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FULL PAPER

Metal ion recognition. The interaction of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) with N-benzylated macrocycles incorporating O_2N_2-, O_3N_2- and O_2N_3-donor sets†

Jeong Kim,*[a] Tae-Ho Ahn,[a] Myungro Lee,[a] Anthony J. Leong,[b] Leonard F. Lindoy,*[c] Brendan R. Rumbel,[c] Brian W. Skelton,[d] Tania Strixner,[b] Gang Wei[c] and Allan H. White[d]

[a] *Department of Chemistry, Seonam University, Namwon, 590-711, Korea*
[b] *School of Pharmacy and Molecular Sciences, James Cook University, Townsville, Qld 4811, Australia*
[c] *Centre for Heavy Metals Research, School of Chemistry, University of Sydney, NSW 2006, Australia*
[d] *Department of Chemistry, The University of Western Australia, Crawley, WA 6009, Australia*

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The interaction of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) with a series of mixed-donor, *N*-benzylated macrocyclic ligands incorporating O_2N_2-, O_3N_2- and O_2N_3-donor sets has been investigated. The log *K* values for the respective 1 : 1 complexes in 95% methanol ($I = 0.1$ mol dm^{-3}; Et_4NClO_4, 25 °C) have been determined potentiometrically and the results compared with the values obtained previously for the parent (non-benzylated) macrocyclic systems. Examples of N-benzylation of individual parent macrocycles leading to enhanced discrimination for silver(I) are presented. In the case of a dibenzylated O_3N_2-ring and a tribenzylated O_2N_3-ring, both 17-membered, high selectivity for this ion was observed relative to the other metal ions investigated. Competitive mixed-metal transport experiments across a bulk chloroform membrane have been performed using the benzylated derivatives as ionophores. For each experiment the source contained equimolar concentrations of the above metal ions and transport was performed against a pH gradient; the aqueous source and receiving phases were buffered at pH 4.9 and 3.0, respectively. In parallel to the log *K* results, transport selectivity for silver(I) was exhibited by the di- and tri-benzylated ligands mentioned above. The remaining ligands proved to be poor ionophores, showing no significant metal ion transport under the conditions employed. In a further study, high silver ion (transport) selectivity was maintained when the above tribenzylated ligand was incorporated as the ionophore in a polymer inclusion membrane system. Single metal and mixed (seven-metal) solvent extraction experiments employing similar aqueous source and chloroform phases to those used in the bulk membrane transport runs have also been performed for the tribenzylated ligand derivative; significant selectivity for silver was again maintained in these solvent extraction experiments. An X-ray study of $[AgL]ClO_4$ (where L is the above-mentioned dibenzylated derivative) confirms that all donor atoms of the macrocycle coordinate to the silver ion; the latter is five-coordinate with the complex cation exhibiting a highly distorted trigonal bipyramidal geometry.

Introduction

In previous studies we have investigated structure–function relationships in the complexation behaviour of selected transition and post transition metal ions with closely related macrocyclic ligands incorporating mixed donor atoms.[1] A motivation for such studies was to elucidate the factors underlying any observed metal ion discrimination by such systems. In our experience, an investigation of metal complexation studies across a range of related ligands has provided a useful background on which to base further ligand design.[2]

Recently we have investigated the effects of N-benzylation of amine-containing macrocyclic ligands on their relative binding affinities towards a range of transition and post transition metal ions.[3–5] Usually N-alkylation of a secondary-amine-containing macrocycle leads to a decrease in the thermodynamic stabilities of the resulting complexes, reflecting the presence of increased steric hindrance.[6] N-Alkylation will of course also lead to both electronic and solvation changes that will influence coordination behaviour towards individual metal ions.[7,8]

As a part of our continuing program in the area of metal-ion recognition, we now present the results of a comparative investigation of the interaction of the related mixed-donor, N-benzylated macrocycles, **2**, **3**, **5**, **7** and **9**[9] towards cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II), with the results obtained compared with the corresponding data for the parent (unsubstituted) rings, **1**, **4**, **6** and **8**.[10–16]

In a preliminary report,[3] we have described how tri-N-benzylation (and to a lesser degree, tri-N-methylation) of the 17-membered, N_3O_2-donor macrocycle **8** led to cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and lead(II) complexes of lower stability (the value for the copper complex could not be determined due to precipitation) while the stability of the corresponding silver(I) complex was little affected (it increased slightly in the case of the tribenzylated derivative).

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† Electronic supplementary information (ESI) available: metal ion transport fluxes for seven-metal competitive transport across a bulk chloroform membrane employing **5** and **9** as ionophores; metal ion transport fluxes for seven-metal competitive transport across a polymer inclusion membrane employing **9** as ionophore; metal ion percent extraction in seven-metal competitive (water–chloroform) extraction employing **9** as extractant. See http://www.rsc.org/suppdata/dt/b2/b206106f/

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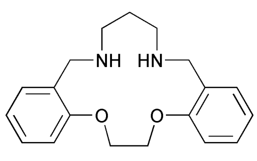

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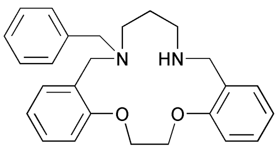

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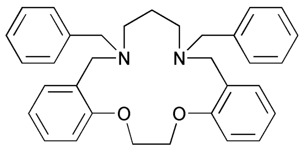

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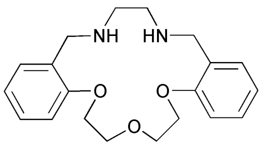

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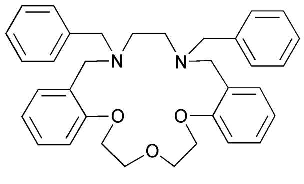

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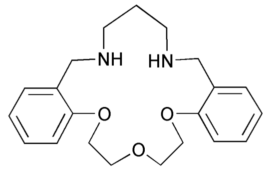

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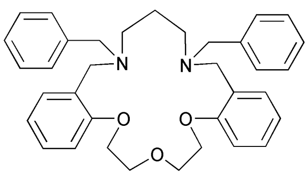

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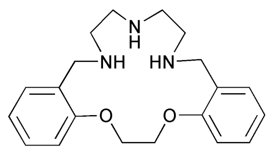

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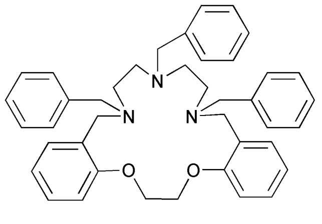

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Such a mechanism for achieving metal ion recognition was termed '*selective detuning*' – on benzylation the parent ring has effectively been 'detuned' towards all of the ions investigated except silver(I). We have since documented similar behaviour towards silver for other N-benzylated amine-containing (mixed donor) macrocyclic ligands.[4] While the origin of such behaviour is clearly less than straight-forward,[17] it is noted that particular tertiary amines have been shown previously to bind more strongly to silver(I) than do secondary amines and that the relative binding strengths can be solvent dependent.[18] A motivation for the present study was thus to both document and evaluate the concept of 'selective detuning' in the context of metal complexation by the above N-benzylated ligand series.

Experimental

Where available, all commercial reagents were of analytical reagent grade. The electrospray ionisation mass spectrum was obtained on a Finnigan Mat LCQ spectrometer.

Macrocycle and complex synthesis

The synthesis and characterisation of the benzylated macrocyclic ligands **2**, **3**, **5**, **7** and **9** have been described elsewhere.[9]

[Ag(5)]ClO$_4$. Silver perchlorate (0.1 g) in acetonitrile (10 cm^3) was added to a stirred solution (10 cm^3) of **5** in acetonitrile at room temperature. Stirring was continued for 30 minutes. The solution was filtered and allowed to stand at room temperature in the absence of light. Colourless crystals separated from the solution (Found: C, 55.9; H, 5.3; N, 3.5. $C_{34}H_{38}AgClN_2O_7$ requires C, 55.9; H, 5.3; N, 3.8%). Mass spectrum (e.s.) parent peak $[Ag(\mathbf{5})]^+$, *m*/*z* 629.

Stability constants

The protonation constants and metal stability constants (Table 1) were determined by potentiometric (pH) titration as described previously.[1]

All metal complex log *K* values are the mean of between two and five individual determinations at varying metal : macrocycle ratios. All measurements were performed in 95% methanol at 25 ± 0.1 °C. Analytical grade methanol was fractionated and distilled over magnesium before use. As was the case in a number of previous investigations, the methanol–water (95 : 5) solvent system was employed since its use helps to overcome the general low solubility of ligands of the present type (and/or their metal complexes) in water. The potentiometric titration apparatus consisted of a water-jacketed titration vessel and a water-jacketed calomel reference electrode, connected by a salt bridge. A Philips glass electrode (GA-110) was used for all pH measurements. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the background electrolyte. This solution was also used in the salt bridge, while the calomel reference contained tetraethylammonium perchlorate (0.09 mol dm^{-3}) and tetraethylammonium chloride (0.01 mol dm^{-3}) in 95% methanol. Methanol-saturated nitrogen was bubbled through the solution in the measuring cell; tetraethylammonium hydroxide solution was introduced into the cell using a Metrohm Dosimat 665 automatic titration apparatus under PC control. A Corning model 130 Research pH meter was employed for the pH determinations. Individual stability measurements were performed on duplicate sets of the potentiometric apparatus; each apparatus was calibrated daily by titration with a solution of standard base. In nearly all cases it was not possible to obtain complete titration curves because of either precipitation or competing hydrolysis reactions. The titration data corresponding to the lower portions of respective titration curves refined satisfactorily assuming 1 : 1 metal to macrocycle complexation.

Membrane transport and solvent extraction experiments

Bulk membrane transport (water/chloroform/water) experiments employed a 'concentric cell' in which the aqueous source phase (10 cm^3) and receiving phase (30 cm^3) were separated by a chloroform phase (50 cm^3). Details of the cell design have been reported.[19] For each experiment both aqueous phases and the chloroform phase were stirred separately at 10 revolutions min^{-1}; the cell was enclosed by a water jacket and thermostatted at 25 °C. In each case the aqueous source phase (buffered at pH 4.9 ± 0.1; acetic acid/sodium acetate buffer) contained a mixture of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) nitrates, each at a concentration of 10^{-2} mol dm^{-3}. The chloroform phase contained the macrocycle (1×10^{-3} mol dm^{-3}) as well as hexadecanoic acid (4×10^{-3} mol dm^{-3}). A major role of the latter is to aid the transport process by providing a lipophilic counter ion in the organic phase (after proton loss to the aqueous source phase) for charge neutralisation of the metal cation being transported; in this manner the need for uptake of lipophobic nitrate anions into the organic phase is avoided. The receiving phase was buffered at pH 3.0 (formic acid/sodium formate buffer). All transport runs were terminated after 24 hours and atomic absorption spectroscopy was used to determine the amount of metal ion transported over this period. The transport fluxes are in mol 24 h^{-1} and represent mean values measured over 24 h.

Table 1 Ligand protonation constants and metal stability constants (ML^{n+}) for **1**–**9** in 95% methanol; I = 0.1 mol dm^{-3}, $(C_2H_5)_4NClO_4$, 25 °C[a]

				$\log K_{ML}$						
Ligand	log K_1	log K_2	log K_3	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Cd^{II}	Ag^{I}	Pb^{II}
1	9.85[b]	6.78[b]		<3.6[b]	4.8[b]	7.3[b]	<4.5[b]	<4[b]	–[c]	–[c]
2	9.71	4.64		<4	<4	6.4	<4	<4	4.4	5.0
3	8.71	5.09		<4	<4	5.2	<4	<4	4.0	4.2
4	9.24[d]	6.06[d]		4.6[d]	6.2[d]	9.7[d]	4.7[e]	5.2[e]	6.7[e]	4.9[e]
5	8.96	3.24		<4	<4	5.4	<4	<4	8.9	4.4
6	10.24[d]	7.37[d]		<4.2[d]	4.4[d]	7.7[d]	<5[e]	4.1[e]	6.0[e]	6.1[e]
7	8.96	5.82		<4	<4	5.3	<4	<4	5.1	≈4.4
8	9.69[f]	8.45[f]	≈2.01[f]	7.7[f]	10.0[f]	14.2[g]	7.5[h]	8.7[h]	8.7[i]	8.1[i]
9	8.80	5.88	≈1.53	<4	<4	–[j]	<4	<4	9.3	4.3

[a] All ligand log K values ±0.05 and metal complex values ±0.1 unless otherwise indicated. [b] Values from ref. 10. [c] Value not available. [d] Values from ref. 11. [e] Values from ref. 12. [f] Values from ref. 13. [g] Values from ref. 14. [h] Values from ref. 15. [i] Values from ref. 16. [j] Precipitation prevented log K determination.

The polymer inclusion membrane transport studies used a cell design based on that described by Izatt *et al.*[20] The aqueous source (130 cm^3) and receiving phases (130 cm^3) were identical to those used for the bulk membrane studies; both phases were stirred at 50 cycles min^{-1}. Each transport experiment was terminated after 24 h. Construction of the polymer membrane was based on a procedure described by Lamb *et al.*;[21] it was cast in a 4 cm petri dish by addition of a solution (9 cm^3) that had been prepared in the following manner. Cellulose triacetate (0.3125 g) was dissolved in dichloromethane (25 cm^{-3}) and 4 cm^3 of this solution was added to a solution consisting of 3 cm^3 of a 0.01 mol dm^{-3} dichloromethane solution of **9**, 1.5 cm^3 of a 10 percent (v/v) dichloromethane solution of 2-nitrophenyloctylether and 0.5 cm^3 of a 10 percent (v/v) dichloromethane solution of tris(2-butoxyethyl)phosphate (proportionally smaller quantities were employed to construct the 'thin' polymer membrane mentioned in the Results and discussion section). The resulting solution was left to evaporate in the petri dish for 18 h. After this time, the gel-like polymer membrane was removed and clamped between two half-cell compartments that subsequently served to contain the aqueous source and receiving phases.

Transport fluxes of less than 20 × 10^{-7} mol 24 h^{-1} are within experimental error of zero and were ignored in the present studies.

The solvent extraction experiments involving **9** were performed by shaking equal volumes of an aqueous phase and a chloroform phase for one hour (at 22 °C). For the competitive seven-metal extractions the aqueous phase and chloroform phases were similar to those employed for the corresponding transport run. For the single metal runs the aqueous phase contained each one of the seven metals in turn at a concentration of ≈10^{-2} mol dm^{-3}; the chloroform phase was identical to that for the competitive runs.

Structure determination, [Ag(5)](ClO$_4$)

A full sphere of CCD area-detector diffractometer data was measured (Bruker AXS instrument; monochromatic Mo-Kα radiation, λ = 0.71073 Å; ω-scans, $2\theta_{max}$ = 58°; T *ca.* 300 K), 39106 reflections merging to 15960 unique (R_{int} = 0.024) after 'empirical'/multiscan absorption correction (proprietary software), 9244 with $F > 4\sigma(F)$ being used in the full matrix least squares refinement. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})H being constrained at estimates. The oxygen atoms of both anions were modelled as disordered over two sets of sites, those for anion 2 rotationally disordered about Cl(2)–O(21) (occupancies: 0.60(1), 0.58(2) and complements); methylene groups lnl (n = 1, 2) of cation 1 were also disordered over two sets of sites, occupancies 0.82(1) and complement. Conventional residuals on $|F|$ at convergence were R = 0.040, R_w = 0.040. Neutral atom complex scattering factors were used within the context of the Xtal 3.5 program system.[22] Pertinent results are presented below and in Table 2 and Fig. 1; the latter figure shows 20% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Crystal data. $C_{34}H_{38}AgClN_2O_7$, M = 730.0, triclinic, space group $P1$ (C^1_i, no. 2), a = 11.932(1), b = 14.663(1), c = 19.441(2) Å, α = 98.247(2), β = 95.733(2), γ = 94.399(2)°, V = 3335 Å^3. D_c (Z = 4) = 1.45$_4$ g cm^{-3}. μ_{Mo} = 7.3 cm^{-1}; specimen: 0.17 × 0.13 × 0.07 cm; 'T'$_{min/max}$ = 0.83, 0.93.

CCDC reference number 188417.

See http://www.rsc.org/suppdata/dt/b2/b206106f/ for crystallographic data in CIF or other electronic format.

Results and discussion

The interaction of the benzylated derivatives **2**, **3**, **5**, **7** and **9** with the previously mentioned transition and post-transition metal ions has been investigated by means of potentiometric stability constant determinations, bulk membrane transport experiments and, in one case, an X-ray structure determination.

Stability constant determinations

The protonation constants and 1 : 1 (metal : ligand) metal stability constants (95% methanol, I = 0.1 mol dm^{-3}; Et_4NClO_4) for the respective benzylated derivatives are summarised in Table 1. For comparison, previously reported protonation and stability data for the parent (unsubstituted) mixed-donor systems **1**, **4**, **6** and **8**, measured under identical conditions, are also included in Table 1.[10–16]

The log K values for the benzylated derivatives (**2**, **3**, **5**, **7** and **9**) of the above metal ions exhibit some clear differences when compared with those obtained for the complexes of the parent ligands (**1**, **4**, **6** and **8**). Thus, the magnitudes of the respective log K values are in most instances strongly affected by the addition of the benzyl substituents to the corresponding parent ligands. For example, inspection of the log K values for **1**, **2** and **3** (incorporating zero, one and two benzyl substituents) indicates that benzylation lowers the values for copper(II) and lead(II) complexation, in accordance with increased steric hindrance inhibiting metal ion binding. For silver(I) a similar trend is evident on passing from the monobenzylated derivative **2** to the dibenzylated derivative **3** but the difference between these two is significantly less marked (0.4 log units) than in the case of copper (1.2 log units) or lead (0.8 log units). As a consequence, dibenzylation of **1** results in silver binding being somewhat enhanced (in relative terms) compared with the binding of copper(II) or lead(II). On moving to **5**, incorporating a dimethylene bridge between the nitrogen donors as well as an additional oxygen donor in its backbone, clear selectivity for silver(I) is observed. Relative to its parent **4**, the stabilities of all complexes of the present metal ion series are lowered except for silver whose complex instead shows a stability enhancement of

Table 2 Selected geometries, [Ag(**5**)](ClO_4)

(a) The silver(I) environments[a]

Atom	r/Å	O(n13)	O(n23)	N(n15)	N(n25)
O(n0)	2.360(3)	67.3(1)	66.0(1)	143.1(1)	135.6(1)
	2.388(3)	68.1(1)	66.6(1)	142.2(1)	137.9(1)
O(n13)	2.688(3)		132.3(1)	81.4(1)	134.3(1)
	2.584(4)		133.9(1)	80.0(1)	136.7(1)
O(n23)	2.753(3)			145.7(1)	78.1(1)
	2.711(4)			145.2(1)	77.8(1)
N(n15)	2.346(3)				80.5(1)
	2.367(4)				79.6(1)
N(n25)	2.369(4)				
	2.375(4)				

(b) Ligand string torsion angles (°)[b]

String	11	12	21	22
1–O(0)–1–2	−174.0(6), −177(3)	164.3(6), 177(3)	−170.6(6)	169.5(6)
O(0)–1–2–O(3)	−67.2(7), 41(3)	53.5(8), −63(3)	−62.8(8)	51.4(9)
1–2–O(3)–31	155.1(3), 98(2)	81.1(7)	159.0(6)	84.6(8)
2–O(3)–31–36	−176.4(4)	−178.0(4)	176.4(5)	179.6(5)
O(3)–31–36–4	−3.9(6)	−1.8(6)	−6.5(6)	−4.5(6)
31–36–4–N(5)	83.9(5)	82.4(5)	78.5(6)	81.5(5)
36–4–N(5)–6	64.1(4)	72.5(5)	69.7(5)	76.4(5)
4–N(5)–6–*6*	−159.6(4)	−163.4(4)	−162.2(4)	−161.3(4)
N(5)–6–*6*–*N(5)*	65.4(5)	–	62.2(6)	–

(c) Coordination plane parameters[c]

	Plane 1[d]		Plane 2	
String	11	12	21	22
Atom deviation				
δAg	−0.114(1)		−0.067(1)	
δC(1)	0.487(10)	−1.219(9)	0.399(10)	−1.086(10)
δC(2)	1.782(8)	−1.423(8)	1.642(10)	−1.260(10)
δO(3)	1.604(5)	−1.403(5)	1.479(6)	−1.294(6)
δC(31)	2.659(5)	−2.508(6)	2.590(6)	−2.456(7)
δC(36)	2.375(6)	−2.330(6)	2.355(6)	−2.327(6)
δC(4)	1.038(6)	−1.029(7)	0.999(7)	−1.020(7)
δC(5)	−1.292(6)	1.317(7)	−1.349(7)	1.341(7)
δC(51)	−1.917(7)	1.886(8)	−1.946(8)	1.854(7)
δC(6)	0.375(5)	−0.366(5)	0.368(6)	−0.336(6)
Interplanar dihedral angles				
θ_3	73.0(2)	72.5(2)	81.3(2)	76.7(2)
θ_5	31.8(2)	22.5(2)	32.3(2)	22.3(2)
$\theta_{3/5}$	78.1(3)	56.8(3)	88.1(3)	82.2(3)

[a] Values for cation $n = 2$ are given below those for cation $n = 1$; r/Å is the silver–ligand atom distance, other entries in the matrix being the angles (°) subtended by the relevant atoms at the head of the row and column. [b] Double entries under strings 1m are for the primed components of the disordered section. Carbon atoms are denoted by number only within string nm. *Italicized* atoms lie in the other section. [c] δÅ are atom deviations from the O(0)N_2 plane about each silver atom; θ_n ° are interplanar dihedral angles to the phenyl C_6 rings, $\theta_{3.5}$ between them. [d] Deviations of C(111', 121') are 1.37(4), −0.20(4) Å.

2.2 log units. Indeed, the affinity of **5** for silver is some 3.5 log units greater than for the next metal ion (copper) and equal to or greater than 4.5 log units for the remaining metal ions investigated. Interestingly, when the dimethylene bridge between nitrogens in **5** is replaced by a trimethylene bridge to yield **7** (giving rise to the prospect of a less stable 6-membered chelate ring rather than 5-membered chelate ring on metal binding), the relative affinity for silver(I) is reduced; now the affinity for copper(II) falls slightly ahead of that for silver. However, selectivity for silver over the remaining ions is maintained.

It is of interest that a change in the donor set from O_3N_2 in **5** to O_2N_3 in **9** (both rings are 17-membered) leads to only a modest increase in stability of the corresponding silver complexes, while generally similar behaviour is maintained towards the remaining metal ions.

Finally, comparison of the log K values for **8** with those for its tribenzylated analogue **9** provides a further example of selective detuning.[3] Unfortunately precipitation during the attempted determination of the log K value for the copper(II) complex of **9** precluded a successful determination for this ion. Nevertheless, **9** exhibits discrimination of 10^5 for silver(I) over lead(II), with discrimination over cobalt(II), nickel(II), zinc(II) and cadmium(II) being even more impressive at > $10^{5.3}$.

Membrane transport and related solvent extraction studies

Competitive mixed-metal transport experiments have been undertaken across a bulk chloroform membrane incorporating a millimolar concentration of ionophore chosen from **2**, **3**, **5**, **7** or **9**. 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), each at 10^{-2} mol dm^{-3}. As mentioned in the Experimental section, transport was performed against a back gradient of protons, maintained by buffering the source and receiving phases at pH 4.9 and 3.0, respectively. Under the conditions employed, **2**, **3** and **7** were observed to be inefficient ionophores for all the metal ions mentioned above; in each case negligible transport (transport fluxes of less than 20×10^{-7} mol 24 h^{-1}) occurred. The transport results for **5** and **9** indicated that, under the conditions

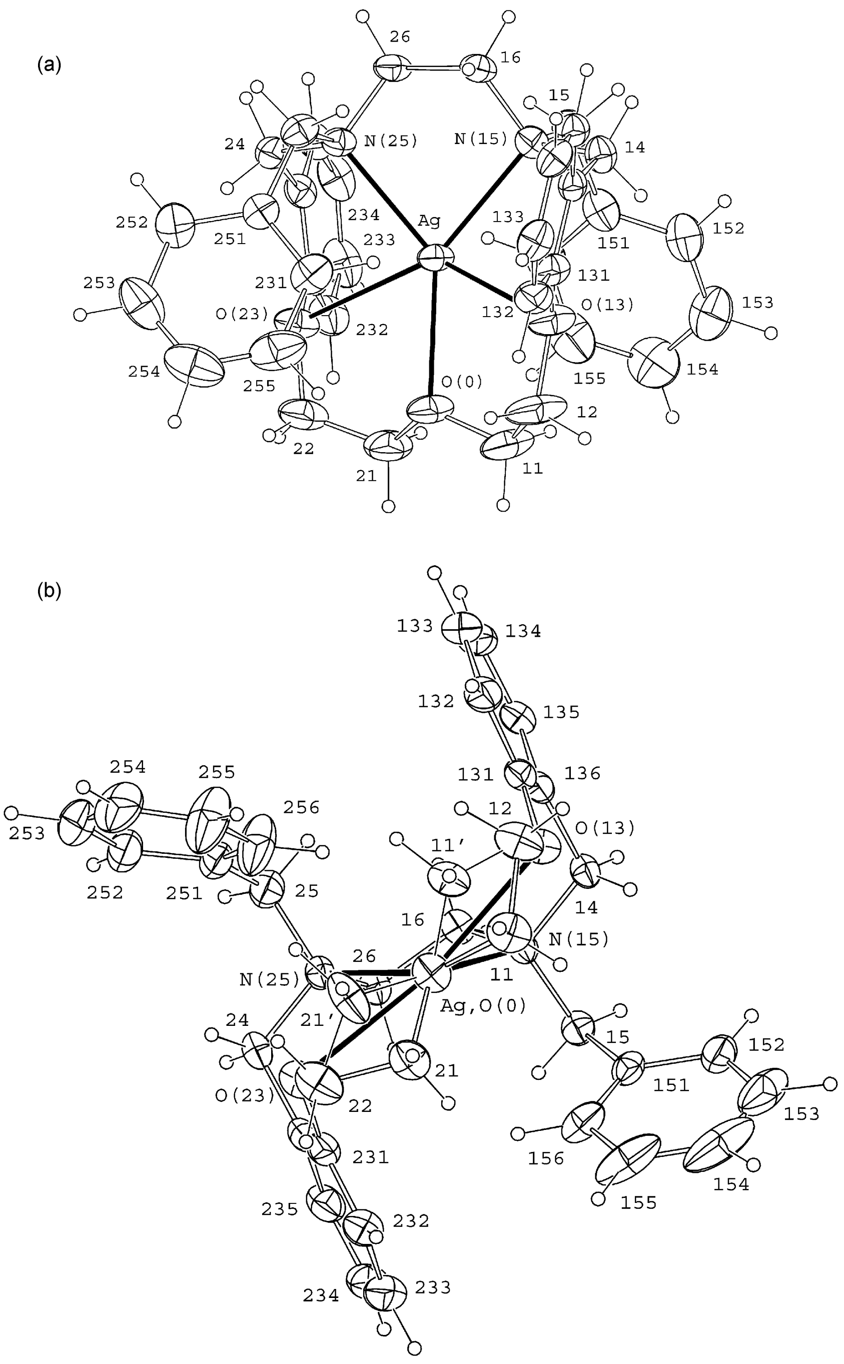

Fig. 1 Projections of cations 2 (a) and 1 (b), normal to and down the Ag–O(0) bond respectively showing the ligand conformations and the nature of the disorder found in cation 1.

employed, sole selectivity for silver(I) was observed in each case – within experimental error no amount of any of the other six metals present in the source phase were observed in the receiving phase after 24 h. The respective silver(I) transport fluxes were (**5**) 3.82 × 10^{-5} and (**9**) 3.98 × 10^{-5} mol 24 h^{-1}. Even though theory does not dictate that it need be the case,[23] these results parallel those from the log *K* studies discussed above in that, overall, **2**, **3** and **7** tend to yield significantly lower metal complex stabilities than the remaining benzylated ligands **5** and **9**. Similarly, from the available stability data, both **5** and **9** show their strongest affinity for silver(I) and both these 17-membered rings also exhibit *sole* transport selectivity for this ion over the remaining six metal ions present in the respective source phases.

In view of the above results a parallel study was instigated in which both **5** and **9** were chosen as ionophores for incorporation in polymer inclusion membranes based on a cellulose triacetate matrix. Details of the preparation of the membrane and of the cell employed are given in the Experimental section. In each case identical source and receiving phases were employed to those used in the liquid membrane studies; both liquid phases were stirred, and each experiment was again run for 24 hours. For the initial runs a membrane thickness of ≈1.5 mm was employed.

Once again, under the conditions employed, similar sole selectivity for silver(I) over the other six metals present was observed for the respective polymer inclusion membrane systems incorporating **5** and **9**. Although it is clearly not valid to compare the transport efficiencies of the liquid and polymer membrane transport types in a quantitative sense, qualitatively both systems based on **5** and **9** yielded significant transport rates coupled with high selectivity for silver(I) over the other ions present in the respective source phases. In order to gauge the influence of polymer membrane thickness on transport behaviour, the above polymer membrane experiment was repeated in which the membrane incorporating **9** was replaced with one whose thickness had been reduced by about one third to ≈1 mm. This had little effect on the performance of the system – excellent silver(I) selectivity and transport efficiency was once again maintained in this case. In keeping with the results so far, when **7** (incorporating three methylene groups between its oxygen donors) replaced **5** (or **9**) as the ionophore in the polymer membrane system, transport efficiency dropped dramatically, with negligible transport of any metal occurring over the 24 hours employed for the experiment.

A competitive (seven) metal solvent extraction study incorporating the tribenzylated derivative **9** as extractant was also carried out. The aqueous source phase and chloroform phase conditions were similar to those used in the bulk membrane transport runs. The selectivity for silver exhibited by this ligand in the transport studies was once again maintained in this study, although smaller amounts of copper(II), cadmium(II) and a trace of zinc(II) were also extracted. A second set of comparative extraction experiments were carried out under related conditions in which the source phase contained only a single metal ion (at 0.01 mol dm^{-3}), chosen in turn from each of the above seven metals. Once again, **9** was found to be a significantly better extractant for silver(I) than any of the other six ions investigated.

X-Ray study

The results of the room-temperature single crystal X-ray study are consistent, in terms of stoichiometry and connectivity, with the formulation of $[Ag(\mathbf{5})](ClO_4)$ as given, two formula units devoid of crystallographic symmetry comprising the asymmetric unit of the structure. The metal atom environments in the two cations are similar (Table 2(a)), the dominant feature of the five-coordinate arrangement about the metal being the trigonal planar array formed by the central oxygen and the two nitrogen atoms, all at similar distances from the metal (range: 2.346(3)–2.388(3) Å) with associated angle sums of $359_{.2}$, $359_{.7}$°. The other two oxygen atoms are more loosely bound with greater divergences in 'equivalent' distances and angles.

The latter variations may be a concomitant of a variation in the ligand conformations. Shorn of the $(CH_2)_2$ bridges to either side of the central oxygen of each ligand, the remainder of each cation comprises an array whereby the remaining bridges and their substituents comprise aggregates whose deviations from the $O(0)N_2$ planes constitute chiral arrays, very similar in their defining components (Fig. 1; Table 2), and, excepting differences in the inclinations of rings 15*n* *vis-à-vis* the $O(0)N_2$ plane and each other, comprising good approaches to 2-symmetry in both cases. Inclusion of the $(CH_2)_2$ bridges to either side of O(0) in conformity with this symmetry would require a trigonal planar O(0); in reality, these bridges are disposed in a manner which breaks this symmetry, the O(0) environment being pyramidal. This situation is clear-cut in cation 2 (Fig. 1(a)); in cation 1, minor disorder, seemingly concerted, is found in the two bridges in C(*n*1), the disordered components, lying to the other side of the $O(0)N_2$ plane also not in conformity with 2-symmetry (Fig. 1(b)). The disorder has no apparent ramifications further afield; disorder is also found in the anions, the components having similar site occupancies in the two independent moieties, different from that of the cations.

Concluding remarks

The log *K*, transport and extraction results clearly parallel each other for the present ligand series, with evidence for enhanced relative stability (and associated selectivity) being evident for silver(I) complexation over complexation of the range of other transition and post-transition metals investigated. Within this context, the concept of 'selective detuning' as a means of achieving metal ion selectivity is well exemplified by the results for silver(I) involving the 17-membered membered, benzylated derivatives **5** and **9**.

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