Metal ion recognition. Interaction of a series of successively N-benzylated derivatives of 1,4,8,11-tetraazacyclotetradecane (cyclam) with selected transition and post-transition metal ions

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The interaction of a series of N-benzylated cyclam ligand derivatives incorporating from one to four *N*-benzyl groups with cobalt(II), zinc(II), cadmium(II), lead(II) and silver(I) nitrates is reported; the results are compared with those obtained in a prior study involving the formation of the corresponding complexes of nickel(II) and copper(II) with this ligand series. The isolation of a selection of 1 : 1 (metal : ligand) complexes has been carried out and X-ray diffraction structures of five such products have been determined. In each complex the metal ion is coordinated to the N_4-donor set of the cyclam ring with the latter adopting either a *trans*-I or a *trans*-V configuration; monodentate or bidentate nitrato ligands complete the respective coordination spheres. Coordination numbers range from five in a zinc(II) complex, through six in two cadmium(II) complexes, to eight in two lead(II) complexes. Competitive bulk membrane transport experiments (water/chloroform/water) have been carried out in which each of the five benzylated ligands were in turn employed as the ionophore in the chloroform phase. The respective aqueous source phases (buffered at pH 4.9) contained an equimolar mixture of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) nitrates. The aqueous receiving phase was buffered at pH 3.0. Under these conditions, high selectivity for copper(II) was observed for each of the ionophores incorporating one or two *N*-benzyl groups whereas no transport for any of the seven metals present in the source phase was observed for the tribenzylated derivative. In marked contrast to the above behaviour, the tetra-*N*-benzyl derivative yielded sole transport selectivity for silver(I) under similar conditions. ^{1}H NMR and ^{13}C NMR titration experiments in CD_3CN–$CDCl_3$ confirmed the 1 : 1 stoichiometry of the silver(I) tetra-*N*-benzylcyclam complex in this solvent mixture.

Introduction

Owing to the presence of a central cavity, macrocyclic ligands have long been employed as selective hosts for a wide range of guest molecules and ions.[1] Thus, macrocyclic systems have been employed as selective extractants/ionophores for transition and post-transition metal ions in a range of solvent extraction[2,3] and bulk membrane transport studies.[3,4] In this context, the modification of tetraaza macrocyclic ligands to control and tune the properties of coordinated metal centres has also been the subject of much interest.[1] For example, in previous studies we have documented that N-benzylation of the nitrogen donors in individual mixed oxygen–nitrogen donor macrocycles leads to enhanced metal ion determination for silver(I) relative to cobalt(II), nickel(II), copper(II), zinc(II), cadmiun(II) and lead(II)—a phenomenom we refer to as 'selective detuning'.[5,6]

In a recent study[7] we have investigated the interaction of nickel(II) and copper(II) with N-benzylated derivatives **1**–**5** (Scheme 1), with emphasis on the relationship between the electrochemical, spectrophotometric and structural features of the corresponding complexes. The present report represents an extension of this latter study.

Experimental

Where available, commercial reagents and solvents were of analytical (or HPLC) grade. The preparation of ligands **1**–**5** have been reported previously.[8]

Physical methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX300 spectrometer. Low resolution (ES) spectra were
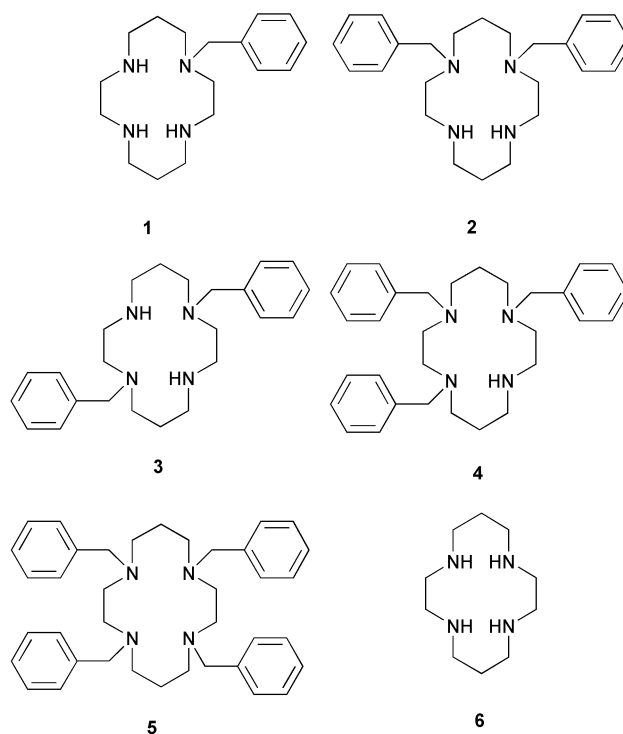
Scheme 1

obtained on a Finnigan LCQ-8 spectrometer. AAS data were collected on a SpectrAA·800, solid state UV-Vis spectra were measured on a CARY 1E UV-Visible Spectrophotometer, and solution UV-Vis spectra on a CARY 5E UV-Vis-NIR

Spectrophotometer. X-Ray diffraction data were obtained on a Bruker SMART 1000 CCD diffractometer.

Membrane transport

The transport experiments employed a 'concentric cell' in which the aqueous source phase (10 cm³) and receiving phase (30 cm³) were separated by a chloroform phase (50 cm³). 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 thermostated at 25 °C. The aqueous source phase was buffered (CH₃CO₂H–CH₃CO₂Na) at pH 4.9 (±0.1)[10] and contained an equimolar mixture of the nitrate salts of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), lead(II) and silver(I), each at a concentration of 1×10^{-2} mol dm⁻³. The chloroform phase contained the ligand (1×10^{-3} mol dm⁻³), as well as palmitic acid (4×10^{-3} mol dm⁻³). The receiving phase consisted of a buffer (HCO₂H–HCO₂Na) solution[10] at pH 3.0 ± 0.1. Atomic absorption spectroscopy was used to determine the amount of metal ion transported over this period. Transport rates (*J* values) are in mol/24 h; they represent the total number of moles of each metal ion present in the aqueous receiving phase at the end of the 24 h period used for the experiment divided by 24. The transport results are quoted as the average values obtained from duplicate runs (errors *ca.* ±10% of reported value). The hydrophilicity of **6** (cyclam) led to bleeding of this ionophore to the aqueous phases and, as a consequence, runs involving this species were aborted. A 'control' experiment containing only palmitic acid in the chloroform membrane phase confirmed that no metal ion transport took place in the absence of the macrocyclic ionophore.

X-Ray structure determinations

Full sphere data were collected at 150(2) K, with the exception of the Pb complex with **3** for which data were collected at 294(2) K. Data were collected with ω scans to 56° 2θ using a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å). The data integration and reduction were undertaken with SAINT and XPREP,[11] and subsequent computations were carried out with the teXsan,[12] WinGX[13] and XTAL[14] graphical user interfaces. A recollection of the reflections in the first 50 CCD frames at the end of the collection showed no significant change in intensities. A Gaussian absorption correction was applied to the data for the Pb(1), Cd(3) and Zn(4) complexes with XPREP,[15,16] and a multiscan empirical correction was applied to these data for the Cd(2) and Pb(3) complexes using SADABS.[17,18]

The structure of [Pb(**1**)(NO₃)₂] was solved by direct methods using SHELXS-97[19] and the other structures were solved using SIR97.[20] The structures were extended and refined with SHELXL-97.[19] In general, the non-hydrogen atoms were modelled with anisotropic thermal parameters and a riding atom model was used for the hydrogen atoms. ORTEP[21] depictions of the molecule with 20% displacement ellipsoids are provided in Figs. 1–5, and pertinent geometry details are provided in Tables 1–5.

The refinement residuals are defined as $R1 = \Sigma ||F_o| - |F_o||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_c^2)^2)^{1/2}$ all reflections where $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, $P = (F_o^2 + 2F_o^2)/3$] and *A* and *B* are as listed below.

Crystal data

[Pb(**1**)(NO₃)₂]: C₁₇H₃₀N₆O₆Pb, $M = 621.66$, triclinic, space group $P\bar{1}$ (#2), $a = 11.847(3)$, $b = 12.448(3)$, $c = 14.959(4)$ Å, $\alpha = 86.322(4)$, $\beta = 89.620(4)$, $\gamma = 87.247(4)°$, $V = 2199.0(10)$ Å³, $D_c = 1.878$ g cm⁻³, $Z = 4$, crystal size $0.508 \times 0.187 \times 0.066$ mm, colour colourless, habit tabular, temperature 150(2) K,

Pb(1)–N(4)	2.445(3)	Pb(1)–N(2)	2.502(3)
Pb(1)–N(3)	2.505(3)	Pb(1)–N(1)	2.646(3)
Pb(1)–O(4)	2.820(3)	Pb(1)–O(1)	2.829(2)
Pb(1)–O(2)	3.044(3)	Pb(1)–O(5)	3.057(3)
Pb(2)–N(8)	2.452(2)	Pb(2)–N(10)	2.483(3)
Pb(2)–N(9)	2.552(3)	Pb(2)–N(7)	2.657(2)
Pb(2)–O(10)	2.842(2)	Pb(2)–O(11)	2.975(2)
Pb(2)–O(8)	3.059(2)	Pb(2)–O(7)	3.102(3)
N(4)–Pb(1)–N(2)	80.18(9)	N(8)–Pb(2)–N(10)	81.33(9)
N(4)–Pb(1)–N(3)	79.33(9)	N(8)–Pb(2)–N(9)	77.79(8)
N(2)–Pb(1)–N(3)	71.12(9)	N(10)–Pb(2)–N(9)	70.33(8)
N(4)–Pb(1)–N(1)	70.49(8)	N(8)–Pb(2)–N(7)	70.61(8)
N(2)–Pb(1)–N(1)	77.78(8)	N(10)–Pb(2)–N(7)	78.24(8)
N(3)–Pb(1)–N(1)	139.68(8)	N(9)–Pb(2)–N(7)	138.14(7)
N(4)–Pb(1)–O(4)	155.58(8)	N(8)–Pb(2)–O(10)	87.48(8)
N(2)–Pb(1)–O(4)	79.85(9)	N(10)–Pb(2)–O(10)	145.70(7)
N(3)–Pb(1)–O(4)	81.02(9)	N(9)–Pb(2)–O(10)	75.64(7)
N(1)–Pb(1)–O(4)	118.33(9)	N(7)–Pb(2)–O(10)	128.04(7)
N(4)–Pb(1)–O(1)	95.59(8)	N(8)–Pb(2)–O(11)	74.22(8)
N(2)–Pb(1)–O(1)	150.09(8)	N(10)–Pb(2)–O(11)	153.67(8)
N(3)–Pb(1)–O(1)	78.99(8)	N(9)–Pb(2)–O(11)	112.80(7)
N(1)–Pb(1)–O(1)	128.97(7)	N(7)–Pb(2)–O(11)	84.49(7)
O(4)–Pb(1)–O(1)	94.73(9)	O(10)–Pb(2)–O(11)	43.78(6)
N(4)–Pb(1)–O(2)	74.53(8)	N(8)–Pb(2)–O(8)	143.24(7)
N(2)–Pb(1)–O(2)	153.55(8)	N(10)–Pb(2)–O(8)	86.66(8)
N(3)–Pb(1)–O(2)	110.90(8)	N(9)–Pb(2)–O(8)	129.99(7)
N(1)–Pb(1)–O(2)	86.48(7)	N(7)–Pb(2)–O(8)	72.97(7)
O(4)–Pb(1)–O(2)	126.56(8)	O(10)–Pb(2)–O(8)	119.62(7)
O(1)–Pb(1)–O(2)	42.89(7)	O(11)–Pb(2)–O(8)	107.20(7)
N(4)–Pb(1)–O(5)	149.95(8)	N(8)–Pb(2)–O(7)	156.52(8)
N(2)–Pb(1)–O(5)	88.69(8)	N(10)–Pb(2)–O(7)	75.69(9)
N(3)–Pb(1)–O(5)	123.33(9)	N(9)–Pb(2)–O(7)	89.87(8)
N(1)–Pb(1)–O(5)	79.92(7)	N(7)–Pb(2)–O(7)	108.68(8)
O(4)–Pb(1)–O(5)	42.83(8)	O(10)–Pb(2)–O(7)	108.94(8)
O(1)–Pb(1)–O(5)	107.34(7)	O(11)–Pb(2)–O(7)	129.24(7)
O(2)–Pb(1)–O(5)	109.52(7)	O(8)–Pb(2)–O(7)	40.66(6)

λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 7.717 mm⁻¹, T(Gaussian)$_{min,max}$ = 0.069, 0.603, $2\theta_{max}$ = 56.20, *hkl* range −15 to 15, −16 to 16, −19 to 19, $N = 20115$, $N_{ind} = 9607$ ($R_{merge} = 0.0314$), $N_{obs} = 8472$ ($I > 2\sigma(I)$), $N_{var} = 565$, residuals $R1(F) = 0.0194$, $wR2(F^2) = 0.0454$ ($A = 0.02$, $B = 0.5$), GoF(all) = 1.201, $\Delta\rho_{min,max} = -0.830$, 0.968 e⁻ Å⁻³.

Specific details: the amine hydrogens were located and modelled isotropically.

[Cd(**2**)(NO₃)]NO₃·0.5MeOH: C₂₄.₅H₃₈CdN₆O₆.₅, $M = 633.01$, triclinic, space group $P\bar{1}$ (#2), $a = 9.537(6)$, $b = 11.146(7)$, $c = 13.097(8)$ Å, $a = 94.789(11)$, $\beta = 93.115(11)$, $\gamma = 93.292(11)°$, $V = 1382.6(15)$ Å³, $D_c = 1.521$ g cm⁻³, $Z = 2$, crystal size $0.389 \times 0.354 \times 0.160$ mm, colour colourless, habit prism, temperature 150(2) K, λ(Mo-Kα) = 0.71069 Å, μ(Mo-Kα) = 0.841 mm⁻¹, T(SADABS)$_{min,max}$ = 0.84, 1.00, $2\theta_{max}$ = 56.40, *hkl* range −12 to 12, −14 to 14, −17 to 17, $N = 13482$, $N_{ind} = 6350$ ($R_{merge} = 0.0212$), $N_{obs} = 5702$ ($I > 2\sigma(I)$), $N_{var} = 334$, residuals $R1(F) = 0.0297$, $wR2(F^2) = 0.0685$ ($A = 0.02$, $B = 0.05$), GoF(all) = 1.369, $\Delta\rho_{min,max} = -0.800$, 0.968 e⁻ Å⁻³.

Specific details: the asymmetric unit contains a complex molecule with a coordinated nitrate counter ion, a disordered non-coordinated nitrate counter ion and a partially occupied methanol solvate site. The disordered nitrate counter ion was modelled with three rigid bodies having partial occupancies that were refined and then fixed. The methanol molecule site occupancies were also refined and then fixed. The partially occupied non-hydrogen sites were modelled with isotropic displacement parameters, and the two amine hydrogen sites were located and modelled isotropically.

[Cd(**3**)(NO₃)]NO₃·MeOH: C₂₅H₄₀CdN₆O₇, $M = 649.03$, monoclinic, space group $P2_1/c$ (#14), $a = 8.330(2)$, $b = 15.976(4)$, $c = 22.011(6)$ Å, $\beta = 97.475(4)$, $V = 2904.3(14)$ Å³, $D_c = 1.484$ g cm⁻³, $Z = 4$, crystal size $0.442 \times 0.397 \times 0.375$ mm, colour colourless, habit priamatic, temperature 150(2) K, λ(Mo-Kα) =

Table 2 Pertinent geometry details (bond lengths in Å angles in °) for [Cd(**2**)(NO₃)]NO₃·0.5MeOH

Cd(1)–N(3)	2.283(2)	Cd(1)–N(4)	2.307(2)
Cd(1)–N(1)	2.320(2)	Cd(1)–N(2)	2.364(2)
Cd(1)–O(1)	2.369(2)	Cd(1)–O(2)	2.460(2)
N(3)–Cd(1)–N(4)	92.40(8)	N(1)–Cd(1)–O(1)	142.78(6)
N(3)–Cd(1)–N(1)	129.59(8)	N(2)–Cd(1)–O(1)	97.14(8)
N(4)–Cd(1)–N(1)	80.78(9)	N(3)–Cd(1)–O(2)	140.06(7)
N(3)–Cd(1)–N(2)	78.41(7)	N(4)–Cd(1)–O(2)	95.29(8)
N(4)–Cd(1)–N(2)	163.66(8)	N(1)–Cd(1)–O(2)	90.34(7)
N(1)–Cd(1)–N(2)	94.59(7)	N(2)–Cd(1)–O(2)	100.42(7)
N(3)–Cd(1)–O(1)	87.43(8)	O(1)–Cd(1)–O(2)	52.84(6)
N(4)–Cd(1)–O(1)	95.91(9)		

Hydrogen bond geometry

Donor	Hydrogen	Acceptor	D–H/Å	H ⋯ A/Å	D ⋯ A/Å	D–H ⋯ A/°
N(3)	H(3N)	O(1^a)	0.84(3)	2.23(3)	2.936(3)	143(2)
N(4)	H(4N)	O(6)	0.82(3)	2.26(3)	2.947(5)	142(3)
N(4)	H(4N)	O(5)	0.82(3)	2.32(3)	3.114(5)	162(3)
N(4)	H(4N)	O(10)	0.82(3)	2.47(3)	3.152(6)	141(2)
O(13)	H(13A)	O(10)	0.84	1.96	2.770(9)	161.7
O(13)	H(13A)	O(7)	0.84	2.15	2.891(8)	146.7

^{a} $1 - x, 1 - y, -z$.

Table 3 Pertinent geometry details (bond lengths in Å angles in °) for [Cd(**3**)(NO₃)]NO₃·MeOH

Cd(1)–N(4)	2.2589(16)	Cd(1)–N(2)	2.2671(16)
Cd(1)–N(3)	2.3718(16)	Cd(1)–N(1)	2.3692(16)
Cd(1)–O(1)	2.3603(14)	Cd(1)–O(2)	2.4837(14)
N(4)–Cd(1)–N(2)	127.40(6)	O(1)–Cd(1)–N(3)	96.81(5)
N(4)–Cd(1)–O(1)	138.81(5)	N(1)–Cd(1)–N(3)	162.51(5)
N(2)–Cd(1)–O(1)	93.79(5)	N(4)–Cd(1)–O(2)	86.18(5)
N(4)–Cd(1)–N(1)	80.06(6)	N(2)–Cd(1)–O(2)	146.17(5)
N(2)–Cd(1)–N(1)	93.10(6)	O(1)–Cd(1)–O(2)	52.76(4)
O(1)–Cd(1)–N(1)	99.77(5)	N(1)–Cd(1)–O(2)	88.61(5)
N(4)–Cd(1)–N(3)	91.12(6)	N(3)–Cd(1)–O(2)	105.98(5)
N(2)–Cd(1)–N(3)	80.22(5)		

Hydrogen bond geometry

Donor	Hydrogen	Acceptor	D–H/Å	H ⋯ A/Å	D ⋯ A/Å	D–H ⋯ A/°
N(2)	H(2N)	O(6^a)	0.82(2)	2.42(2)	3.139(3)	146.0(18)
N(4)	H(4N)	O(5)	0.781(19)	2.624(19)	3.331(2)	151.5(17)
N(4)	H(4N)	O(4)	0.781(19)	2.23(2)	2.931(2)	150.5(17)
O(7)	H(7O)	O(6)	0.91(3)	2.21(3)	3.054(3)	155(3)

^{a} $-x, y + 1/2, 3/2 + z$.

Table 4 Pertinent geometry details (bond lengths in Å angles in °) for [Pb(**3**)(NO₃)₂]·H₂O

Pb(1)–N(2^a)	2.448(2)	Pb(1)–N(2)	2.448(2)
Pb(1)–N(1)	2.583(2)	Pb(1)–N(1)	2.583(2)
Pb(1)–O(2)	2.968(3)	Pb(1)–O(1)	3.066(3)
N(2^a)–Pb(1)–N(2)	80.47(11)	N(1^a)–Pb(1)–O(2)	86.77(8)
N(2)–Pb(1)–N(1)	78.20(7)	N(2^a)–Pb(1)–O(1)	155.15(8)
N(2)–Pb(1)–N(1^a)	71.86(7)	N(2)–Pb(1)–O(1)	99.68(10)
N(1)–Pb(1)–N(1^a)	140.51(10)	N(1)–Pb(1)–O(1)	83.78(9)
N(2^a)–Pb(1)–O(2)	155.58(8)	N(1^a)–Pb(1)–O(1)	125.75(8)
N(2)–Pb(1)–O(2)	76.58(8)	O(2)–Pb(1)–O(1)	40.58(8)
N(1)–Pb(1)–O(2)	110.89(8)		

Hydrogen bond geometry

Donor	Hydrogen	Acceptor	D–H/Å	H ⋯ A/Å	D ⋯ A/Å	D–H ⋯ A/°
O(4)	H(4O)	O(3)	0.909(19)	1.98(3)	2.823(4)	155(6)
N(2)	H(2N)	O(4^b)	0.91	2.13	3.028(5)	167.1

^{a} $1 - x, y, 3/2 - z$. ^{b} $x, 1 + y, z$.

Table 5 Pertinent geometry details (bond lengths in Å angles in °) for [Zn(**4**)(NO₃)]NO₃·0.5MeOH

Zn(1)–O(1)	2.0442(17)	Zn(1)–O(2)	2.837(2)
Zn(1)–N(1)	2.204(2)	Zn(1)–N(2)	2.109(2)
Zn(1)–N(3)	2.306(2)	Zn(1)–N(4)	2.061(2)
O(1)–Zn(1)–N(4)	120.91(8)	N(2)–Zn(1)–N(3)	84.55(7)
O(1)–Zn(1)–N(2)	102.15(8)	N(1)–Zn(1)–N(3)	173.75(7)
N(4)–Zn(1)–N(2)	136.78(8)	O(1)–Zn(1)–O(2)	49.81(6)
O(1)–Zn(1)–N(1)	96.41(7)	N(4)–Zn(1)–O(2)	71.14(7)
N(4)–Zn(1)–N(1)	84.04(8)	N(2)–Zn(1)–O(2)	151.44(7)
N(2)–Zn(1)–N(1)	95.42(7)	N(1)–Zn(1)–O(2)	93.50(6)
O(1)–Zn(1)–N(3)	89.69(7)	N(3)–Zn(1)–O(2)	89.42(6)
N(4)–Zn(1)–N(3)	91.69(8)		

0.71073 Å, μ(Mo-Kα) = 0.804 mm^{-1}, T(Gaussian)$_{min,max}$ = 0.74, 0.85, $2\theta_{max}$ = 56.62, hkl range −11 to 11, −21 to 21, −29 to 29, N = 28544, N_{ind} = 6914 (R_{merge} = 0.0259), N_{obs} = 5815 ($I > 2\sigma(I)$), N_{var} = 365, residuals $R1(F)$ = 0.0260, $wR2(F^2)$ = 0.0588 (A = 0.02, B = 0.0), GoF(all) = 1.471, $\Delta\rho_{min,max}$ = −0.419, 0.804 e$^-$ Å^{-3}.

Specific details: the amine hydrogen sites were located and modelled with isotropic displacement parameters.

[Pb(**3**)(NO₃)₂]·H₂O: C₂₄H₃₈N₆O₇Pb, M = 729.79, ortho-rhombic, space group $Pbcn$ (#60), a = 16.1228(13), b = 9.4321(7), c = 18.4865(15) Å, V = 2811.3(4) Å³, D_c = 1.724 g cm^{-3}, Z = 4, crystal size 0.326 × 0.294 × 0.264 mm, colour colourless, habit prism, temperature 294(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 6.053 mm^{-1}, T(SADABS)$_{min,max}$ = 0.79, 1.00, $2\theta_{max}$ = 56.54, hkl range −21 to 21, −12 to 12, −23 to 23, N = 27909, N_{ind} = 3412 (R_{merge} = 0.0244), N_{obs} = 2361 ($I > 2\sigma(I)$), N_{var} = 177, residuals $R1(F)$ = 0.0176, $wR2(F^2)$ = 0.0553 (A = 0.02, B = 1.0), GoF(all) = 1.350, $\Delta\rho_{min,max}$ = −0.427, 0.744 e$^-$ Å^{-3}.

Specific details: the water hydrogen atom site was located and modelled with a group isotropic displacement parameter.

[Zn(**4**)(NO₃)]NO₃·0.5MeOH: C₃₁.₅H₄₄.₇₅N₆O₆.₅Zn, M = 676.85, monoclinic, space group $C2/c$ (#15), a = 25.741(14), b = 20.796(11), c = 13.212(7) Å, β = 108.425(9), V = 6710(6) Å³, D_c = 1.340 g cm^{-3}, Z = 8, crystal size 0.487 × 0.132 × 0.055 mm, colour colourless, habit blade, temperature 150(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.784 mm^{-1}, T(Gaussian)$_{min,max}$ = 0.74, 0.96, $2\theta_{max}$ = 56.56, hkl range −34 to 32, −27 to 27, −17 to 17, N = 33034, N_{ind} = 7959 (R_{merge} 0.0483), N_{obs} = 5235 ($I > 2\sigma(I)$), N_{var} = 416, residuals $R1(F)$ = 0.0410, $wR2(F^2)$ = 0.1097 (A = 0.05, B = 0.0), GoF(all) = 1.056, $\Delta\rho_{min,max}$ = −0.374, 1.395 e$^-$ Å^{-3}.

Specific details: the asymmetric unit contains a complex molecule with a coordinated nitrate ion, a non-coordinated nitrate counter ion and a disordered solvent region modelled with two methanol molecules having occupancies refined and fixed at 0.25. The solvate sites were modelled with isotropic displacement parameters, and the amine hydrogen site was located and modelled with an isotropic displacement parameter.

CCDC reference numbers 200929–200933.

See http://www.rsc.org/suppdata/dt/b3/b300002h/ for crystallographic data in CIF or other electronic format.

Metal complex syntheses

All complexes were dried over P₄O₁₀ in a vacuum before microanalysis.

[Co(1)(NO₃)]PF₆. Cobalt(II) nitrate hexahydrate (0.06 g, 0.207 mmol) in methanol (5 cm³) was added to a solution of **1** (0.06 g, 0.207 mmol) in methanol (15 cm³). The solution was refluxed for 1 h under nitrogen and then cooled to room temperature. The volume of the solution was reduced by one third and excess saturated NH₄PF₆ in methanol was added, followed by the dropwise addition of ether to produce an oily solid. The latter was purified by recrystallization from a mixture

of acetone, methanol and ether to give dark-purple crystals (0.052 g, 45%) (Found: C, 36.48; H, 5.58; N, 12.36. Calc. for C₁₇H₃₀CoF₆N₅PO₃: C, 36.70; H, 5.44; N, 12.59%).

[Zn(1)](NO₃)₂. Zinc(II) nitrate hexahydrate (0.045 g, 0.172 mmol) in methanol (5 cm³) was added to **1** (0.05 g, 0.172 mmol) in hot methanol (15 cm³). The solution was warmed for 30 min then allowed to stand at room temperature. The required product formed as colourless crystals (0.046 g, 56%) after recrystallization from methanol (Found: C, 42.48; H, 6.33; N, 17.29. Calc. for C₁₇H₃₀N₆O₆Zn: C, 42.55; H, 6.30; N, 17.51%). ¹H NMR (DMSO-d₆): δ 1.58–1.86 (m, CH_2CH₂NH, 4 H), 2.22–3.08 (m, overlapping signals, CH₂N, 16 H), 3.96–4.02 (m, CH_2C₆H₅, 1 H), 4.15–4.25 (m, CH_2C₆H₅, 1 H), 7.25–7.55 (m, ArH, 5 H). ¹³C NMR (DMSO-d₆): δ 23.71, 23.90, 24.11, 27.62, 28.30, 43.96, 44.52, 44.72, 45.42, 46.34, 46.78, 47.41, 48.14, 48.42, 48.54, 49.18, 49.48, 49.71, 50.51, 50.77, 51.06, 51.31, 52.16, 53.64, 53.91, 54.36, 128.41, 128.55, 128.67, 128.74, 130.77, 131.22, 131.76, 132.42, 132.71.

[Cd(1)](NO₃)PF₆. Cadmium(II) nitrate tetrahydrate (0.054 g, 0.172 mmol) in methanol (5 cm³) was added to a solution of **1** (0.050 g, 0.172 mmol) in methanol (10 cm³). The solution was stirred and heated for 0.5 h, then the solvent was reduced to 10 cm³ and excess saturated NH₄PF₆ in methanol was added. The white powder that formed was filtered off and recrystallized from acetonitrile–isopropanol to yield colourless crystals (0.067 g, 64%) (Found: C, 33.69; H, 5.03; N, 11.50. Calc. for C₁₇H₃₀CdF₆N₅PO₃: C, 33.48; H, 4.96; N, 11.48%). ¹H NMR (CD₃CN): δ 1.57–1.88 (m, CH_2CH₂NH, 4 H), 2.61–3.25 (m, CH₂N, 16 H), 3.88–3.93 (d, CH_2C₆H₅, 1 H), 4.23–4.28 (d, CH_2C₆H₅, 1 H), 7.26–7.40 (dm, ArH, 5 H). ¹³C NMR (CD₃CN): δ 25.62, 29.15, 46.59, 47.71, 47.94, 52.00, 52.85, 53.26, 53.85, 55.03, 56.24, 129.39, 129.54, 131.70, 132.65.

[Pb(1)](NO₃)₂. Lead nitrate (0.048 g, 0.145 mmol) in water (2 cm³) was added to a solution of **1** (0.042 g, 0.145 mmol) in methanol (10 cm³). The solution was heated for 0.5 h and filtered. The filtrate was left to stand in the air overnight and colourless crystals were obtained (0.018 g, 20%). Single crystals suitable for X-ray diffraction were obtained from methanol–water (Found: C, 32.68; H, 4.99; N, 13.67. Calc. for C₁₇H₃₀N₆O₆Pb: C, 32.85; H, 4.86; N, 13.52%).

[Co(2)](NO₃)PF₆. Using a similar procedure to that described for [Co(**1**)(NO₃)]PF₆, cobalt(II) nitrate hexahydrate (0.038 g, 0.132 mmol) and **2** (0.050 g, 0.132 mmol) produced the product as a dark-purple powder (0.034 g, 40%) (Found: C, 44.38; H, 5.82; N, 10.99. Calc. for C₂₄H₃₆CoF₆N₅PO₃: C, 44.59; H, 5.61; N, 10.83%).

[Zn(2)](NO₃)₂. Using a similar procedure to that described for [Zn(**1**)](NO₃)₂, zinc(II) nitrate tetrahydrate (0.035 g, 0.132 mmol) and **2** (0.050 g, 0.132 mmol) yielded the product as colourless crystals (0.025 g, 33%) (Found: C, 50.29; H, 6.25; N, 14.62. Calc. for C₂₄H₃₆N₆O₆Zn: C, 50.58; H, 6.37; N, 14.74%). ¹H NMR (DMSO-d₆): δ 1.56–1.73 (m, CH_2CH₂NH, 2H), 2.25–2.37 (m, CH_2CH₂NH, 2H), 2.61–3.13 (m, CH₂N, 16 H), 4.17–4.36 (m, CH_2C₆H₅, 4 H), 7.37–7.44 (m, ArH, 10 H). ¹³C NMR (DMSO-d₆): δ 20.62, 28.16, 44.42, 44.70, 48.60, 50.97, 52.78, 53.00, 53.45, 54.21, 56.65, 128.45, 128.51, 128.63, 130.74, 132.67, 133.16.

[Cd(2)](NO₃)PF₆. Using a similar procedure to that described for [Cd(**1**)(NO₃)]PF₆, cadmium(II) nitrate tetrahydrate (0.033 g, 0.105 mmol) and **2** yielded the product as colourless crystals (0.024 g, 32%). Single crystals suitable for X-ray diffraction were obtained by diffusion of ether vapour into a methanol solution of the complex (Found: C, 40.99; H, 5.32; N, 9.87. Calc. for C₂₄H₃₆CdF₆N₅O₃P: C, 41.18; H, 5.18; N,

10.01%). ^{1}H NMR (CD$_3$CN): δ 1.80–1.84 (m, CH_2CH$_2$NH, 2 H), 2.01–2.06 (m, CH_2CH$_2$NH, 2 H), 2.73–3.28 (m, CH$_2$N, 16 H), 4.02–4.05 (d, CH_2C$_6$H$_5$, 4 H), 5.98 (br s, NH, 2 H), 7.38–7.45 (m, ArH, 10 H). ^{13}C NMR (CD$_3$CN): δ 22.67, 25.58, 25.63, 46.13, 50.44, 51.63, 52.45, 52.74, 54.27, 55.36, 55.93, 58.09, 129.43, 129.72, 130.03, 130.07, 131.69, 133.04, 133.26.

[Co(3)](NO$_3$)$_2$. Cobalt(II) nitrate hexahydrate (0.154 g, 0.526 mmol) in methanol (10 cm^3) was added to a solution of **3** (0.200 g, 0.526 mmol) in methanol (20 cm^3). The solution was refluxed for 1 h under nitrogen and then cooled to room temperature. After filtration, the clear filtrate was left to stand overnight during which time pink–purple crystals of product formed (0.184 g, 62%) (Found: C, 51.30; H, 6.37; N, 14.95. Calc. for C$_{24}$H$_{36}$CoN$_6$O$_6$: C, 51.15; H, 6.44; N, 14.91%).

[Zn(3)](NO$_3$)$_2$. This was prepared using a similar procedure to that described for [Zn(1)](NO$_3$)$_2$. The initial product was recrystallized from methanol to yield colourless crystals (46%) (Found: C, 50.36; H, 6.17; N, 14.60. Calc. for C$_{24}$H$_{36}$N$_6$O$_6$Zn: C, 50.58; H, 6.37; N, 14.74%). ^{1}H NMR (DMSO-d$_6$): δ 1.64–1.80 (m, CH_2CH$_2$NH, 3 H), 2.33–3.08 (m, CH_2CH$_2$NH, CH$_2$N, 17 H), 3.72–3.84 (dd, CH_2C$_6$H$_5$, 2 H), 4.21–4.34 (dd, CH_2C$_6$H$_5$, 2 H), 7.31–7.44 (m, ArH, 10 H). ^{13}C NMR (DMSO-d$_6$): δ 22.89, 23.87, 44.52, 44.85, 45.25, 49.16, 49.59, 51.86, 52.94, 53.97, 54.92, 56.17, 128.02, 128.19, 128.36, 130.31, 130.69, 131.42, 132.31.

[Cd(3)](NO$_3$)$_2$·0.5MeOH. Using a similar procedure to that described for [Zn(1)](NO$_3$)$_2$, colourless crystals (58%) were obtained following recrystallization of the initial product from methanol (Found: C, 46.28; H, 6.07; N, 13.09. Calc. for C$_{24.5}$H$_{38}$CdN$_6$O$_{6.5}$: C, 46.49; H, 6.05; N, 13.28%). ^{1}H NMR (DMSO-d$_6$): δ 1.73 (br s, CH_2CH$_2$NH, 4 H), 2.42–3.09 (m, overlapping signals, CH$_2$N, 16 H), 3.88–3.93 (d, CH_2C$_6$H$_5$, 2 H), 4.20–4.25 (d, CH_2C$_6$H$_5$, 2 H), 7.32–7.43 (m, ArH, 10 H). ^{13}C NMR (DMSO-d$_6$): δ 24.10, 24.77, 44.67, 44.93, 45.51, 49.11, 50.60, 52.42, 54.04, 55.54, 55.96, 56.68, 128.02, 128.20, 130.46, 131.52, 2.11.

[Pb(3)](NO$_3$)$_2$·0.25H$_2$0. A similar procedure to that described for [Pb(1)(NO$_3$)$_2$] yielded colourless crystals (yield 67.8%). Single crystals suitable for X-ray diffraction were obtained from methanol–water (Found: C, 40.14; H, 4.99; N, 11.67. Calc. for C$_{24}$H$_{36.5}$N$_6$O$_{6.25}$Pb: C, 40.24; H, 5.14; N, 11.73%).

[Co(4)](NO$_3$)PF$_6$. A similar procedure to that described for [Co(1)](NO$_3$)PF$_6$ given a product which was recrystallized from acetone–isopropanol to yield pink–purple crystals (44%) (Found: C, 50.67; H, 5.99; N, 9.36. Calc. for C$_{31}$H$_{42}$CoF$_6$N$_5$O$_3$P: C, 50.55; H, 5.75; N, 9.51%).

[Zn(4)](NO$_3$)$_2$·0.5H$_2$O. A similar procedure to that described for [Zn(1)](NO$_3$)$_2$ was employed. The initial product was recrystallized from methanol–isopropanol to yield colourless crystals (54%). Single crystals suitable for X-ray diffraction were obtained from the same solvent mixture (Found: C, 55.42; H, 6.24; N, 12.34. Calc. for C$_{31}$H$_{43}$N$_6$O$_{6.5}$Zn: C, 55.65; H, 6.48; N, 12.56%). ^{1}H NMR (CD$_3$OD): δ 1.71–1.84 (m, CH_2CH$_2$NH, 2 H), 2.29–2.56 (m, CH_2CH$_2$NH, CH_2NH, 4 H), 2.68–3.27 (m, CH$_2$N, 13 H), 3.61–3.72 (m, CH$_2$N, 1 H), 3.78–4.61 (m, CH_2C$_6$H$_5$, 6 H), 7.35–7.49 (m, ArH, 15 H). ^{13}C NMR (CD$_3$OD): δ 21.87, 24.89, 25.28, 47.24, 51.15, 51.75, 52.11, 52.24, 53.45, 54.20, 55.35, 56.82, 57.89, 58.40, 129.58, 129.69, 129.82, 130.35, 131.62, 132.25, 132.69, 133.14, 133.92.

[Cd(4)](NO$_3$)PF$_6$·0.75H$_2$O. A similar procedure to that described for [Cd(1)](NO$_3$)PF$_6$ was employed. The initial product was recrystallized from acetone–isopropanol to yield colourless crystals (52%) (Found: C, 46.44; H, 5.30; N, 8.55.

Calc. for C$_{31}$H$_{43.5}$CdF$_6$N$_5$O$_{3.75}$P: C, 46.33; H, 5.46; N, 8.72%). ^{1}H NMR (CD$_3$CN): δ 1.73–1.83 (m, CH_2CH$_2$NH, 2 H), 2.09–2.29 (m, CH_2CH$_2$NH, 2 H), 2.42–2.50 (m, CH_2NH, 2 H), 2.60–3.34 (m, CH$_2$N, 14 H), 3.63 (br s, NH, 1 H), 3.95–4.58 (m, CH_2C$_6$H$_5$, 6 H), 7.35–7.51 (m, ArH, 15 H). ^{13}C NMR (CD$_3$CN): δ 22.25, 25.32, 46.63, 51.66, 52–58 (overlapping signals), 129.39, 129.44, 129.71, 129.86, 131.28, 131.44, 132.75, 132.95, 133.47.

[Zn(5)](NO$_3$)$_2$·2H$_2$O. S similar procedure to that described for [Zn(1)](NO$_3$)$_2$ yielded colourless needle-like crystals on recrystallizaton of the initial product from absolute ethanol (43%) (Found: C, 58.23; H, 6.47; N, 10.43. Calc. for C$_{38}$H$_{52}$N$_6$O$_8$Zn: C, 58.05; H, 6.67; N, 10.69%).

[Cd(5)](NO$_3$)$_2$·EtOH·H$_2$O. A similar procedure to that described for [Cd(3)](NO$_3$)$_2$ was employed except that the reaction solvent was changed from methanol to absolute ethanol. Colourless crystals were obtained after recrystallization of the initial product from absolute ethanol (40%) (Found: C, 56.40; H, 6.15; N, 9.87. Calc. for C$_{40}$H$_{56}$CdN$_6$O$_8$: C, 56.49; H, 6.32; N, 10.13%).

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

Results and discussion

Synthesis of complexes

In an effort to obtain crystalline complexes that were suitable for X-ray analysis, the isolation of selected solid complexes of cobalt(II), zinc(II), cadmium(II), silver(I) and lead(II) with **1**–**5** was attempted. The 1 : 1 (metal : ligand) complexes listed in Table 6 were successfully obtained in pure form by mixing hot solutions of the required metal nitrate salt and ligand in methanol, with in some instances excess ammonium hexafluorophosphate being added to induce precipitation. While the copper(II)[7] and palladium(II)[22] complexes of the tetrabenzylated derivative **5** have been reported previously, only zinc(II) and cadmium(II) complexes of this ligand were obtained in the present study. Interestingly, while this later ligand has been employed in a range of host–guest investigations (including studies of alkali, alkaline earth and other metal ion binding),[23–26] it has been proposed that it shows low affinity for cobalt(II), nickel(II), copper(II) and zinc(II) under a variety of reaction conditions,[27,28] with the latter behaviour

Table 6 Conductance values^a for the complexes of cobalt(II), zinc(II), cadmium(II) and lead(II) of **1**–**5** in methanol at 25 °C

Complex	Colour	Λ^a/S cm^2 mol^{-1}
[Co(**1**)](NO$_3$)]PF$_6$	Dark purple	121
[Co(**2**)](NO$_3$)]PF$_6$	Dark purple	–
[Co(**3**)](NO$_3$)]NO$_3$	Pink	75
[Co(**4**)](NO$_3$)]PF$_6$	Pink	92
[Zn(**1**)](NO$_3$)]NO$_3$	Colourless	84
[Zn(**2**)](NO$_3$)$_2$	Colourless	–
[Zn(**3**)](NO$_3$)]NO$_3$	Colourless	76
[Zn(**4**)](NO$_3$)$_2$·0.5H$_2$O	Colourless	75
[Zn(**5**)](NO$_3$)$_2$·2H$_2$O	Colourless	–
[Cd(**1**)[(NO$_3$)]PF$_6$	Colourless	108
[Cd(**2**)](NO$_3$)]PF$_6$	Colourless	84
[Cd(**3**)](NO$_3$)]NO$_3$·0.5MeOH	Colourless	81
[Cd(**4**)](NO$_3$)]PF$_6$·0.75H$_2$O	Colourless	87
[Cd(**5**)](NO$_3$)]]NO$_3$·EtOH·H$_2$O	Colourless	84
[Pb(**1**)](NO$_3$)$_2$]	Colourless	–
[Pb(**3**)](NO$_3$)]NO$_3$·0.25H$_2$O	Colourless	98

^{a} Conductance at 25 °C in methanol at ~10^{-3} mol dm^{-3}; 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}.

being ascribed to the sterically demanding nature of the four pendant benzyl groups.[28]

As with cyclam itself, silver(I) complexes of **1**–**5** proved prone to decomposition and none were obtained in pure form from the synthetic conditions employed.

Where values were obtained, each of the cobalt(II), zinc(II), cadmium(II) and lead(II)] complexes yielded conductances in methanol (Table 6) which approximated these expected for a 1 : 1 electrolyte;[29] thus indicating that, on average, at least one of the anionic groups is coordinated (or ion-paired) with the cation under the conditions employed.

The ^{1}H and ^{13}C NMR spectra of the zinc(II), cadmium(II) complexes of **1**–**5** were recorded in CD$_3$CN, CD$_3$OD or DMSO-d$_6$ (see Experimental section). All spectra showed induced chemical shifts relative to the corresponding free ligands, with the ^{1}H NMR signals shifted up-field in the spectra of the complexes, as is commonly observed for other diamagnetic metal-containing systems. Both the ^{1}H and ^{13}C NMR spectra of the respective complexes are more complicated (reflecting peak broadening and/or splitting) relative to those for the free ligands. For example, the singlets observed for the benzyl methylene protons in the free ligands are split on complex formation to 'doublets' or 'multiplets', in accordance with inhibition of ligand flexibility occurring on metal binding.

As mentioned above, no solid complexes of Ag(I) were isolated free of contamination; however, in view of our interest in the effect of N-benzylation on silver(I) selectivity (see below), both ^{1}H NMR and ^{13}C NMR titration studies of the interaction of silver(I) nitrate with **5** in CD$_3$CN–CDCl$_3$ were performed. The incremental addition of solid silver(I) nitrate to a solution of **5** held in the NMR tube yielded clear 1 : 1 end-points in both sets of spectra (no evidence for other species was obtained up to a molar ratio of [Ag$^+$] : [**5**] of 3.5), confirming the 1 : 1 stoichiometry of this Ag(I) complex.

In accord with the observations discussed above, both the ^{1}H NMR and ^{13}C NMR spectra exhibited a doubling of the benzyl methylene resonance and particular aromatic resonances of the free ligand on addition of silver ion with significant broadening of the proton spectrum also being evident.

Bulk membrane transport

Competitive mixed metal transport experiments (water/chloroform/water) have been undertaken, with the chloroform membrane phase containing an ionophore at 10^{-3} mol dm^{-3} chosen from **1**–**5**, respectively. 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 being 1×10^{-2} mol dm^{-3}. As mentioned in the Experimental section, transport was performed against a back gradient of protons, with palmitic acid (4×10^{-3} mol dm^{-3}) also being present in the organic phase. A main 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 neutralisation of the metal cation being transported; in this manner the need for uptake of hydrophilic nitrate anions into the organic phase may be avoided. Under the conditions employed (and ignoring any apparent transport showing *J* values of $>20 \times 10^{-7}$ mol/24 h as being within experimental error of zero), sole selectivity for copper(II) was observed for the systems incorporating the dibenzylated species **2** ($J = 83 \times 10^{-7}$ mol/24 h) and **3** ($J = 63 \times 10^{-7}$ mol/24 h); as might be expected, the values for these isomeric systems are quite similar. While **1** also solely delivered a significant amount of copper(II) to the receiving phase, in this case a precipitate was observed to form in the organic phase and the results for this system were not considered further. On moving to the system incorporating the tribenzylated species **4**, no transport of any of the seven metal

ions present in the source phase was observed. Clearly, this ligand is a poor ionophore for all seven metal ions under the conditions employed. In contrast, the tetrabenzylated derivative **5** was found to show *high* transport selectivity towards silver(I)—a *J* value of 169×10^{-7} mol/24 h was obtained, with no evidence for transport of any of the other six metals present in the source phase.

In the above context it is noted that a series of single (individual) metal solvent extraction (water/chloroform)[25] and membrane (water/dichloromethane/water)[26] experiments have been reported previously. In parallel with the present findings, it was reported that **5** was the most efficient extractant for AgClO$_4$ relative to the perchlorates of Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Cs$^+$, Ba^{2+} and Pb^{2+}. Similarly, the above silver salt was the only one transported when compared with the attempted transport of the individual perchlorates of Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Cs$^+$, Ba^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in separate experiments. Clearly these results support the present finding that the tetrabenzyl derivative **5** has a prepensity for Ag$^+$ selectivity which persists across the respective experiment types just discussed.

Crystal structures

Single crystal X-ray diffraction studies have been undertaken to determine the crystal structures of [Pb(**1**)(NO$_3$)$_2$], [Cd(**2**)(NO$_3$)]NO$_3$·0.5MeOH, [Cd(**3**)(NO$_3$)]NO$_3$·MeOH, [Pb(**3**)(NO$_3$)$_2$]·H$_2$O and [Zn(**4**)(NO$_3$)]NO$_3$·0.5MeOH.

The structure of [Pb(**1**)(O$_2$NO)$_2$] is illustrated in Fig. 1, and the asymmetric unit contains two crystallographically independent complex molecules, each with two weakly coordinated nitrate counter ions. The cyclam ring adopts the unusual *trans*-V configuration (*RRRR*),[1] presumably reflecting that lead(II) is too large to fit within the macrocyclic ring. The lead ion in this complex is eight coordinated, and the Pb–N bond lengths range from 2.445(3) to 2.657(2) Å (Table 1) and are typical of such Pb–N bond lengths in other related complexes.[30] The benzyl substituent on N(1) atom is responsible for a longer Pb–N coordination bond length. The nitrato oxygen to metal bond distances vary from 2.820(3) to 3.102(3) Å and are slightly longer than the mean length of 2.71 Å recorded on the CSD database.[31]

The asymmetric unit of the cadmium(II) complex of **2** contains a complex molecule with a coordinated nitrate counter ion, a non-coordinated nitrate counter ion disordered over three sites and a partially occupied methanol solvate site. Fig. 2 shows that the complex adopts a *trans*-I (*RSRS*) configuration[1] with bidentate coordination of a nitrato ligand to cadmium(II). The coordination number of the cadmium cation is six. The Cd–N bond lengths (to NCH$_2$Ph) of 2.320(2) and 2.364(2) Å are slightly longer than those of 2.283(2) and 2.307(2) Å (to NH), while the Cd–O distances are 2.369(2) and 2.460(2) Å respectively.

The cadmium(II) complex of **3**, [Cd(**3**)(O$_2$NO)]·NO$_3$·MeOH, incorporates **3** in a *trans*-I (*RSRS*) configuration[1] (Fig. 3). The Cd–N distances range from 2.2589(16) to 2.3718(16) Å, while the Cd–O bond lengths are 2.3603(14) and 2.4837(14) Å, respectively. The coordination number of the cadmium cation is six, consisting of four non-coplanar nitrogen atoms from the macrocycle and two oxygens from one (bidentate) nitrato ligand. There are hydrogen bonding interactions between the hydrogens attached to N(2) and N(4) and the nitrate counter ion, as well as between this nitrate and a methanol solvate molecule (Fig. 3 and Table 3).

The asymmetric unit of the lead(II) complex of **3** contains the complex molecule (located on a 2-fold axis), a weakly coordinated nitrate counter ion and a water molecule (Fig. 4). The macrocycle ring, again, adopts the unusual *trans*-V configuration[1] with the lead ion being again eight coordinated. The substituents on the N(1) atoms are once again reflected by Pb–N
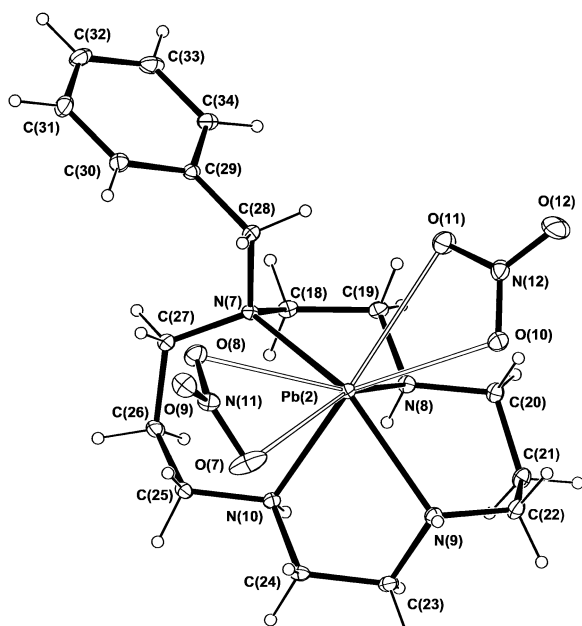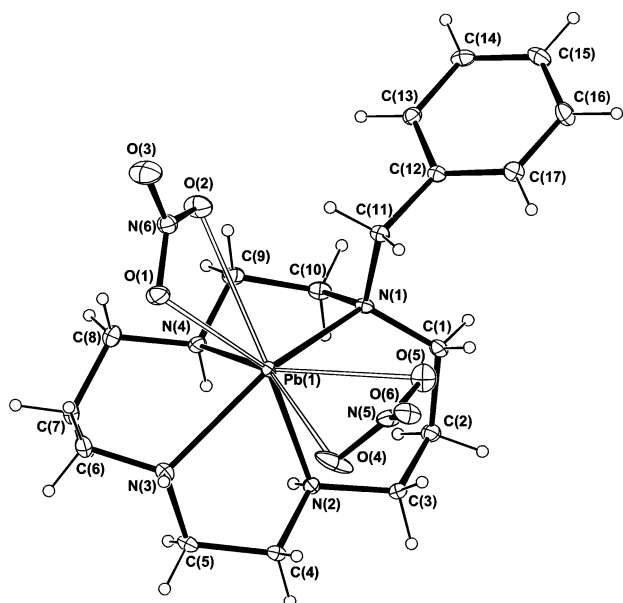
Fig. 1 ORTEP[21] depiction with 20% displacement ellipsoids, of the two independent complex molecules present in the crystal structure of [Pb(**1**)(O₂NO)₂].

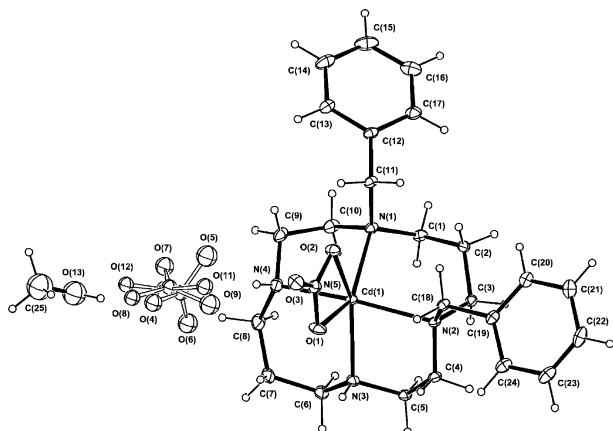**Fig. 2** ORTEP[21] depiction of [Cd(**2**)(O₂NO)]NO₃·0.5MeOH, with 20% displacement ellipsoids.
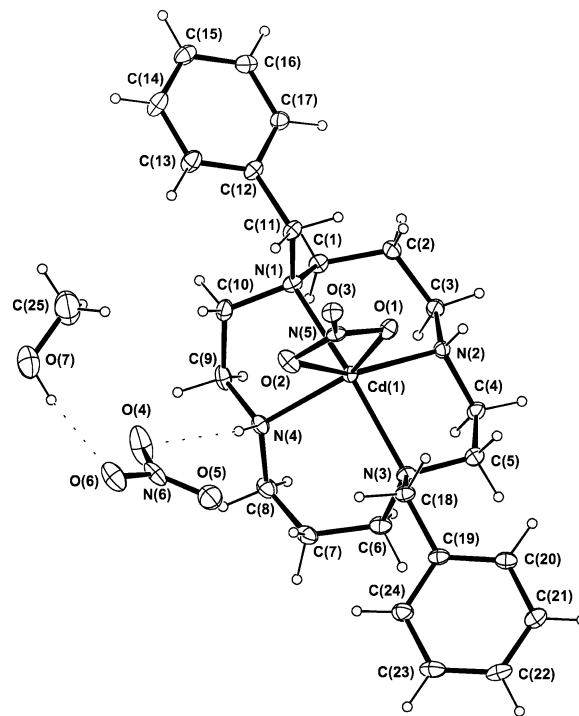
Fig. 3 ORTEP[21] depiction of [Cd(**3**)(O₂NO)]NO₃·MeOH, with 20% displacement ellipsoids. Hydrogen bond interactions are indicated with a dashed line.
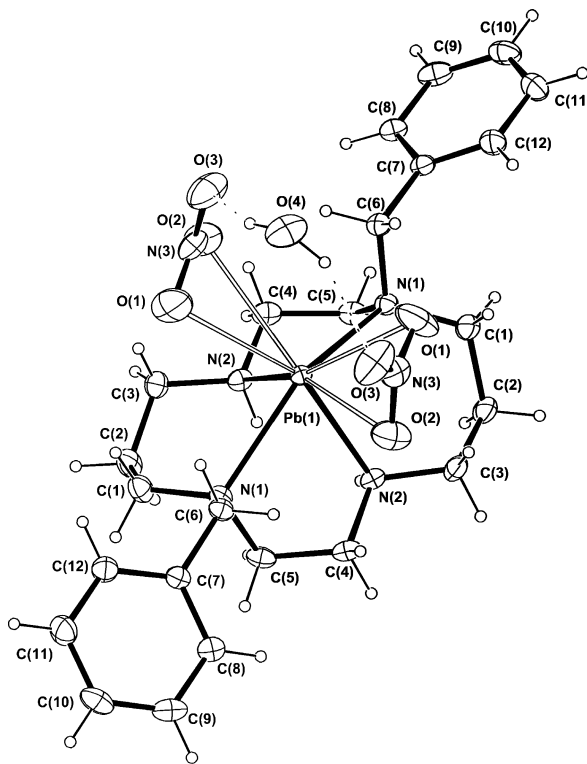
Fig. 4 ORTEP[21] depiction of [Pb(**3**)(O₂NO)₂]·H₂O, with 20% displacement ellipsoids.

bond length (to NCH₂Ph) of 2.583(2) Å that are slightly longer than that of 2.448(2) Å (to NH).

For the zinc(II) complex of the tribenzyl derivative **4**, the asymmetric unit contains a complex molecule with a coordinated nitrato ion, and a non-coordinated nitrate counter ion. In each [Zn(**4**)(ONO₂)]NO₃·0.5MeOH, the macrocycle adopts a *trans*-I configuration[1] (Fig. 5). The Zn–N bond length to the secondary amine is 2.061(2) Å and, for the zinc to the tertiary amine lengths, the range is 2.109(2)–2.306(2) Å; these lengths are similar to those present in other related zinc cyclam
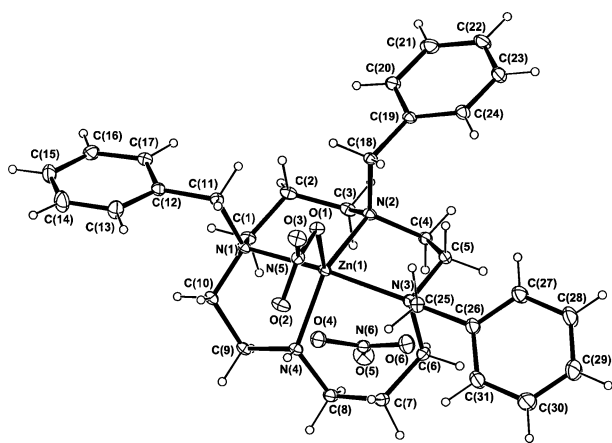
Fig. 5 ORTEP[21] depiction of [Zn(**4**)(ONO$_2$)]NO$_3$·0.5MeOH, with 20% displacement ellipsoids.

derivatives.[32] It is interesting that the Zn–O(1) bond length (2.0442(17) Å) is somewhat shorter than the normal range. The overall coordination geometry of this five-coordinated complex is distorted square pyramidal.

In summary, the five X-ray structures described above show several noteworthy features. Benzylation of nitrogen donors consistently results in longer metal to nitrogen bond lengths than those involving secondary nitrogens, undoubtedly reflecting the steric (as well as electronic) consequences of N-benzylation. As expected, the metal ion is coordinated in each case to the N$_4$-donor set of the macrocyclic cavity with either monodentate or bidentate nitrato ligands completing the respective coordination spheres. Unlike the majority of the nickel(II) and copper(II) complexes of this ligand series whose structures were investigated previously,[7] none of the present complexes has the cyclam ring present in the (usually preferred) *trans*-III configuration[1]—with either the slightly less stable *trans*-I or the unusual *trans*-V arrangement being adopted instead. Finally, the coordination number of the central metal ion expands as its radius increases—from five-coordinate in [Zn(**4**)(ONO$_2$)]NO$_3$· 0.5MeOH in which the nitrato ligand is monodentate, through six-coordinate (incorporating a bidentate nitrato group) for both cadmium(II) complexes to eight-coordinate (bidentate nitrato ligands) in both lead(II) complexes.

Concluding remarks

In the present study we report the results of an investigation of the interaction of **1**–**5** with the above metal ions with emphasis on the effect of successive N-benzylation on the properties of their respective complexes. In contrast to the (competitive) membrane transport behaviour of the partially N-benzylated derivatives **1**–**4**, a corresponding experiment using the tetrabenzylated species **5** as ionophore resulted in sole transfer of silver(I) from the aqueous source phase to the aqueous receiving phase. Although the origins of this selectivity remain unclear, the result parallels our prior observation that the benzylation of secondary amine donors in macrocyclic ligands can give rise to selective behaviour towards silver(I) over the other transition and post-transition metal ions employed in the present study.

Finally, it is noted that a number of groups have explored the effects of N-alkylation of amine ligands in relation to their metal ion recognition properties.[6,33–36] While alkylation of a secondary amine generally results in a reduction of its metal ion affinity due to steric factors, it is known that tertiary amines sometimes bind more strongly to silver(I) than do secondary amines—with the relative affinities being solvent dependent.[33] Similarly, N-alkylation of individual chelating ligands has been reported to result in enhanced binding for lead(II).[37] While, in general, it remains unclear what factors will dominate in a

particular situation, other examples of N-alkylation leading to enhanced selectivity and related behaviour have been reported. Based on studies involving tetraaza cyclam and its tetra-N-methylated derivative, it has been proposed by Meyerstein *et al.*[38,39] that N-alkylation will tend to favour stabilisation of metals in their lower oxidation states—behaviour exemplified electrochemically by the above workers with respect to the stabilisation of copper(I) over copper(II) by the N-tetramethylcyclam derivative. In view of the latter, it also seems likely that a similar effect may contribute to the enhanced recognition for silver(I) observed for the tetra-N-benzylated derivative **5** in both the present and past studies.

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