

## Metal Ion Recognition. Interaction of New Oxygen-Nitrogen Donor Macrocycles with Selected Transition and Post-Transition Metal Ions\*

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### Abstract

As part of an ongoing investigation of the factors influencing metal ion recognition, we have investigated structure/function relationships involving the metal-ion binding by three new *N*-benzyl-substituted, 15- and 16-membered, macrocyclic ligands incorporating N<sub>2</sub>O<sub>3</sub>- and N<sub>3</sub>O<sub>3</sub>-donor sets (with the N<sub>3</sub>O<sub>3</sub>-system consisting of a N<sub>2</sub>O<sub>3</sub>-macrocyclic ring with an attached CH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> pendant arm). Selected solid complexes of the latter ligand were isolated and the X-ray structures of individual Ni(II) and Ag(I) complexes were obtained.

Where solubility permitted, potentiometric titration studies in 95% methanol were employed to investigate the binding affinities of all three ligand derivatives towards Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II). The 15-membered N<sub>2</sub>O<sub>3</sub>-ring was found to be selective for Ag(I) over the other six metals investigated, including Cu(II). However, the presence of a further nitrogen donor in the form of the pendant benzylamine functionality in the N<sub>3</sub>O<sub>3</sub>-donor system results in an increase in its binding affinity for Ag(I) but an even greater increase occurs for Cu(II). As a consequence, the latter ion is now more strongly bound than Ag(I). The factors influencing these respective selectivities are discussed.

### Introduction

For some time now the research of our group has been concerned with an investigation of the factors influencing metal-ion recognition by mixed donor macrocyclic ligands [1]. Our studies have focused on the complexation behaviour of the industrially important ions: Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ag(I) and Pb(II). For a number of systems significant metal-ion recognition has been achieved, with such studies having implications for a number of areas that include the development of new reagents for the sensing and separation of metal ions.

We now report the results of an investigation of structure/function relationships underlying metal-ion binding by the new mixed (oxygen-nitrogen) donor systems 1–3 (Figure 1). In our prior studies mixed donor systems of this type have proved to be especially suitable for investigation of metal-ion recognition in solution since they tend not to exhibit the very high thermodynamic and kinetic stabilities that are often characteristic of all-nitrogen donor macrocyclic ligand complexes [2]. As a consequence of high thermodynamic and kinetic stabilities, solution measurements have often been found to be less than a straight forward.

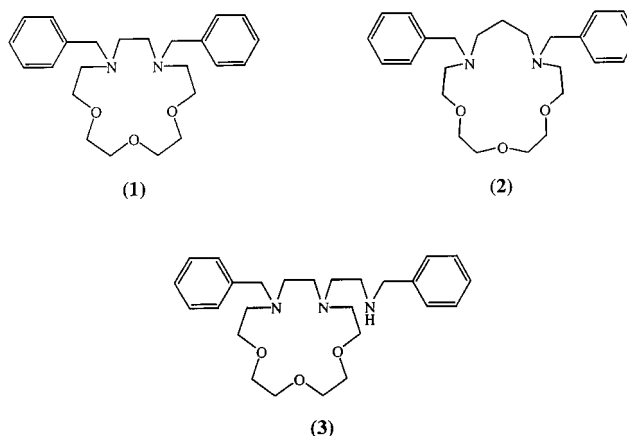


Figure 1. Structures of macrocycles used in this study.

While the variation of ring size in crown and azacrown macrocycles sometimes allows preferential binding of selected metal ions, it is now well understood that such selectivity may be moderated by other factors [2]. Indeed, some or all of the following may contribute to discrimination behaviour: the number and type of donor atoms available and their positions in the ring in terms of spacing and sequence; the electronic and structural aspects associated with the ligand's backbone; the formal charge and/or the presence or absence of dipoles (permanent or induced) on the bound ligand; and

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changes in solvation of the ligand and/or metal ion on complexation. In the case of transition metal ions, crystal field effects will also influence stabilities.

It is normally expected that *N*-alkylation of a macrocycle will result in a lowering of the stability of individual complexes due to an increase in steric hindrance on complex formation [3], although such alkylation may also influence coordination behaviour in a number of other ways [4]. In this context we have been interested in investigating the effect of *N*-benzylation of mixed donor macrocycles on the relative thermodynamic stabilities of the corresponding complexes of the metal ions listed above [1, 5]. For example, in the case of one 17-membered, N<sub>3</sub>O<sub>2</sub>-donor macrocycle, tri-*N*-benzylation led to complexes of lower stability in all cases except for Ag(I) (with the value for Cu(II) not be determined because of precipitation) [1]. Overall, such behaviour amounts to the selective ‘detuning’ of the parent ring towards all the ions investigated except silver(I). While related behaviour towards silver has now also been documented on *N*-benzylation of other amine-containing macrocyclic ligands [5], it should be noted that the origins of such behaviour are not well understood, even though it has been known for some time that tertiary amine nitrogens sometimes bind more strongly to Ag(I) than do secondary amine nitrogens (the relative binding strengths can be solvent dependant) [6]. Such phenomena may also parallel previously reported observations that tetra-*N*-methylation of the N<sub>4</sub>-donors of cyclam and related open-chain derivatives [7] results in stabilisation of the monovalent state of copper relative to its divalent state.

The goal of the present research was to synthesise the *N*-benzylated derivatives **1–3** and to investigate their binding properties towards individual transition and post-transition metal ions of the type mentioned above.

## Experimental

### Materials and methods

NMR spectra were acquired on a Bruker 200 MHz spectrometer in CDCl<sub>3</sub>. UV-Vis spectra were obtained in acetonitrile on a Cary 5E spectrophotometer. A Finnigan LCQ-8 spectrometer was employed for low resolution ESMS while HRMS spectra were obtained on a VG Autospec in EI mode. The ESR spectrum was obtained on a powdered sample at ambient temperature using a Bruker EMX ESR spectrometer at 9.475 GHz (X-band). Magnetic susceptibility was measured on a Sherwood Scientific magnetic susceptibility balance (Cambridge Research Laboratories). The ligand protonation and stability constants were determined by potentiometric titration in 95% methanol (*I* = 0.1 mol dm<sup>-3</sup>; NEt<sub>4</sub>ClO<sub>4</sub>) as previously described [5]. The data were processed using a local version of MINQUAD [8] with selected data also being processed with SUPERQUAD [9]; both programs yielded near identical log *K* values in each case. All quoted log *K* values represent the mean of data from at least two (and up to five) titrations performed at different metal to ligand ratios.

The syntheses of *N,N'*-dibenzyl-1,2-ethanediamine [10], *N,N'*-dibenzyl-1,2-propanediamine [11], 1,7-dibenzyl-diethylenetriamine [12], and tetraethylene glycol ditosylate [13] have been described previously.

### Structures determinations

Full spheres of low-temperature CCD area-detector diffractometer data were measured (*T* ca 153 K; Bruker AXS instrument,  $\omega$ -scans, monochromatic Mo K $\alpha$  radiation,  $\lambda$  = 0.71073 Å) yielding *N*<sub>(total)</sub> reflections, merging to *N* unique (*R*<sub>int</sub> quoted) after empirical/multiscan absorption correction (proprietary software), *N*<sub>o</sub> (*F* > 4 $\sigma$ (*F*)) being considered ‘observed’ and used in the full matrix least squares refinement, refining anisotropic thermal parameter forms for the non-hydrogen atoms. (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> were refined for the nickel adduct and constrained at estimates for the silver. In the nickel adduct, nitrate 2 was modeled with N(2), O(23) disordered over two sets of sites of equal occupancy, component separations 0.20(1), 1.020(7) Å respectively. Conventional residuals *R*, *R*<sub>w</sub> (weights: (( $\sigma^2$ (*F*) + 0.0004*F*<sup>2</sup>)<sup>-1</sup>) on |*F*| are quoted at convergence. Computation used the Xtal 3.6 program system, [14] neutral atom complex scattering factors being employed. Pertinent results are given in the Figures 2a and 2b as well as Tables 2 and 3, *cif* depositions 167432, 167433 being made with the Cambridge Crystallographic Data Centre Crystal/refinement data.

[NiL(OH<sub>2</sub>)](NO<sub>3</sub>)<sub>2</sub> (**L = 3**). C<sub>26</sub>H<sub>41</sub>N<sub>5</sub>NiO<sub>10</sub>, *M* = 642.3. Monoclinic, space group *C*2/*c* (*C*<sub>2h</sub><sup>6</sup>, *a* = 33.507(5), *b* = 11.628(2), *c* = 15.456(2) Å,  $\beta$  = 106.107(2)°, *V* = 5785 Å<sup>3</sup>. *D*<sub>c</sub> (*Z* = 8) = 1.475 g cm<sup>-3</sup>.  $\mu_{\text{Mo}}$  = 7.4 cm<sup>-1</sup>; specimen: 0.32 × 0.26 × 0.09 mm; *T*'<sub>min,max</sub> = 0.77, 0.90. 2 $\theta$ <sub>max</sub> = 58°; *N*<sub>t</sub> = 34322, *N* = 7438 (*R*<sub>int</sub> = 0.025), *N*<sub>o</sub> = 6224. | $\Delta\rho_{\text{max}}$ | = 0.45(3) e Å<sup>-3</sup>.

[AgL](NO<sub>3</sub>) (**L = 3**). C<sub>26</sub>H<sub>39</sub>AgN<sub>4</sub>O<sub>6</sub>, *M* = 611.5. Orthorhombic, space group *Pbca* (*D*<sub>2h</sub><sup>15</sup>, No. 61), *a* = 20.072(9), *b* = 12.237(5), *c* = 21.624(9) Å, *V* = 5311 Å<sup>3</sup>. *D*<sub>c</sub> (*Z* = 8) = 1.529 g cm<sup>-3</sup>.  $\mu_{\text{Mo}}$  = 8.1 cm<sup>-1</sup>; specimen: 0.40 × 0.32 × 0.02 mm; *T*'<sub>min,max</sub> = 0.46, 0.93. 2 $\theta$ <sub>max</sub> = 50°; *N*<sub>t</sub> = 63789, *N* = 4680 (*R*<sub>int</sub> = 0.017), *N*<sub>o</sub> = 2942. | $\Delta\rho_{\text{max}}$ | = 1.72(7) e Å<sup>-3</sup>.

### Synthesis

**Macrocycle 1** Sodium hydrogen carbonate (4.3 g, 0.05 mol) and *N,N'*-dibenzyl-1,2-ethylenediamine (2.64 g, 0.01 mol) were added to tetraethylene glycol ditosylate (5.18 g, 0.01 mol) in acetonitrile (500 mL) and the solution was refluxed for two days. The reaction mixture was filtered and then concentrated by evaporation under reduced pressure to give the crude product as an oil. Any non tertiary amines were derivatised by the addition of acetyl chloride (5 mL) in chloroform (20 mL) and then stirring the solution for 2 hours. The product was then extracted into dilute hydrochloric acid (50 mL) and the acid solution was washed with chloroform (2 × 50 mL). The pH of the aqueous phase was adjusted to

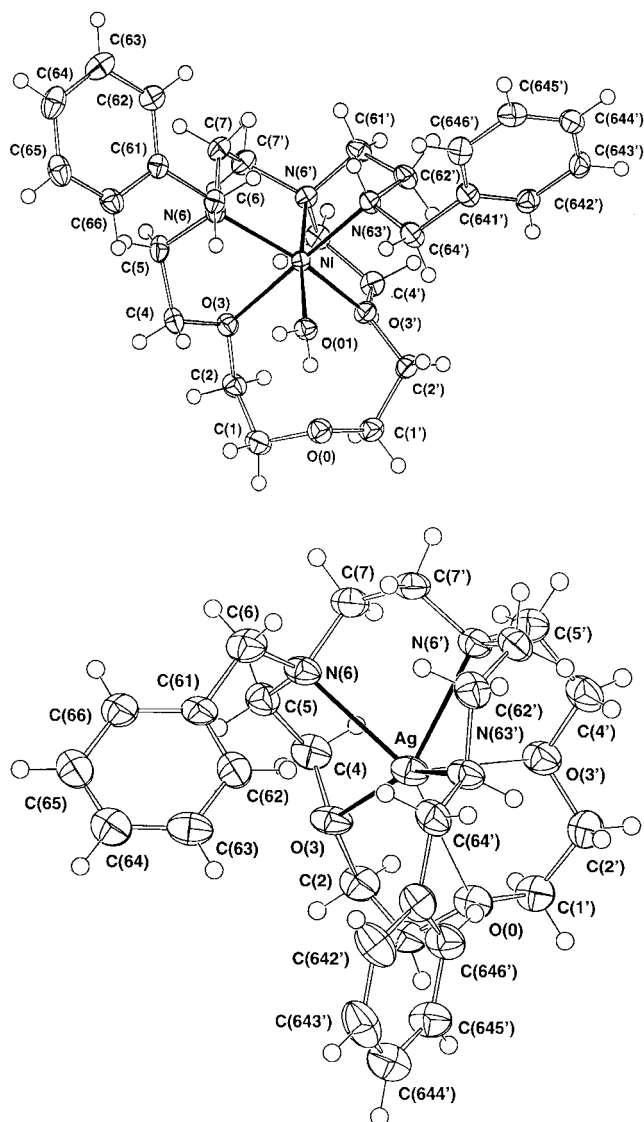


Figure 2. Projections of the (a)  $[\text{LNi}(\text{OH}_2)_2]^{2+}$  and (b)  $[\text{LAg}]^+$  cations ( $L = 3$ ), showing 50% thermal ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. About the nickel atom, Ni–O(01), O(3,3')N(6,6',63') are 2.023(1), 2.235(1), 2.122(1), 2.115(1), 2.055(1), 2.104(1) Å, the 'cis'-angles ranging between 78.94(4) (O(3)–Ni–N(6)) and 102.00(5)° (N(6)–Ni–N(63')), and the 'trans' being 157.45(4) (N(6)–Ni–O(3')), 172.85(5) (N(6')–Ni–O(01)), 179.05(6)° (O(3)–Ni–N(63')). About the silver atom, Ag–N(6,6',63) are 2.543(6), 2.464(6), 2.336(6) with Ag–O(0,3,3') 2.796(5), 2.448(5), 2.912(5) Å; O(3)–Ag–N(6,6',63) are 71.1(2), 127.5(2), 155.4(2), N(6)–Ag–N(6',63) 76.3(2), 120.3(2) and N(6')–Ag–N(63) 77.1(2)°.

~14 and the neutral product was extracted back into chloroform ( $3 \times 50$  mL), which was dried over anhydrous sodium sulfate. The solution was evaporated to dryness under reduced pressure to give the product as an oil. Yield: 1.27 g, 32%. [Found  $M^+$ ,  $m/z$  398.2571 (EI).  $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_3$  requires 398.2569].  $^1\text{H}$  NMR  $\delta$  2.71 (t, 4H,  $J = 5$ ), 2.80 (s, 4H), 3.59 (s, 4H), 3.63 (m, 12H), 7.17–7.33 (m, 10H).  $^{13}\text{C}$  NMR  $\delta$  52.35, 53.58, 60.07, 70.24, 71.14, 126.74, 128.13, 128.92, 139.39.

**Macrocycle 2** Using a similar procedure to the above in which *N,N'*-dibenzyl-1,2-propanediamine (2.64 g,

0.01 mol) was substituted for *N,N'*-dibenzyl-1,2-ethylenediamine gave the product as an oil. Yield: 2.19 g, 24%. [Found  $M^+$ ,  $m/z$  412.27255 (EI).  $\text{C}_{25}\text{H}_{36}\text{N}_2\text{O}_3$  requires 412.27259].  $^1\text{H}$  NMR  $\delta$  1.70 (quintet, 2H,  $J = 7$ ), 2.61–2.70 (m, 8H), 3.57–3.68 (m, 16H), 7.17–7.33 (m, 10H).  $^{13}\text{C}$  NMR  $\delta$  24.32, 52.40, 53.11, 70.22, 70.40, 71.16, 126.65, 128.06, 128.85, 140.02.

**Macrocycle 3** Sodium hydrogen carbonate (4.2 g, 0.05 mol) and 1,7-dibenzyl-diethylenetriamine (2.89 g, 0.01 mol) were added to tetraethylene glycol ditosylate (5.06 g, 0.01 mol) in acetonitrile (500 mL), and the mixture was heated at reflux for two days. The reaction mixture was then concentrated to near dryness by evaporation under reduced pressure. Water (100 mL) was added and the solution made acidic (pH ~1) by the dropwise addition of hydrochloric acid, then the solution was shaken with dichloromethane ( $3 \times 100$  mL). The aqueous phase was separated and sodium hydroxide was added until the pH was ~14. This aqueous phase was then extracted with dichloromethane ( $3 \times 50$  mL) and the organic phase then dried over anhydrous sodium sulfate with subsequent removal of the solvent under reduced pressure to yield a pale oil (3.08 g).

The product was purified by means of its nickel(II) nitrate complex. Nickel(II) nitrate hexahydrate (4.36 g, 0.015 mol) in warm ethanol (5 mL) was added to the oil (3.08 g) in warm ethanol (10 mL). Fine light blue crystals formed on letting the solution stand overnight at 4 °C. The crystals were then removed by filtration, washed with a minimum of chilled ethanol and then diethyl ether. The blue nickel complex was added to an aqueous solution of ethylenediaminetetraacetic acid at pH ~13 (50 mL, 0.1 M). The resultant solution was extracted with dichloromethane ( $3 \times 100$  mL) and the organic phase was dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure to yield the product as an oil. Yield: 1.79 g, 40%. [Found:  $[\text{L}-\text{H}]^+$ ,  $m/z$  440.29140 (EI).  $\text{C}_{26}\text{H}_{38}\text{N}_3\text{O}_3$  requires 440.29131]  $^1\text{H}$  NMR  $\delta$  1.56 (s, HOD), 2.72 (m, 8H), 3.77 (m, 4H), 7.21–7.30 (m, 10H).  $^{13}\text{C}$  NMR  $\delta$  47.03, 52.99, 53.12, 53.63, 53.97, 54.04, 54.39, 55.52, 60.25, 70.10, 70.41, 70.52, 71.24, 71.28, 126.74, 126.79, 128.13, 128.28, 128.81, 139.81, 140.61.

**$[\text{NiL}(\text{H}_2\text{O})](\text{NO}_3)_2$  ( $L = 3$ )** Nickel(II) nitrate hexahydrate (0.43 g, 1.5 mmol) in warm ethanol (5 mL) was added to **3** (0.44 g, 1.0 mmol) in warm ethanol (10 mL). Fine light blue crystals formed on letting the solution stand overnight at 4 °C. The crystals were removed by filtration washed with chilled ethanol, and dried under vacuum over phosphorus pentoxide to yield the required nickel(II) nitrate complex. Yield: 0.47 g, 63% [Found  $\text{NiLNO}_3^+$ ,  $m/z$  561.2 (ES)  $\text{C}_{26}\text{H}_{40}\text{N}_4\text{O}_6\text{Ni}$  requires 561.2] (Found: C, 48.55; H, 6.52; N, 11.04. Calc. For  $\text{C}_{26}\text{H}_{40}\text{N}_5\text{O}_9\text{Ni}\cdot\text{H}_2\text{O}$ : C, 48.62; H, 6.43; N, 10.90%). Crystals suitable for X-ray study were obtained by recrystallisation of the above product from ethanol.

**[ML](PF<sub>6</sub>)<sub>2</sub> (L = 3; M = Co, Cu and Zn) and [CdL]NO<sub>3</sub>PF<sub>6</sub>·½H<sub>2</sub>O (L = 3)** The appropriate metal(II) nitrate (1.5 mmol) in methanol (5 mL) was added to a solution of **3** (1.0 mmol) in methanol (5 mL). Saturated aqueous solution of ammonium hexafluorophosphate was added dropwise to each stirred solution until precipitation ceased. The respective solids were removed by filtration and taken up in acetonitrile. Crystallisation occurred on diffusion of ether vapour into the respective solutions. The products were removed by filtration and dried under vacuum over phosphorus pentoxide. Yields 50–65%.

**[CoL](PF<sub>6</sub>)<sub>2</sub> (L = 3)** [Found (CoL-H)<sup>+</sup>, *m/z* 499.3 (ES) C<sub>26</sub>H<sub>38</sub>N<sub>3</sub>O<sub>3</sub>Co requires 499.2] (Found: C, 39.50; H, 4.92; N, 5.37. Calc. For C<sub>26</sub>H<sub>39</sub>N<sub>3</sub>O<sub>3</sub>CoP<sub>2</sub>F<sub>12</sub>: C, 39.51; H, 4.97; N, 5.32%).

**[CuL](PF<sub>6</sub>)<sub>2</sub> (L = 3)** [Found (CuL-PF<sub>6</sub>)<sup>+</sup>, *m/z* 648.7 (ES) C<sub>26</sub>H<sub>39</sub>N<sub>3</sub>O<sub>3</sub>CuPF<sub>6</sub> requires 649.2] (Found: C, 39.47; H, 4.84; N, 5.27. Calc. For C<sub>26</sub>H<sub>39</sub>N<sub>3</sub>O<sub>3</sub>CuP<sub>2</sub>F<sub>12</sub>: C, 39.28; H, 4.94; N, 5.28%).

**[ZnL](PF<sub>6</sub>)<sub>2</sub> (L = 3)** [Found (ZnL-H)<sup>+</sup>, *m/z* 504.3 (ES) C<sub>26</sub>H<sub>38</sub>N<sub>3</sub>O<sub>3</sub>Zn requires 504.2] (Found: C, 39.03; H, 4.80; N, 5.16. Calc. For C<sub>26</sub>H<sub>39</sub>N<sub>3</sub>O<sub>3</sub>ZnP<sub>2</sub>F<sub>12</sub>: C, 39.19; H, 4.93; N, 5.27%).

**[CdL]NO<sub>3</sub>PF<sub>6</sub>·½H<sub>2</sub>O (L = 3)** [Found (CdL-H)<sup>+</sup>, *m/z* 554.3 (ES) C<sub>26</sub>H<sub>38</sub>N<sub>3</sub>O<sub>3</sub>Cd requires 554.2] (Found: C, 40.44; H, 5.05; N, 7.04. Calc. For C<sub>26</sub>H<sub>39</sub>N<sub>4</sub>O<sub>6</sub>CdPF<sub>6</sub>·½H<sub>2</sub>O: C, 40.56; H, 5.24; N, 7.28%).

**[AgL]NO<sub>3</sub> (L = 3)** Silver(I) nitrate (0.17 g, 1.0 mmol), in warm ethanol (5 mL) was added to **3** (0.44 g, 1.0 mmol) in warm ethanol (10 mL) and ether vapour was allowed to slowly diffuse into the solution. All operations were performed in the presence of subdued light. After several days colourless crystals were obtained; these were isolated and used directly for the X-ray diffraction study discussed below. [Found (AgL)<sup>+</sup>, *m/z* 548.2 (ES) C<sub>26</sub>H<sub>39</sub>N<sub>3</sub>O<sub>3</sub>Ag requires 548.2]

## Results and discussion

### Ligand synthesis

Condensation of ditosylated polyethylene glycols with substituted di- and triamines has been a common procedure for the preparation of aza-substituted crown ether macrocycles which has been reported previously [15]. In the present work, a similar procedure was employed in which the amine precursors incorporated *N*-terminal benzyl groups. All three of the aza-substituted products **1–3** were isolated as pale yellow oils. For ligands **1** and **2**, the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra were readily assigned and the mass spectral parent ion for each were found to be in accord with the proposed structures. However, for the synthesis of **3**, initial analysis of the crude product by <sup>1</sup>H NMR spectroscopy revealed a

series of complex overlaying peaks suggesting that a mixture of products was present. However, reaction of the mixture with nickel(II) nitrate in ethanol led to isolation of a single nickel complex as a crystalline blue product. Its FTIR infrared spectrum revealed a broad band at 3600–3000 cm<sup>-1</sup> indicative of the presence of water but was otherwise uninformative. The free ligand was isolated from the nickel complex by treatment with ethylenediaminetetraacetic acid (EDTA) under alkaline conditions followed by extraction into dichloromethane. This product was again obtained as an oil. Both the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectra of the free ligand did not correspond to the expected triaza-18-crown-6 derivative and both spectra proved difficult to assign with certainty. In view of this, an X-ray diffraction study of the nickel complex (see later) was undertaken and confirmed the structure given by **3** for the above product. The formation of **3** may be a reflection of the greater nucleophilic character of the central nitrogen relative to the terminal (benzyl substituted) amines, although steric considerations may also play a part.

### Metal complexes

During the course of the study, attempts were made to isolate crystalline metal complexes of **1–3** that might be suitable for X-ray diffraction analysis. Initial attempts involving the N<sub>2</sub>O<sub>3</sub>-donor systems **1** and **2** were unsuccessful whereas the more strongly binding (see later) N<sub>3</sub>O<sub>3</sub>-donor system **3** readily yielded 1:1 (M:L) species on mixing this ligand and the corresponding metal nitrate in methanol or ethanol. Except for the Ni(II) and Ag(I) species, hexafluorophosphate anion was added to the solution to induce crystallisation. The complexes isolated are listed in Table 1 along with their physical data.

The conductance values in acetonitrile (Table 1) for the complexes of Co(II), Ni(II), Cu(II) and Zn(II) indicate 2:1 electrolytes whereas the values for the Cd(II) and Ag(I) species correspond to 1:1 electrolytes [16]. The results suggest that the mixed-anion Cd(II) complex is best formulated as [CdLNO<sub>3</sub>]PF<sub>6</sub> in view of the low coordinating ability of hexafluorophosphate over nitrate anion.

The magnetic moment (Table 1) of the pink cobalt complex confirms its high spin nature; while its visible spectrum in acetonitrile shows a broad (composite) band with maxima at 480(sh), 505 (ε = 25) and 570(sh) nm, consistent with an octahedral coordination geometry [17]. The blue nickel complex yielded a magnetic moment (Table 1) in the range expected for high spin Ni(II). The solution spectra in acetonitrile contains absorptions at 380(sh), 580 (ε = 22) and 950 (ε = 25) nm, consistent with that expected for a (pseudo) octahedral geometry. The magnetic moment (Table 1) of the pale blue copper complex falls in the normal range for a Cu(II) species with S = ½; the visible spectrum (acetonitrile) shows a broad absorbance with a maximum centred at 710 nm (ε = 150). The featureless nature of this band results in it being of little value for the assignment of the geometry of the coordination sphere. The EPR spectrum of a powdered sample of this complex at ambient temperature yielded a *g* value of 2.076.

Table 1. Physical properties of the complexes of **3**

Complex (L = <b>3</b> )	Colour	$\Delta^a$	$\mu^b$	Electronic spectra <sup>c</sup>
[CoL](PF <sub>6</sub> ) <sub>2</sub>	Pink	279	4.75	480(sh), 505( $\epsilon$ = 25), 570(sh)
[NiLOH <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Blue	219	3.33	380(sh), 580( $\epsilon$ = 22), 950( $\epsilon$ = 25)
[CuL](PF <sub>6</sub> ) <sub>2</sub>	Pale Blue	288	1.90	710br ( $\epsilon$ = 150)
[ZnL](PF <sub>6</sub> ) <sub>2</sub>	Colourless	293		
[CdLNO <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub> · $\frac{1}{2}$ H <sub>2</sub> O	Colourless	171		
[AgL]NO <sub>3</sub>	Colourless	158		

<sup>a</sup>Conductance (S cm<sup>2</sup> mol<sup>-1</sup>) at 20 °C in acetonitrile; expected range for a 1:1 electrolyte in acetonitrile is 120–160 S cm<sup>2</sup> mol<sup>-1</sup> while that for a 2:1 electrolyte is 220–300 S cm<sup>2</sup> mol<sup>-1</sup> (see reference 16).

<sup>b</sup>Magnetic moment (BM) at 25 °C.

<sup>c</sup>In acetonitrile.

Table 2. Metal atom environments in [NiL(OH<sub>2</sub>)](NO<sub>3</sub>)<sub>2</sub> (L = **3**) and [AgL]NO<sub>3</sub> (L = **3**). Values for the nickel complex are given above those for the silver; atom 'X' is the water molecule oxygen O(1) for the former and O(0) for the latter

Atom	<i>r</i>	O(3)	O(3')	N(6)	N(6')	N(63')
X	2.023(1)	85.32(4)	92.82(5)	100.81(5)	172.85(5)	94.35(5)
	2.796(5)	65.8(2)	58.8(1)	135.7(2)	123.3(2)	103.5(2)
O(3)	2.235(1)		84.42(4)	78.94(4)	95.85(4)	179.05(6)
	2.448(5)		90.1(2)	71.1(2)	127.5(2)	155.4(2)
O(3')	2.122(1)			157.45(4)	80.29(5)	94.71(5)
	2.912(5)			112.6(2)	65.9(2)	103.3(2)
N(6)	2.115(1)				86.33(5)	102.00(5)
	2.543(6)				76.3(2)	120.3(2)
N(6')	2.055(1)					84.37(5)
	2.464(6)					77.1(2)
N(63')	2.104(1)					
	2.336(6)					

Table 3. L = **3** macrocycle torsion angles (degrees). The two values in each entry are for the nickel and silver complexes, respectively

C(1')–O(0)–C(1)–C(2)	–69.3(8),	–76.6(8)	C(1)–O(0)–C(1')–C(2')	125.0(1),	155.4(6)
O(0)–C(1)–C(2)–O(3)	–59.5(2),	–62.9(8)	O(0)–C(1')–C(2')–O(3')	–60.0(2),	–65.5(8)
C(1)–C(2)–O(3)–C(4)	–75.1(2),	158.4(6)	C(1')–C(2')–O(3')–C(4')	–101.1(2),	176.8(6)
C(2)–O(3)–C(4)–C(5)	–156.1(6),	164.3(6)	C(2')–O(3')–C(4')–C(5')	168.6(1),	–163.0(6)
O(3)–C(4)–C(5)–N(6)	–53.6(2),	62.6(7)	O(3')–C(4')–C(5')–N(6')	44.0(2),	65.5(8)
C(4)–C(5)–N(6)–C(7)	138.2(2),	82.1(7)	C(4')–C(5')–N(6')–C(7')	–166.4(1),	–164.3(6)
C(5)–N(6)–C(7)–C(7')	–76.0(2),	–161.4(6)	C(5')–N(6')–C(7')–C(7)	153.6(1),	80.5(7)
M–O(0)–C(1)–C(2)		53.7(6)	M–O(0)–C(1')–C(2')		34.8(8)
M–O(3)–C(2)–C(1)	66.0(2),	34.6(7)	M–O(3')–C(2')–C(1')	84.9(2),	61.6(6)
M–O(3)–C(4)–C(5)	53.4(1),	–63.4(6)	M–O(3')–C(4')–C(5')	–16.3(1),	–45.9(6)
M–N(6)–C(5)–C(4)	24.4(2),	–25.3(6)	M–N(6')–C(5')–C(4')	–50.5(2),	–47.3(7)
M–N(6)–C(7)–C(7')	42.2(1),	–49.3(6)	M–N(6')–C(7')–C(7)	38.1(1),	–44.1(6)
M–N(6)–C(6)–C(61)	179.4(1),	–60.2(8)	M–N(6')–C(61')–C(62')	19.6(2),	–32.6(7)
M–N(63')–C(62')–C(61')	48.5(1),	–54.2(6)	M–N(63')–C(64')–C(641')	172.2(1),	53.3(8)
N(6)–C(7)–C(7')–N(6')	–56.3(2),	71.2(8)			

Table 4. Ligand protonation constants and metal stability constants for **1–3**<sup>a</sup>

Ligand	Log $K_H$			Log $K_{ML}^b$						
	Log $K_1$	log $K_2$	log $K_3$	Co <sup>2+</sup>	Ni <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Cu <sup>2+</sup>	Ag <sup>+</sup>	Pb <sup>2+</sup>
<b>1</b>	9.11 (0.05)	3.24 (0.05)	–	<4	<4.5	<4	5.3 (0.1)	7.0 (0.1)	– <sup>c</sup>	5.3 (0.1)
<b>2</b>	8.84 (0.05)	5.90 (0.05)	–	<4	<4.5	– <sup>c</sup>	4.4 (0.1)	5.3 (0.1)	7.1 (0.1)	4.3 (0.1)
<b>3</b>	9.91 (0.05)	6.90 (0.05)	2.37 (0.05)	6.4 (0.1)	7.0 (0.2)	7.1 (0.1)	8.8 (0.1)	13.0 (0.3)	10.3 (0.2)	8.6 (0.2)

<sup>a</sup>In 95% methanol;  $I = 0.1$ , (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NClO<sub>4</sub>, 25 °C; uncertainties in parenthesis.

<sup>b</sup>Each value is the mean of at least two (and up to five) determinations at different metal:ligand ratios rounded to the first decimal place.

<sup>c</sup>Precipitation, slow approach to equilibrium or competing hydrolysis inhibited log  $K$  determination in this case.

### Crystal structures

The results of low temperature single crystal X-ray structure determinations of the above nickel(II) and silver(I) nitrate complexes of **3** are consistent with their formulation as 1:1 adducts, L in combination with M (and a water molecule in the case of M = Ni) forming a mononuclear cation, all nitrates being counterions in both structures. In the two complexes the binding and conformations of the ligand within the two cations are very different (Figure 2). The nickel ion is quasi-octahedrally six-coordinated by the three nitrogen and two oxygen atoms of the ligand *plus* the water molecule oxygen, the latter bond the shortest; O(0) is not bound. In the unsolvated silver complex, the bonding is irregular and the coordination number ambiguous about the larger metal atom, involving the six possible donors of the ligand at various distances with M–N(63') now long and M–O(0) the shortest of the M–O contacts; there is no dominant pair of interactions and among the six putative donors, the largest 'trans' angle is O(3)–Ag–N(63') (155.4(2)°).

### Stability constants

The protonation constants for ligands **1–3** were obtained by potentiometric (pH) titration in 95% methanol ( $I = 0.1$  mol dm<sup>–3</sup>; NEt<sub>4</sub>ClO<sub>4</sub>) and are given in Table 4. As in previous studies, this solvent system was employed to overcome the generally restricted solubility of ligands of the present type (and/or their metal complexes) in water [18].

Comparison of the corresponding protonation log  $K$  for **1** and **2** illustrates the effect of electrostatic interaction between the adjacent (protonated) nitrogen sites. While the higher log  $K$  values are quite similar, the lower values differ considerably. The difference is in accord with greater repulsion occurring between the nitrogen sites in the case of **1** (which has two methylene groups linking adjacent nitrogens) relative to **2** in which these donors are linked by three methylene groups. The overall complexation pattern for ligands **1** and **2** are quite similar, with the expected decrease in metal binding being evident for **2** relative to **1**; the latter being very likely due to the formation of a less-stable, six-membered chelate ring in each of the complexes of **1** relative to those of **2** (for which only five-membered rings are possible).

A full set of values was able to be obtained for **3** and it is observed that the first four log  $K$  values (Table 4) follow the Irving-Williams stability order of Co(II) < Ni(II) < Cu(II) > Zn(II). The presence of the extra (pendant) donor clearly increases the overall metal-ion binding of this ligand relative to that of the parent ring **1** (Table 4). While this undoubtedly reflects the donation of the pendant nitrogen to the central metal, in particular instances there may also be a contribution from the increased flexibility of this system allowing better accommodation of the steric dictates of the central metal.

Unfortunately a log  $K$  value for the Ag(I) complex was unable to be obtained for **1** due to precipitation during the attempted determination; however, its larger ring analogue **2** proved to be more tractable and yielded a value for the (1:1) complex of this ion. Significantly, this di-*N*-benzylated derivative is selective for silver over the other six metals investigated. Such behaviour very likely reflects both the predominance of ether oxygen donors in the N<sub>2</sub>O<sub>3</sub>-donor set (such ether donors have now been well documented to show quite low affinity for copper in its divalent state) and the previously mentioned propensity for Ag(I) to be relatively less sensitive to the 'detuning' effect of *N*-benzylation than the other metals investigated [5]. However, as might be predicted, addition of a further nitrogen donor in the form of the pendant benzylamine functionality to **1** (to yield **3**, with a N<sub>3</sub>O<sub>3</sub>-donor set) results in a significant increase in the binding constant for Ag(I) while showing an even greater increase for Cu(II) – so much so that this ligand now binds Cu(II) more strongly than Ag(I).

### Concluding remarks

Overall, the present study serves to illustrate the manner by which variation of donor atom set coupled with choice of donor substituent can be employed to fine tune metal-ion selectivity towards metals of the present type.

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