water-jacketed calomel reference electrode connected by a salt bridge. A solution of base (tetraethylammonium hydroxide) was introduced into the measuring cell by means of a Metrohm dosimat 665 automatic titrator under personal computer control.

The protonation constants for the respective ligands and the corresponding metal stability constants were obtained in 95% methanol ($I = 0.1$, Et_4NClO_4), with the data processed using a local version of MINQUAD.⁴ The titration data for the metal complexation were successfully refined assuming the presence of only 1 : 1 metal–ligand species in solution; in virtually all cases only data corresponding to the lower portions of the titration curves were employed for the calculations in order to avoid complications arising from competing hydrolysis/precipitation at higher pH values. Quoted $\log K$ values (see Table 4, later) are the mean of two or three separate determinations obtained at different metal to ligand ratios (in each case measured on duplicate sets of potentiometric titration apparatus). Unless otherwise specified, all $\log K$ values obtained in separate titrations fell within ± 0.1 units (and usually within ± 0.05 units) of the mean value for a given metal/ligand system.

Crystal structure determinations

Diffraction data were collected at 150(2) K with a Bruker SMART 1000 CCD diffractometer employing graphite monochromated Mo-K α radiation generated from a sealed tube. The data integration and reduction were undertaken with SAINT and XPREP⁵ and subsequent computations were carried out with the teXsan,⁶ WinGX,⁷ and Xtal⁸ graphical user interfaces. In general a Gaussian absorption correction^{5,9} was applied to the data obtained from the crystals, with the exception of the $[\text{Ni}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot 0.8\text{CH}_3\text{OH}\cdot 0.2\text{H}_2\text{O}$ data for which an empirical correction determined with SADABS¹⁰ was applied. The structures were solved by direct

methods with SIR97,¹¹ with the exception of complex $[\text{AgNO}_3(\text{I})\text{Ag}(\text{I})\text{AgNO}_3]\text{NO}_3\cdot\text{H}_2\text{O}$ which was solved using SHELXS-97,¹² and the solutions were extended and refined with SHELXL-97.¹² Fully occupied non-hydrogen sites were modelled with anisotropic displacement parameters and in general a riding atom model was used for hydrogen atoms. The methanol hydrogen atom positions were located and the atoms modelled with isotropic displacement parameters for the structure of $[\text{Co}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot\text{CH}_3\text{OH}$. The amine hydrogen sites were located and isotropically modelled for the $[\text{Co}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot\text{CH}_3\text{OH}$, $[\text{Ni}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot 0.8\text{CH}_3\text{OH}\cdot 0.2\text{H}_2\text{O}$, $[\text{Cu}(\text{I})(\text{NO}_3)_2]\text{CH}_3\text{OH}$ and $[\text{Cd}(\text{I})(\text{NO}_3)]\cdot 0.5\text{Cd}(\text{NO}_3)_4$ structures. The absolute structure for $[\text{Zn}(\text{I})(\text{NO}_3)_2]\text{CH}_3\text{OH}\cdot 0.8\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ was established with the Flack parameter¹³ refining to 0.027(9). The structure of $[\text{Ni}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot 0.8\text{CH}_3\text{OH}\cdot 0.2\text{H}_2\text{O}$ differs from that of $[\text{Co}(\text{I})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3\cdot\text{CH}_3\text{OH}$ in having a partially occupied water oxygen site. The nitrate counterion for the bridging silver ion in the $[\text{AgNO}_3(\text{I})\text{Ag}(\text{I})\text{AgNO}_3]\text{NO}_3\cdot\text{H}_2\text{O}$ structure is disordered over three sites, and a rigid body taken from the CSD¹⁴ was used to model this counterion. The asymmetric unit for this structure additionally contains a water molecule disordered over two sites. For all compounds with partially occupied solvents, occupancies were initially refined then fixed. Crystal structure determination details are summarised in Tables 1 and 2.

CCDC reference numbers 178685–178690.

See <http://www.rsc.org/suppdata/dt/b2/b201195f/> for crystallographic data in CIF or other electronic format.

Ligand synthesis

The synthesis of 2,6-bis(2-formylphenoxy)methylpyridine has been described previously,^{15,16} as has that of 2,6-bis(2'-formyl-4'-*tert*-butylphenoxy)methylpyridine.¹⁷

Macrocycle 1. 2,6-Bis(2-formylphenoxy)methylpyridine (3.30 g, 9.50 mmol) was dissolved in warm methanol (1000 mL); activated 3 Å molecular sieves were added, and diethylenetriamine (0.98 g, 9.50 mmol) in methanol (500 mL) was added dropwise to the warm solution over 2 h. The reaction mixture was then refluxed for 30 min and sodium borohydride (1.80 g, 47.5 mmol) was carefully added to the hot solution. The reaction solution was refluxed for a further 30 min, filtered hot, and the solvent removed under reduced pressure. The crude reaction mixture was taken up in sodium hydroxide solution (50 mL, 1 M) and the mixture was extracted into chloroform (3 × 50 mL); the chloroform extracts were dried over anhydrous sodium sulfate. The dried solution was filtered and then

Table 2 Crystal structure determination details for complexes [Cu(1)](NO₃)₂·CH₃OH, [Cd(1)(NO₃)]·0.5Cd(NO₃)₄ and [AgNO₃(1)Ag(1)AgNO₃]-NO₃·H₂O

	[Cu(1)](NO ₃) ₂ ·CH ₃ OH	[Cd(1)(NO ₃)]·0.5Cd(NO ₃) ₄	[AgNO ₃ (1)Ag(1)AgNO ₃]-NO ₃ ·H ₂ O
Model formula	C ₂₆ H ₃₄ CuN ₆ O ₉	C ₂₅ H ₃₀ Cd _{1.50} N ₇ O ₁₁	C ₅₀ H ₆₂ Ag ₃ N ₁₁ O ₁₄
Model molecular weight	638.13	773.16	1364.72
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c (no. 15)	C2/c (no. 15)	P1̄ (no. 2)
a/Å	28.340(8)	29.273(6)	14.470(3)
b/Å	8.324(2)	8.4920(17)	20.354(5)
c/Å	24.685(7)	23.673(5)	10.173(2)
α°			79.900(4)
β°	100.890(5)	97.575(3)	108.100(4)
γ°			100.973(4)
V/Å ³	5719(3)	5833(2)	2774.0(11)
Z	8	8	2
μ(Mo-Kα)/mm ⁻¹	0.827	1.175	1.122
N	24727	26575	27139
N _{ind}	6545(R _{merge} 0.0436)	6928(R _{merge} 0.0259)	12729(R _{merge} 0.0364)
N _{obs}	5636 [I > 2σ(I)]	6006 [I > 2σ(I)]	8768 [I > 2σ(I)]
Residuals R1 (F), wR2 (F ² all data)	0.0342, 0.0894	0.0223, 0.0522	0.0445, 0.0998

evaporated on a rotary evaporator to yield the crude product as a pale yellow oil. This was dissolved in ethanol (50 mL) and concentrated hydrochloric acid (3.8 mL, 10 M) was added dropwise to the stirred solution. The solution was left to stand overnight in a refrigerator. The crude hydrochloride salt that formed was removed by filtration. This white solid was then purified *via* Soxhlet extraction employing refluxing ethanol (100 mL); the ethanol solution that resulted being placed in a refrigerator overnight. The hydrochloride salt of **1** that crystallised was isolated by filtration as a white microcrystalline powder.

The above salt was taken up in water (50 mL) and chloroform (50 mL) was added. The pH of the aqueous phase was adjusted to ≈13 by addition of sodium hydroxide. The mixture was shaken and the organic phase was separated. The aqueous phase was further shaken with chloroform (3 × 25 mL); the organic fractions were combined, and the solution dried over anhydrous sodium sulfate. The solvent was then removed under reduced pressure to yield **1** as a pale yellow oil. (2.45 g, 62%) [Found M⁺, 419.2465 (EI). C₂₅H₃₀N₄O₄ requires 419.2447]. δ_H (CDCl₃, 300 MHz) 2.15 (3H, br, NH), 2.50 (8H, s, NHCH₂-CH₂NH), 3.78 (4H, s, ArCH₂NH), 5.18 (4H, s, ArCH₂O), 6.91–7.31 (8H, m, ArH), 7.47 (2H, d, J 8, ArH), 7.81 (1H, t, J 8, ArH). δ_C (CDCl₃, 75 MHz) 48.4, 48.9, 50.0, 72.1, 113.0, 121.5, 122.2, 128.7, 129.4, 130.9, 137.7, 156.5, 157.2. A report of a related preparation of this macrocycle and its use as an ionophore for the membrane transport of alkali metal ions has recently appeared.¹⁸

Macrocycle 2. 2,6-Bis(2'-formyl-4'-*tert*-butylphenoxy-methyl)pyridine (6.07 g, 13.2 mmol) was dissolved in refluxing methanol (600 mL). Diethylenetriamine (1.36 g, 13.2 mmol) was dissolved in methanol (200 mL) and this solution was added dropwise over 2 h to the refluxing solution of the dialdehyde. The reaction mixture was then heated at the reflux for a further 30 min. Sodium borohydride (2.27 g, 60.0 mmol) was carefully added and the reaction mixture was heated at the reflux for a further 2 h. The mixture was cooled to room temperature and the solvent removed under reduced pressure. The residue was partitioned between dichloromethane (200 mL) and 1 M sodium hydroxide solution (200 mL). The dichloromethane layer was separated and the aqueous layer was extracted twice more with dichloromethane. The organic extracts were combined and washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and the solvent again removed under reduced pressure. The crude product was taken up in methanol and acidified to pH < 2 with concentrated hydrochloric acid. The solvent was removed under vacuum and the white solid that remained was washed with chloroform.

This product was slurried in chloroform and the slurry was shaken with 1 M sodium hydroxide solution whereupon the white solid dissolved in the organic layer. The chloroform phase was separated, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure to yield **2** (5.00 g, 67%) as a white solid, mp 124.5–126 °C. This product analysed as its hemihydrate. (Found: C, 73.0; H, 8.7; N, 10.4. C₃₃H₄₆N₄O₂·0.5H₂O requires C, 73.43; H, 8.78; N, 10.38%). Found MH⁺ 531.3796 (ES). C₃₃H₄₆N₄O₂ requires MH⁺ 531.3693. δ_H (CDCl₃, 300 MHz) 1.28 [18H, s, C(CH₃)₃], 2.49 (8H, m, NHCH₂-CH₂NH), 3.74 (4H, s, ArCH₂NH), 5.15 (4H, s, ArCH₂O), 6.96 (2H, d, J 8, ArH), 7.22 (2H, dd, J 2,8, ArH), 7.27 (2H, d, J 2, ArH), 7.44 (2H, d, J 8, ArH), 7.81 (1H, t, J 8, ArH). δ_C (CDCl₃, 75 MHz) 31.4, 34.0, 48.5, 48.8, 50.2, 72.0, 112.4, 122.1, 125.1, 127.9, 128.4, 137.5, 144.0, 154.8, 156.5.

Macrocycle 3. 2,6-Bis(2'-formyl-4'-*tert*-butylphenoxy-methyl)pyridine (6.09 g, 13.3 mmol) was dissolved in methanol (1.25 L) and heated to reflux under a nitrogen atmosphere. 2,6-Bis(aminomethyl)pyridine (1.82 g, 13.3 mmol) in methanol (250 mL) was added dropwise over 2 h to the refluxing solution. Solid sodium borohydride (2.95 g, 78.5 mmol) was then added slowly and the reaction mixture heated at the reflux for a further 2 h. The solvent was removed under reduced pressure and the resulting residue was partitioned between dichloromethane and water. The dichloromethane phase was separated and the aqueous layer extracted twice with further dichloromethane. The organic extracts were combined and washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and the solvent again removed on a rotary evaporator. This crude product was purified by chromatography on silica gel [elution with NH₃(aq)–methanol–dichloromethane, 1 : 2 : 97] to yield **3** as a pale yellow oil (2.29 g, 31%) which was dried under vacuum. (Found: C, 73.0; H, 7.8; N, 9.3. C₃₆H₄₄N₄O₂·1.5H₂O requires C, 73.07; H, 8.01; N, 9.47%). δ_H (CDCl₃, 300 MHz) 1.32 [18H, s, C(CH₃)₃], 3.76 (4H, s, NHCH₂Ar), 3.96 (4H, s, ArCH₂NH), 5.12 (4H, s, ArCH₂O), 6.92 (2H, d, J 8 ArH), 7.00 (2H, d, J 8, ArH), 7.25–7.40 (9H, m, ArH), 7.74 (1H, t, J 8, ArH). δ_C (CDCl₃, 75 MHz) 31.6, 34.1, 50.3, 54.2, 71.6, 112.2, 120.3, 121.8, 125.4, 127.9, 136.2, 137.5, 143.9, 154.7, 156.2, 157.8.

Metal complex synthesis

Cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) nitrate complexes of 1. The appropriate hydrated metal(II) nitrate (1.5 mmol) in warm methanol (2 mL) was added to a solution of **1** (1.5 mmol) in warm methanol (2 mL). The solution was then filtered and crystallisation of the metal complex was induced by diffusion of ether vapour into the reaction

Table 3 Physical properties of the complexes of **1** and **2**

Complex	Colour	$\Lambda^a/S \text{ cm}^2 \text{ mol}^{-1}$	μ^b/μ_B	Electronic spectra $\epsilon/\text{nm} (\epsilon/\text{M}^{-1} \text{ cm}^{-1})$
[Co(1)](NO ₃) ₂ ·1.5H ₂ O	Pink	155	4.83	470(sh), 490 ($\epsilon = 35$), 520(sh)
[Ni(1)](NO ₃) ₂ ·3CH ₃ OH·0.5H ₂ O	Pale blue	104	3.27	380(sh), 590 ($\epsilon = 8$), 990 ($\epsilon = 13$)
[Cu(1)](NO ₃) ₂ ·CH ₃ OH·0.5H ₂ O	Blue	158	1.80	605br ($\epsilon = 72$)
[Zn(1)](NO ₃) ₂ ·CH ₃ OH·1.5H ₂ O	Colourless	102		
[Cd(1)](NO ₃) ₂ ·0.5Cd(NO ₃) ₄	Colourless	191		
[Ag ₃ (1) ₂](NO ₃) ₃ ·2C ₂ H ₅ OH	Colourless	^d		
[Cu(2)](ClO ₄) ₂	Blue	156	1.77	607br ($\epsilon = 97$)
[Cu(2)](NO ₃) ₂	Blue	144	1.99	603br ($\epsilon = 101$)
[Zn(2)](NO ₃) ₂ ·2.5H ₂ O	Colourless	114		
[Cd(2)](NO ₃) ₂	Colourless	159		

^a Conductance at 25 °C in methanol; expected range for a 1 : 1 electrolyte in methanol is 80–115 S cm² mol⁻¹ while that for a 2 : 1 electrolyte is 160–220 S cm² mol⁻¹ (see ref. 21). ^b Magnetic moment at 25 °C. ^c In methanol. ^d Precipitation.

solution. The product was removed by filtration and dried under vacuum over phosphorus pentoxide. Yields 50–65%. Crystals suitable for X-ray crystallography were grown by slow diffusion of ether into a methanol solution of the respective complexes.

[Co(**1**)](NO₃)₂·1.5H₂O. [Found (CoL–H)⁺, m/z 476.1 (ES). C₂₅H₂₉CoN₄O₂ requires 476.2]. (Found: C, 47.9; H, 5.3; N, 13.3. Calc. for C₂₅H₃₀CoN₄O₈·1.5H₂O: C, 47.78; H, 5.29; N, 13.37%).

[Ni(**1**)](NO₃)₂(CH₃OH)₂·NO₃·CH₃OH·0.5H₂O. [Found (NiL)²⁺, m/z 238.1 (ES). C₂₅H₃₀N₄NiO₂ requires 238.1]. (Found: C, 47.7; H, 5.9; N, 12.1. Calc. for C₂₈H₄₂N₆NiO₁₁·0.5H₂O: C, 47.61; H, 6.14; N, 11.90%).

[Cu(**1**)](NO₃)₂·CH₃OH·0.5H₂O. [Found (CuLNO₃)⁺, m/z 543.0 (ES). C₂₅H₃₀CuN₅O₅ requires 543.2]. (Found: C, 48.1; H, 5.2; N, 13.2. Calc. for C₂₆H₃₄CuN₆O₉·0.5H₂O: C, 48.26; H, 5.45; N, 13.99%).

[Zn(**1**)](NO₃)₂·CH₃OH·1.5H₂O. [Found (ZnL–H)⁺, m/z 481.1 (ES). C₂₅H₂₉N₄O₂Zn requires 481.2]. (Found: C, 46.6; H, 5.4; N, 12.8. Calc. for C₂₆H₃₄N₆O₉Zn·1.5H₂O: C, 46.82; H, 5.59; N, 12.60%).

[Cd(**1**)](NO₃)₂·0.5Cd(NO₃)₄. [Found (CdL–H)⁺, m/z 531.2 (ES). C₂₅H₂₉CdN₄O₂ requires 531.1]. (Found: C, 38.7; H, 4.1; N, 12.6. Calc. for C₂₅H₃₀CdN₅O₅·0.5Cd(NO₃)₄: C, 38.84; H, 3.91; N, 12.68%).

[AgNO₃(**1**)Ag(**1**)AgNO₃](NO₃)₂·2C₂H₅OH. Silver(I) nitrate (1.5 mmol) in ethanol (6 mL) was added to a solution of **1** (1.5 mmol) in ethanol (2 mL). The solution was then filtered and crystallisation of the metal complex occurred on the diffusion of ether vapour into the solution. The product was removed by filtration and dried under vacuum over phosphorus pentoxide. Yield, 0.11 g, 15%. [Found (AgL)⁺, m/z 525.3 (ES). C₂₅H₃₀AgN₄O₂ requires 525.1]. (Found: C, 44.9; H, 4.9; N, 10.7. Calc. for C₅₀H₆₀Ag₃N₁₁O₁₁·2C₂H₅OH: C, 45.08; H, 5.04; N, 10.68%). Crystals suitable for X-ray crystallography were grown by slow diffusion of ether into an ethanol solution of the above complex.

[Cu(**2**)](ClO₄)₂. A mixture of **2** (0.086 g, 0.162 mmol) and Cu(ClO₄)₂·6H₂O (0.060 g, 0.162 mmol) was dissolved in hot methanol (≈5 mL) and the solution was stirred at ≈60 °C for ≈10 min, filtered, and then allowed to cool. Slow evaporation of the solution yielded a blue crystalline product (0.043 g, 33%) that was removed by filtration, washed with cold methanol (≈2 mL), and dried under vacuum over phosphorus pentoxide. Yield, 0.043 g, 33%. [Found (CuLClO₄)⁺, m/z 692.1 (ES). C₃₃H₄₆ClCuN₄O₆ requires 692.3]. (Found: C, 49.8; H, 5.9; N, 6.9. Calc. for C₃₃H₄₆Cl₂CuN₄O₁₀: C, 49.97; H, 5.85; N, 7.06%). Crystals suitable for X-ray crystallography were isolated and the structure was solved.

Copper(II), zinc(II) and cadmium(II) nitrate complexes of 2. The appropriate hydrated metal(II) nitrate (0.1 mmol) and **2** were dissolved in hot methanol (≈5 mL) and the solution was

stirred at ≈60 °C for ≈10 min. The solution was then filtered, allowed to cool, and crystallisation of the metal complex was induced by diffusion of ether vapour into the reaction solution. The product was removed by filtration and dried under vacuum over phosphorus pentoxide. Yields 55–85%.

[Cu(**2**)](NO₃)₂. [Found (CuLNO₃)⁺, m/z 655.1 (ES). C₃₃H₄₆CuN₅O₅ requires 655.3]. (Found: C, 55.3; H, 6.8; N, 11.6. C₃₃H₄₆CuN₆O₈ requires C, 55.18; H, 6.45; N, 11.70%).

[Zn(**2**)](NO₃)₂·2.5H₂O. [Found (ZnL–H)⁺, m/z 593.4 (ES). C₃₃H₄₅N₄O₂Zn requires 593.3]. (Found: C, 51.7; H, 7.0; N, 11.0. C₃₃H₄₆N₆O₈Zn·2.5H₂O requires C, 51.80; H, 6.72; N, 10.98%).

[Cd(**2**)](NO₃)₂. [Found (CdL–H)⁺, m/z 643.3 (ES). C₃₃H₄₅N₄O₂Cd requires 643.3]. (Found: C, 51.8; H, 6.2; N, 10.7. C₃₃H₄₆CdN₆O₈ requires C, 51.67; H, 6.04; N, 10.95%).

Results and discussion

Ligand synthesis

Macrocycles **1** and **2** were synthesised *via* Schiff-base condensation between 2,6-bis(2-formylphenoxy)methylpyridine or the corresponding di-*tert*-butyl substituted derivative and diethylenetriamine, followed by reduction of the product *in situ* with sodium borohydride. In this context it is noted that attempts to use linear polyamines in such Schiff-base condensations have been shown in some cases to result in a secondary amine reacting in concert with one primary amine and an aldehyde group to yield a 1,3-diazapentane derivative.¹⁹ Nevertheless, reduction of such a product results in generation of the required linear amine backbone incorporating only secondary amine groups.²⁰ Macrocycle **3** was obtained by a related procedure to that employed for **2** except that 2,6-bis(amino-methyl)pyridine was substituted for diethylenetriamine in the initial Schiff-base condensation step.

From mass spectral and NMR evidence, a small yield of the analogous (large ring) 2 : 2 macrocycle was also observed to be formed during the synthesis of **1**. Initially, this larger-ring product proved somewhat difficult to remove; however, success was obtained *via* a selective Soxhlet extraction of the mixed hydrochloride salts using refluxing ethanol.

Metal complexes

In an attempt to obtain crystalline products suitable for X-ray diffraction studies, a range of solid metal complexes of both **1** and **2** were isolated and characterised (Table 3). In each case the synthetic procedure involved the interaction of the ligand with the required metal(II) salt in hot methanol or ethanol. Crystals suitable for X-ray structural analysis were obtained in the case of the cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and silver(I) complexes (all nitrates) with ligand **1**; each of these was grown by slow diffusion of ether vapour into a methanol or ethanol solution of the corresponding complex.

With the exception of the cadmium(II) and silver(I) complexes **1** (see later), all of the remaining solid complexes of **1**

Table 4 Ligand protonation constants and metal stability constants for **1–7**^a

Ligand	Log K_H			Log K_{ML}^b						
	Log K_1	log K_2	log K_3	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺	Ag ⁺	Pb ²⁺
1	9.86	8.58	—	9.2	≈10	>14	9.4	9.5	>13	9.8
2	9.98	8.76	—	9.1	—	>14	9.7	9.7	>13	9.7
3	9.60	7.94	—	9.4	^c	>14	9.5	9.8	>13	≈9.3
4 ^d	9.69	8.45	≈2.0	7.7	10.0	14.2	7.5	8.7	8.7	8.1
5 ^d	9.65	8.33	—	7.4	^c	14.0	7.5	8.8	8.6	7.9
6 ^e	9.08	6.17	2.5	4.5	6.7	13.9	5.9	8.7	10.3 ^f	4.9 ^f
7	9.95	8.32	2.7	8.7 ^g	^c	≈16 ^g	≈9.3 ^h	8.9 ^h	8.1 ^h	9.6 ^h

^a In 95% methanol; $I = 0.1$, (C₂H₅)₄NClO₄, 25 °C; uncertainties in parentheses. ^b Each value is the mean of two or three separate determinations at different metal : ligand ratios rounded to the first decimal place. ^c Precipitation and/or competing hydrolysis inhibited log K determination in this case. ^d From ref. 23. ^e From ref. 24. ^f This study. ^g From ref. 25. ^h From ref. 26.

and **2** were shown to have a 1 : 1 (metal : macrocycle) stoichiometry by microanalysis.

The conductance values in methanol (Table 3) for the complexes of cobalt(II), copper(II) and cadmium(II) approximate those expected for 2 : 1 electrolytes. Thus the first two complexes have both nitrates essentially ionised under the conditions employed; however, the situation for the cadmium complex is not as straightforward owing to the presence of a [Cd(NO₃)₄]²⁻ ion for each two complex cations in the solid state. In contrast, the values for the nickel(II) and zinc(II) complexes indicate that they behave as 1 : 1 electrolytes, consistent with one nitrate ion remaining coordinated in these species.²¹

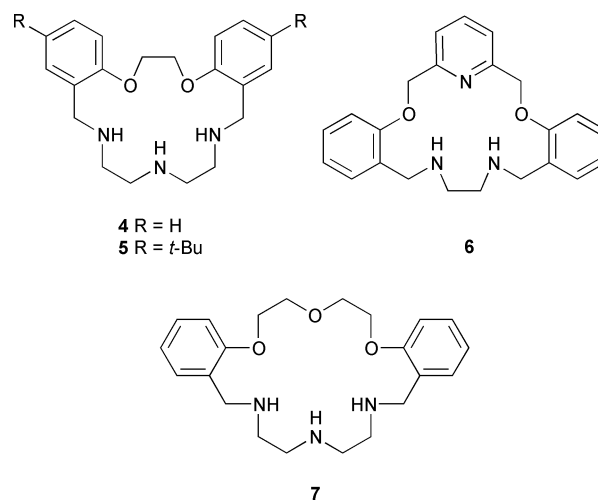
The magnetic moments (Table 3) of the pink cobalt complex and the blue nickel complex of **1** confirms their high spin nature. The visible spectra in methanol are consistent with both complexes having pseudo-octahedral coordination geometries.²²

The magnetic moments (Table 3) of the blue copper complexes [Cu(**1**)](NO₃)₂·CH₃OH·0.5H₂O, [Cu(**2**)](ClO₄)₂ and [Cu(**2**)](NO₃)₂ all fall in the normal range for a copper(II) species with $S = 1/2$; the visible spectra (methanol) in each case show broad featureless absorbances that are of little value for the assignment of the coordination geometries. The EPR spectrum of the above copper(II) complexes at ambient temperature yielded 'normal' g values of 2.05, 2.05 and 2.06 respectively. A spectrophotometric titration involving the incremental addition of **2** to a solution of copper(II) nitrate in dimethylsulfoxide gave a clear 1 : 1 endpoint when monitored at 650 nm. There was no evidence for additional endpoints up to a ligand : metal molar ratio of 3 : 1.

Stability constants

The protonation constants for the respective macrocycles were obtained by potentiometric (pH) titration in 95% methanol ($I = 0.1$, NEt₄ClO₄) and are listed in Table 4. As in previous studies, this solvent was employed to overcome the generally restricted solubility of ligands of the present type (and/or their metal complexes) in water. Log K values corresponding to the formation of 1 : 1 (metal : ligand) species were obtained in each case by analysis of the initial portions of the respective titration curves. The log K data are summarised in Table 4 and, for comparison, stability data for the mixed-donor systems **4**,²³ **5**,²³ **6**,²⁴ and **7**^{25,26} are also included.

The following observations may be made concerning the relative stabilities of the complexes of **1–7** (Table 4). First, for **1**, **4** and **6**, the Irving–Williams stability order²⁷ of cobalt(II) < nickel(II) < copper(II) > zinc(II) is seen to apply and, despite the absence of log K values for the nickel complexes of the other remaining ligands in the series, it seems likely that this order will hold across all systems listed in Table 4. Second, comparison of the values for **1** with its di-*tert*-butyl derivative **2** confirms that substitution of *tert*-butyl groups on the periphery of the ring has little effect on the respective log K values (a result that



parallels the behaviour of **4** relative to its similarly substituted derivative **5**). Third, the presence of an additional secondary amine in **1** and **2** relative to **6**, leads to a substantial increase in the respective log K values for most complexes in the series. Fourth, the addition of a pyridinyl nitrogen donor in the ring system between the oxygen donors of **4** or **5** to yield **1** or **2** in the main leads to a smaller increase in the respective log K values for **1** and **2**; an exception is the silver(I) complex where the increase is greater than five log units for each of the latter ligands. Fifth, substitution of a pyridinyl group for the 'centre' aliphatic –NH– of **1** to yield **3**, leads to only a marginal change in the corresponding log K values for the complexes of **3**. Finally, substitution of the pyridinyl group in **1** by an 'aliphatic' ether oxygen group to give the corresponding N₃O₃-donor analogue **7** also results in only a minor decrease in each of the corresponding metal complex stabilities — with an exception being for the complexation of silver(I). In this latter case a decrease of greater than 5.9 log units is observed.

From the above discussion, it is clear that the incorporation of a O–N(pyridinyl)–O donor fragment in ligands of the present type in most cases results in only minor variations in the respective log K values for each of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and lead(II) while it very significantly enhances selectivity towards silver(I) relative to these ions.

X-Ray structures

Crystal structures have been determined for the complexes of **1** with zinc(II), cobalt(II), nickel(II), copper(II), cadmium(II) and silver(I) (see Tables 1 and 2). Coordination sphere bond lengths and angles for the complexes of [Zn(**1**)(NO₃)₂]·CH₃OH·0.8C₂H₅OC₂H₅, [Co(**1**)(NO₃)(CH₃OH)₂]NO₃·CH₃OH, [Ni(**1**)(NO₃)(CH₃OH)₂]NO₃·0.8CH₃OH·0.2H₂O, [Cu(**1**)](NO₃)₂·CH₃OH, [Cd(**1**)(NO₃)]·0.5Cd(NO₃)₄ and [AgNO₃(**1**)Ag(**1**)–

Table 5 Coordination sphere bond lengths (Å) for [Zn(1)(NO₃)₂·CH₃OH·0.8C₂H₅OC₂H₅], [Co(1)(NO₃)(CH₃OH)₂]NO₃·CH₃OH and [Ni(1)(NO₃)(CH₃OH)₂]NO₃·0.8CH₃OH·0.2H₂O

[Zn(1)(NO ₃) ₂ ·CH ₃ OH·0.8C ₂ H ₅ OC ₂ H ₅]			
Zn(1)–O(3)	2.284(2)	Zn(1)–N(1)	2.117(2)
Zn(1)–O(4)	2.288(2)	Zn(1)–N(2)	2.133(2)
Zn(1)–O(6)	2.059(2)	Zn(1)–N(3)	2.103(2)
[Co(1)(NO ₃)(CH ₃ OH) ₂]NO ₃ ·CH ₃ OH			
Co(1)–O(3)	2.0941(12)	Co(1)–N(1)	2.1985(13)
Co(1)–O(4)	2.1103(12)	Co(1)–N(2)	2.1306(14)
Co(1)–O(5)	2.1828(12)	Co(1)–N(3)	2.1418(13)
[Ni(1)(NO ₃)(CH ₃ OH) ₂]NO ₃ ·0.8CH ₃ OH·0.2H ₂ O			
Ni(1)–O(3)	2.0940(11)	Ni(1)–N(1)	2.1578(12)
Ni(1)–O(4)	2.0787(10)	Ni(1)–N(2)	2.0730(12)
Ni(1)–O(5)	2.1427(11)	Ni(1)–N(3)	2.0983(13)

Table 6 Coordination sphere bond lengths (Å) for [Cu(1)(NO₃)₂·CH₃OH], [Cd(1)(NO₃)₂·0.5Cd(NO₃)₄] and [AgNO₃(1)Ag(1)AgNO₃]NO₃·H₂O

[Cu(1)(NO ₃) ₂ ·CH ₃ OH]			
Cu(1)–O(1)	2.3480(13)	Cu(1)–N(2)	1.9898(15)
Cu(1)–O(2)	2.3252(13)	Cu(1)–N(3)	2.0368(16)
Cu(1)–N(1)	2.0531(15)	Cu(1)–N(4)	2.0584(15)
[Cd(1)(NO ₃) ₂ ·0.5Cd(NO ₃) ₄]			
Cd(1)–O(1)	2.5208(13)	Cd(1)–N(1)	2.3875(16)
Cd(1)–O(2)	2.4472(13)	Cd(1)–N(2)	2.3710(15)
Cd(1)–O(3)	2.5026(14)	Cd(1)–N(3)	2.4413(16)
Cd(1)–O(4)	2.6851(14)	Cd(1)–N(4)	2.4043(14)
[AgNO ₃ (1)Ag(1)AgNO ₃]NO ₃ ·H ₂ O			
Molecule A		Molecule B	
Ag(1)–O(1)	2.716(3)	Ag(3)–O(6)	2.690(3)
Ag(1)–O(3)	2.544(3)	Ag(3)–O(8)	2.703(4)
Ag(1)–N(1)	2.417(3)	Ag(3)–N(6)	2.364(3)
Ag(1)–N(2)	2.340(3)	Ag(3)–N(7)	2.340(4)
Ag(1)–N(4)	2.254(3)	Ag(3)–N(9)	2.237(3)
Ag(2)–N(3)	2.170(3)	Ag(4)–N(8)	2.188(3)

Table 7 Coordination sphere bond angles (°) for [Zn(1)(NO₃)₂·CH₃OH·0.8C₂H₅OC₂H₅], [Co(1)(NO₃)(CH₃OH)₂]NO₃·CH₃OH and [Ni(1)(NO₃)(CH₃OH)₂]NO₃·0.8CH₃OH·0.2H₂O

[Zn(1)(NO ₃) ₂ ·CH ₃ OH·0.8C ₂ H ₅ OC ₂ H ₅]			
O(6)–Zn(1)–O(3)	80.13(9)	O(6)–Zn(1)–N(2)	166.13(9)
O(6)–Zn(1)–O(4)	82.46(9)	O(6)–Zn(1)–N(3)	107.73(9)
N(3)–Zn(1)–N(1)	110.01(8)	N(1)–Zn(1)–O(3)	100.85(7)
N(1)–Zn(1)–N(2)	83.08(8)	N(2)–Zn(1)–O(3)	86.01(8)
N(3)–Zn(1)–N(2)	84.13(8)	N(3)–Zn(1)–O(3)	146.09(7)
O(6)–Zn(1)–N(1)	99.01(9)		
[Co(1)(NO ₃)(CH ₃ OH) ₂]NO ₃ ·CH ₃ OH			
O(3)–Co(1)–O(4)	92.16(5)	O(5)–Co(1)–N(1)	86.07(4)
O(3)–Co(1)–O(5)	81.23(4)	O(3)–Co(1)–N(2)	94.07(5)
O(4)–Co(1)–O(5)	90.05(4)	O(4)–Co(1)–N(2)	173.46(5)
N(2)–Co(1)–N(1)	81.06(5)	O(3)–Co(1)–N(3)	89.31(5)
N(3)–Co(1)–N(1)	102.78(5)	O(4)–Co(1)–N(3)	95.51(5)
N(2)–Co(1)–N(3)	82.63(5)	N(2)–Co(1)–O(5)	92.82(4)
O(3)–Co(1)–N(1)	166.18(5)	N(3)–Co(1)–O(5)	169.21(5)
O(4)–Co(1)–N(1)	93.29(5)		
[Ni(1)(NO ₃)(CH ₃ OH) ₂]NO ₃ ·0.8CH ₃ OH·0.2H ₂ O			
O(4)–Ni(1)–O(3)	90.64(4)	O(5)–Ni(1)–N(1)	87.46(4)
O(4)–Ni(1)–O(5)	91.55(4)	O(4)–Ni(1)–N(3)	93.86(4)
O(3)–Ni(1)–O(5)	81.14(4)	O(3)–Ni(1)–N(3)	89.04(5)
N(3)–Ni(1)–N(1)	101.94(5)	N(2)–Ni(1)–O(4)	175.16(4)
N(2)–Ni(1)–N(1)	82.69(5)	N(2)–Ni(1)–O(3)	93.87(5)
N(2)–Ni(1)–N(3)	84.49(5)	N(2)–Ni(1)–O(5)	90.86(4)
O(4)–Ni(1)–N(1)	93.23(4)	N(3)–Ni(1)–O(5)	168.85(5)
O(3)–Ni(1)–N(1)	168.06(5)		

Table 8 Coordination sphere bond angles (°) for [Cu(1)(NO₃)₂·CH₃OH], [Cd(1)(NO₃)₂·0.5Cd(NO₃)₄] and [AgNO₃(1)Ag(1)AgNO₃]NO₃·H₂O

[Cu(1)(NO ₃) ₂ ·CH ₃ OH]			
O(2)–Cu(1)–O(1)	150.22(4)	N(3)–Cu(1)–O(2)	102.20(5)
N(2)–Cu(1)–N(3)	84.95(6)	N(1)–Cu(1)–O(2)	87.59(5)
N(2)–Cu(1)–N(1)	84.51(6)	N(4)–Cu(1)–O(2)	76.90(5)
N(3)–Cu(1)–N(1)	166.85(6)	N(2)–Cu(1)–O(1)	107.05(6)
N(2)–Cu(1)–N(4)	177.07(6)	N(3)–Cu(1)–O(1)	89.05(5)
N(3)–Cu(1)–N(4)	97.72(6)	N(1)–Cu(1)–O(1)	86.54(5)
N(1)–Cu(1)–N(4)	93.01(6)	N(4)–Cu(1)–O(1)	74.30(5)
N(2)–Cu(1)–O(2)	101.39(6)		
[Cd(1)(NO ₃) ₂ ·0.5Cd(NO ₃) ₄]			
O(1)–Cd(1)–O(4)	112.87(5)	N(4)–Cd(1)–O(2)	65.99(5)
O(2)–Cd(1)–O(1)	129.86(4)	N(3)–Cd(1)–O(2)	75.21(5)
O(3)–Cd(1)–O(1)	149.60(5)	N(2)–Cd(1)–O(3)	81.37(5)
O(2)–Cd(1)–O(3)	71.96(5)	N(1)–Cd(1)–O(3)	75.54(5)
O(2)–Cd(1)–O(4)	69.39(4)	N(4)–Cd(1)–O(3)	121.98(5)
O(3)–Cd(1)–O(4)	49.25(4)	N(3)–Cd(1)–O(3)	116.99(5)
N(2)–Cd(1)–N(1)	74.68(6)	N(2)–Cd(1)–O(1)	97.75(5)
N(2)–Cd(1)–N(4)	155.84(5)	N(1)–Cd(1)–O(1)	74.96(5)
N(1)–Cd(1)–N(4)	114.71(5)	N(4)–Cd(1)–O(1)	65.69(4)
N(2)–Cd(1)–N(3)	73.34(5)	N(3)–Cd(1)–O(1)	91.34(5)
N(1)–Cd(1)–N(3)	142.97(5)	N(2)–Cd(1)–O(4)	124.96(5)
N(4)–Cd(1)–N(3)	88.95(5)	N(1)–Cd(1)–O(4)	71.08(5)
N(2)–Cd(1)–O(2)	122.51(5)	N(4)–Cd(1)–O(4)	78.88(4)
N(1)–Cd(1)–O(2)	139.39(5)	N(3)–Cd(1)–O(4)	144.54(5)
[AgNO ₃ (1)Ag(1)AgNO ₃]NO ₃ ·H ₂ O			
Molecule A		Molecule B	
O(3)–Ag(1)–O(1)	147.13(10)	O(6)–Ag(3)–O(8)	150.79(11)
N(4)–Ag(1)–N(2)	130.60(11)	N(9)–Ag(3)–N(7)	132.51(12)
N(4)–Ag(1)–N(1)	135.07(11)	N(9)–Ag(3)–N(6)	134.26(13)
N(2)–Ag(1)–N(1)	78.64(10)	N(7)–Ag(3)–N(6)	80.73(12)
N(4)–Ag(1)–O(3)	108.78(12)	N(9)–Ag(3)–O(6)	70.09(12)
N(2)–Ag(1)–O(3)	105.22(12)	N(7)–Ag(3)–O(6)	100.39(11)
N(1)–Ag(1)–O(3)	89.73(11)	N(6)–Ag(3)–O(6)	73.93(10)
N(4)–Ag(1)–O(1)	70.02(10)	N(9)–Ag(3)–O(8)	115.35(15)
N(2)–Ag(1)–O(1)	98.38(10)	N(7)–Ag(3)–O(8)	95.49(13)
N(1)–Ag(1)–O(1)	72.68(9)	N(6)–Ag(3)–O(8)	84.74(12)

Table 9 Metal to ligand CSD^a bond distance data^b

	Mean	Min.	Max.	N _{obs}
Zn–O(nitrate)	2.210	1.938	2.400	29
Zn–N(amine)	2.143	2.052	2.513	188
Co–O(nitrate)	2.149	1.890	2.310	34
Co–O(methanol)	2.127	2.059	2.264	46
Co–N(amine)	1.980	1.818	2.354	1678
Ni–O(nitrate)	2.137	1.991	2.321	66
Ni–O(methanol)	2.117	2.049	2.235	60
Ni–N(amine)	2.093	1.850	2.355	1020
Cu–O(ether)	2.415	2.009	2.832	117
Cu–N(pyridine)	2.061	1.860	2.842	1492
Cu–N(amine)	2.051	1.888	2.597	501
Cd ⁸ –O(ether)	2.562	2.336	2.896	66
Cd ⁸ –O(nitrate)	2.488	2.266	2.816	24
Cd ⁸ –N(pyridine)	2.460	2.332	2.745	110
Cd ⁸ –N(amine)	2.462	2.258	2.575	8
Ag ⁵ –O(nitrate)	2.575	2.329	2.861	22
Ag ⁵ –O(ether)	2.547	2.203	2.883	48
Ag ⁵ –N(pyridine)	2.374	2.143	2.757	87
Ag ⁵ –N(amine)	2.463	2.353	2.557	10
Ag ² –N(amine) ^c	2.166	2.081	2.356	22

^a See ref. 14. ^b Metal coordination number is six unless otherwise indicated by a superscript. At least one representative ligand was present in each complex included in the search. ^c There were no two-coordinate Ag(I) complexes with a secondary amine ligand listed on the October 2001 release of the CSD. A general amine search was accordingly undertaken.

AgNO₃]NO₃·H₂O are provided in Tables 5–8, and a summary of comparable coordination sphere bond lengths taken from the CSD¹⁴ is provided in Table 9. The coordination sphere bond lengths of the complexes of **1** are in each case unremark-

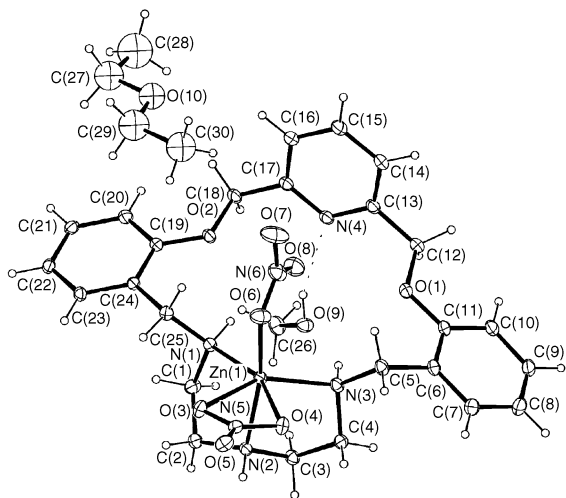


Fig. 1 ORTEP depiction of $[\text{Zn}(\mathbf{1})(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH} \cdot 0.8\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$, with 20% atomic displacement ellipsoids. The populations of the isotropically modelled diethyl ether solvate molecule were initially refined and then fixed at 0.8.

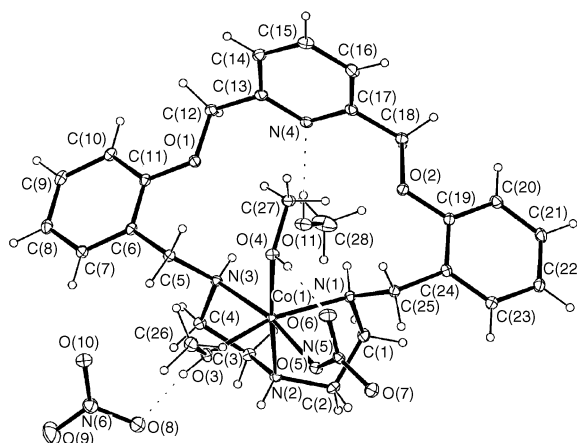


Fig. 2 ORTEP depiction of $[\text{Co}(\mathbf{1})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3 \cdot \text{CH}_3\text{OH}$, with 20% atomic displacement ellipsoids and dotted lines illustrating hydrogen bonds. $[\text{Ni}(\mathbf{1})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3 \cdot 0.8\text{CH}_3\text{OH} \cdot 0.2\text{H}_2\text{O}$ is essentially isostructural and has the same numbering scheme.

able. ORTEP²⁸ depictions of the molecules showing the numbering schemes are provided in Figs. 1 to 5. The copper(II), cadmium(II) and silver(I) ions, coordinate to **1** *via* all of its donor sites. In contrast, this macrocycle only coordinates to cobalt(II), nickel(II) and zinc(II) *via* its secondary amine sites.

In addition to the secondary amines of **1**, two nitrate ions coordinate to the zinc atom in $[\text{Zn}(\mathbf{1})(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH} \cdot 0.8\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ to complete a distorted pseudo-octahedral coordination geometry (Fig. 1 and Tables 5 and 7). One of the nitrate ions coordinates in a bidentate fashion in the equatorial plane, while the other is monodentate and occupies an axial position. Two methanol molecules replace the bidentate nitrate ligand in the above structure in the case of $[\text{Co}(\mathbf{1})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3 \cdot \text{CH}_3\text{OH}$ and $[\text{Ni}(\mathbf{1})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3 \cdot 0.8\text{CH}_3\text{OH} \cdot 0.2\text{H}_2\text{O}$; in these essentially isostructural complexes the coordination geometry is more conventional (see Fig. 2, and Tables 5 and 7). In all three structures the three secondary amine coordination sites of the macrocycle define the vertices of one face of a distorted octahedral coordination sphere, and the macrocyclic ring pyridine is free to form a hydrogen bond with a methanol solvate molecule (Table 10). In $[\text{Co}(\mathbf{1})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3 \cdot \text{CH}_3\text{OH}$ and $[\text{Ni}(\mathbf{1})(\text{NO}_3)(\text{CH}_3\text{OH})_2]\text{NO}_3 \cdot 0.8\text{CH}_3\text{OH} \cdot 0.2\text{H}_2\text{O}$ there are also hydrogen bond interactions between the two metal-coordinated methanol molecules and the two nitrate

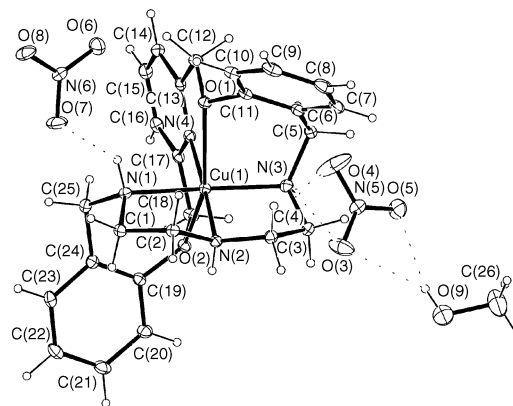


Fig. 3 ORTEP depiction of $[\text{Cu}(\mathbf{1})(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH}$, with 20% atomic displacement ellipsoids.

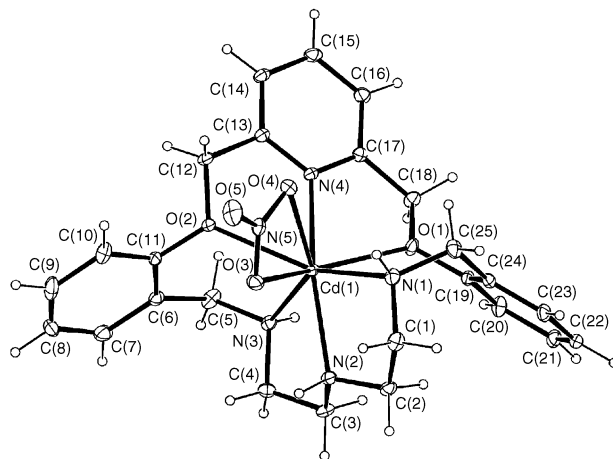


Fig. 4 ORTEP depiction of $[\text{Cd}(\mathbf{1})(\text{NO}_3)_2] \cdot 0.5\text{Cd}(\text{NO}_3)_4$, with 20% atomic displacement ellipsoids. A $[\text{Cd}(\text{NO}_3)_4]^{2-}$ anion residing on a two-fold axis provides a counterion for the macrocyclic complex.

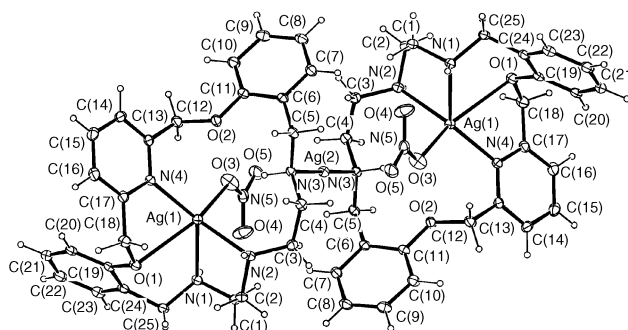


Fig. 5 ORTEP depictions, with 20% atomic displacement ellipsoids, of the two crystallographically independent molecules in the crystal structure of $[\text{AgNO}_3(\mathbf{1})\text{Ag}(\mathbf{1})\text{AgNO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$. The bridging silver ions are located on inversion centres.

counterions. The crystal structure of the $[\text{Zn}(\mathbf{1})(\text{NO}_3)_2] \cdot \text{CH}_3\text{OH} \cdot 0.8\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ also includes a diethyl ether molecule that is not coordinated.

Table 10 Hydrogen bond geometries for the [Zn(1)(NO₃)₂] \cdot CH₃OH \cdot 0.8C₂H₅OC₂H₅, [Co(1)(NO₃)(CH₃OH)₂]₂NO₃ \cdot CH₃OH, [Ni(1)(NO₃)(CH₃OH)₂]₂NO₃ \cdot 0.8CH₃OH \cdot 0.2H₂O, [Cu(1)](NO₃)₂ \cdot CH₃OH, [Cd(1)(NO₃)]₂ \cdot 0.5Cd(NO₃)₄ and [AgNO₃(1)Ag(1)AgNO₃]₂NO₃ \cdot H₂O complexes

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA angle/°
[Zn(1)(NO ₃) ₂] \cdot CH ₃ OH \cdot 0.8C ₂ H ₅ OC ₂ H ₅						
O(9) ^m	H(9O)	N(4)	0.84	2.03	2.840(3)	161.3
[Co(1)(NO ₃)(CH ₃ OH) ₂] ₂ NO ₃ \cdot CH ₃ OH						
O(3) ^m	H(3O)	O(8) ⁿ	0.83(2)	1.84(2)	2.6638(19)	172(2)
O(3) ^m	H(3O)	O(10) ⁿ	0.83(2)	2.51(2)	3.1021(19)	129.9(18)
O(4) ^m	H(4O)	O(6) ⁿ	0.78(2)	1.95(2)	2.7000(18)	162(2)
O(11) ^m	H(11O)	N(4)	0.78(2)	2.04(2)	2.817(2)	174(2)
N(1)	H(1N)	O(2)	0.862(19)	2.390(19)	2.9922(18)	127.3(15)
N(1)	H(1N)	O(11) ^m	0.862(19)	2.412(19)	3.128(2)	140.8(16)
N(2)	H(2N)	O(5) ⁿ	0.815(19)	2.465(19)	3.1401(17)	140.9(16)
N(2)	H(2N)	O(7) ⁿ	0.815(19)	2.626(18)	3.2122(19)	130.2(15)
N(3)	H(3N)	O(11) ^m	0.814(19)	2.388(19)	3.138(2)	153.5(16)
N(3)	H(3N)	O(1)	0.814(19)	2.586(18)	3.0831(17)	120.9(15)
[Ni(1)(NO ₃)(CH ₃ OH) ₂] ₂ NO ₃ \cdot 0.8CH ₃ OH \cdot 0.2H ₂ O						
O(3) ^m	H(3O)	O(8) ⁿ	0.84	1.84	2.6695(19)	171.0
O(3) ^m	H(3O)	O(10) ⁿ	0.84	2.49	3.0871(18)	128.5
O(4) ^m	H(4O)	O(6) ⁿ	0.84	1.89	2.6865(16)	157.0
O(11) ^m	H(11O)	N(4)	0.84	1.98	2.8180(18)	174.8
N(1)	H(1N)	O(2)	0.87(2)	2.418(19)	3.0044(16)	125.3(15)
N(1)	H(1N)	O(11) ^m	0.87(2)	2.35(2)	3.0876(18)	142.8(16)
N(2)	H(2N)	O(5) ⁿ	0.87(2)	2.40(2)	3.1305(16)	141.6(16)
N(2)	H(2N)	O(7) ⁿ	0.87(2)	2.623(19)	3.2551(18)	130.3(15)
N(3)	H(3N)	O(11) ^m	0.82(2)	2.35(2)	3.1080(18)	154.5(17)
N(3)	H(3N)	O(1)	0.82(2)	2.596(19)	3.0926(16)	120.4(15)
[Cu(1)](NO ₃) ₂ \cdot CH ₃ OH						
O(9) ^m	H(9O)	O(5) ⁿ	0.84	2.32	3.137(3)	164.9
O(9) ^m	H(9O)	O(3) ⁿ	0.84	2.35	3.042(3)	139.9
N(1)	H(1N)	O(7) ⁿ	0.91(2)	2.171(19)	2.916(2)	138.2(16)
N(2)	H(2N)	O(6) ⁿ	0.79(2)	2.13(2)	2.900(2)	166.3(19)
N(3)	H(3N)	O(4) ⁿ	0.79(2)	2.36(2)	3.066(2)	149.3(19)
N(3)	H(3N)	O(3) ⁿ	0.79(2)	2.39(2)	3.111(2)	152.3(19)
[Cd(1)(NO ₃)] ₂ \cdot 0.5Cd(NO ₃) ₄						
N(3)	H(3N)	O(6) ⁿ	0.788(19)	2.478(19)	3.219(2)	157.5(17)
N(2)	H(2N)	O(3) ⁿ	0.89(2)	2.30(2)	3.069(2)	144.2(17)
N(1)	H(1N)	O(5) ⁿ	0.87(2)	2.34(2)	3.029(2)	135.4(18)
N(1)	H(1N)	O(4) ⁿ	0.87(2)	2.40(2)	2.958(2)	121.8(17)
[AgNO ₃ (1)Ag(1)AgNO ₃] ₂ NO ₃ \cdot H ₂ O						
N(1)	H(1)	O(4) ⁿ	0.93	2.21	2.917(5)	132.0
N(3)	H(3)	O(2)	0.93	2.43	3.029(4)	121.8
N(3)	H(3)	O(3) ⁿ	0.93	2.49	3.188(4)	132.2
N(6)	H(6)	O(9) ⁿ	0.93	2.18	2.960(5)	140.4
N(8)	H(8A)	O(7)	0.93	2.43	3.009(4)	120.2
N(8)	H(8A)	O(8) ⁿ	0.93	2.63	3.283(5)	128.2

^a 1 – x, –y, –z. ^b –x, 1 – y, 2 – z. ^c x, y – 1, z. ^d –x + 1/2, –y + 1/2, –z. ^e (2) –x + 1/2, 3/2 – y, –z. ^m Methanol. ⁿ Nitrate.

In [Cu(1)](NO₃)₂ \cdot CH₃OH all of the macrocyclic donor sites of **1** are bound to the copper ion to yield a moderately distorted octahedral coordination geometry (Fig. 3). The two nitrate counter ions do not coordinate to the metal, they do however participate in hydrogen bond interactions with the secondary amine hydrogens of the macrocycle (Table 10). One of these nitrate ions also forms a hydrogen bond with a methanol solvate molecule. Crystal structure details for a perchlorate salt of a copper(II) complex of **2** have been independently deposited with the Cambridge Crystallographic Data Centre (CCDC reference number 177950) and, not surprisingly, the copper(II) complexes of **1** and **2** have very similar structures. In addition to the six donor atoms of **1**, a bidentate nitrate ion also coordinates to the cadmium in [Cd(1)(NO₃)]₂ \cdot 0.5Cd(NO₃)₄, which is accordingly eight coordinate (Fig. 4). The coordination of the nitrate group is asymmetric, with metal to oxygen distances of 2.5026(14) and 2.6851(14) Å. Charge balance for the complex is provided by a [Cd(NO₃)₄]^{2–} ion residing on a nearby two-fold axis. There are no solvate molecules in this structure.

The crystal structure of [AgNO₃(1)Ag(1)AgNO₃]₂NO₃ \cdot H₂O contains two crystallographically independent tri-nuclear silver(I) complexes (Fig. 5). The trinuclear species are comprised of two macrocyclic ligand complexes linked by a bridging silver(I) ion located on an inversion site. Each macrocycle has a silver(I) ion coordinated within the macrocycle to an ether residue, two secondary amine residues and the pyridine residue. The internally bound silver ion is also coordinated to a monodentate nitrate counterion, with a metal to oxygen distance of 2.544(3) Å in one complex and 2.703(4) Å in the second. The longer metal to nitrate bond in the second complex may be associated with a hydrogen bond interaction between the coordinated nitrate ligand and a nearby water molecule. As far as we are aware, [AgNO₃(1)Ag(1)AgNO₃]₂NO₃ \cdot H₂O provides the first crystal structure incorporating a two-coordinate Ag(I) complex involving secondary amine ligands. There are however 21 two-coordinate silver complexes with sp³ nitrogen donor ligands listed in the October 2001 CSD release.

Acknowledgements

We thank the Australian Research Council for support.

References

- 1 I. M. Atkinson, J. D. Chartres, G. W. Everett, X.-K. Ji, L. F. Lindoy, O. A. Matthews, G. V. Meehan, B. W. Skelton, G. Wei and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 1191 and refs. therein.
- 2 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, *Chem. Rev.*, 1985, **85**, 271; R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721; J. S. Bradshaw, K. R. Krakowiak and R. M. Izatt, *Aza-Crown Macrocycles*, Wiley, New York, 1993; R. M. Izatt, K. Pawlak and J. S. Bradshaw, *Chem. Rev.*, 1995, **95**, 2529.
- 3 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989.
- 4 P. Gans, A. Sabatini and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.
- 5 Bruker, SMART, SAINT and XPREP. Area detector control and data integration and reduction software, Bruker Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA, 1995.
- 6 Molecular Structure Corporation, teXsan for Windows: Single Crystal Structure Analysis Software, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1997–1998.
- 7 WinGX, L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
- 8 S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, eds., Xtal3.6 System, University of Western Australia, 1999.
- 9 P. Coppens, L. Leiserowitz and D. Rabinovich, *Acta Crystallogr.*, 1965, **18**, 1035.
- 10 G. M. Sheldrick, SADABS. Empirical absorption correction program for area detector data, University of Göttingen, Germany, 1996; R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
- 11 A. Altomare, M. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
- 12 G. M. Sheldrick, SHELX97. Programs for Crystal Structure Analysis, University of Göttingen, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- 13 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876; G. Bernardinelli and H. D. Flack, *Acta Crystallogr., Sect. A*, 1985, **41**, 500.
- 14 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31; J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Info. Comp. Sci.*, 1991, **31**, 187.
- 15 L. T. Battaglia, A. Bonamartini Corradi and A. Mangia, *Inorg. Chim. Acta*, 1980, **42**, 191.
- 16 N. A. Bailey, D. E. Fenton, S. J. Kitchen, T. H. Lilley, M. G. Williams, P. A. Tasker, A. J. Leong and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, 1991, 2989.
- 17 I. M. Atkinson, A. R. Carrol, R. J. A. Janssen, L. F. Lindoy, O. A. Matthews and G. V. Meehan, *J. Chem. Soc., Perkin Trans. 1*, 1997, 295.
- 18 B. Zhao, F. Q. Wang and L. J. Tian, *J. Heterocycl. Chem.*, 2001, **38**, 781; B. Zhao, F. Q. Wang, M. Xia and L. J. Tian, *Chin. Chem. Lett.*, 2001, **12**, 31.
- 19 R. Menif, A. E. Martell, P. J. Squattrito and A. Clearfield, *Inorg. Chem.*, 1993, **29**, 4723; M. Pietraszkiwicz and R. Gasiorowski, *Chem. Ber.*, 1990, **123**, 405.
- 20 S. Tamburini, P. A. Vigato, D. Chiarello and P. Traldi, *Inorg. Chim. Acta*, 1989, **156**, 271.
- 21 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
- 22 F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, *Advanced Inorganic Chemistry*, 6th edn., Wiley, New York, 1999.
- 23 J.-H. Kim, A. J. Leong, L. F. Lindoy, J. Kim, J. Nachbaur, A. Nezhadali, G. Rounaghi and G. Wei, *J. Chem. Soc., Dalton Trans.*, 2000, 3453 and refs. therein.
- 24 N. A. Bailey, D. E. Fenton, S. J. Kitchen, T. H. Lilley, M. G. Williams, P. A. Tasker, A. J. Leong and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, 1991, 627; H. Adams, N. A. Bailey, D. E. Fenton, I. G. Ford, S. J. Kitchen, M. G. Williams, P. A. Tasker, A. J. Leong and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, 1991, 1665; N. A. Bailey, D. E. Fenton, S. J. Kitchen, T. H. Lilley, M. G. Williams, P. A. Tasker, A. J. Leong and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, 1991, 2989.
- 25 C. A. Davis, P. A. Duckworth, A. J. Leong, L. F. Lindoy, A. Bashall and M. McPartlin, *Inorg. Chim. Acta*, 1998, **273**, 372.
- 26 C. A. Davis, A. J. Leong, L. F. Lindoy, J. Kim and S. S. Lee, *Aust. J. Chem.*, 1998, **51**, 189.
- 27 H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3194.
- 28 C. K. Johnson, ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.