Macrocyclic Ligand Design. Effect of Donor-set and Ring-size Variation on Silver(I)/Lead(II) Discrimination within an Extended Series of Dibenzo Substituted Rings†

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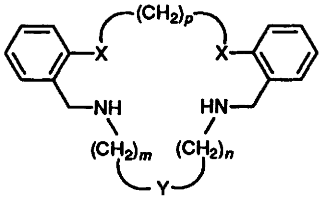
The effect of systematic variation of the donor-atom set within dibenzo-substituted, 17- to 20-membered macrocycles on their ability to discriminate between silver(I) and lead(II) has been investigated. The log *K* values for the respective complexes, determined potentiometrically in 95% methanol ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4), show that successive replacement of either nitrogen or oxygen heteroatoms by thioether donors leads to increasing affinity for silver(I) relative to lead(II), as does the incorporation of an 'aliphatic' NON or NSN donor sequence in the structure. For the 17-membered system incorporating a S_2N_2S-donor set, exceptional discrimination (of the order of 10^9) was observed. The characterisation of selected complexes has included the crystal structure of the silver perchlorate complex of the 17-membered ON_2S_2 macrocycle (L^{17}). The silver ion in $[AgL^{17}]ClO_4$ has a very distorted trigonal-bipyramidal geometry with all metal to donor bond lengths appearing normal. The complex crystallises in the monoclinic space group $P2_1/n$ with lattice parameters $a = 19.410(4)$, $b = 9.602(2)$, $c = 12.747(3)$ Å, $\beta = 103.67(2)°$ and $Z = 4$.

Over recent years considerable effort has been directed towards the design and synthesis of new macrocycles in order to investigate their co-ordination preferences towards particular transition and post-transition ions.[1] We have developed strategies for achieving discrimination between ions of this type (largely using mixed-donor rings) and, more importantly, for understanding the nature of the discrimination when it is attained.[2]

One approach in the above studies has been to investigate metal-ion complexation across a matrix (or part of a matrix) of related macrocycles and to search for stability maxima at different points within the matrix. The structures comprising the matrix normally bear a stepwise relationship to each other. For a given investigation, not all members of such a matrix need necessarily be synthesised. Nevertheless, our experience is that metal-ion discrimination effects are usually much better understood when an investigation of the co-ordination chemistry of the macrocyclic system of interest is undertaken in conjunction with stability measurements.[2]

Although isolated examples of macrocyclic ligands displaying significant discrimination for silver(I) over lead(II) are known,[3] in general less attention has been given to the factors influencing such discrimination. We now report an extension of our previous studies[2] in which the variation of the donor set and macrocycle ring size within the series L^1–L^{20} has been used to investigate the factors influencing discrimination for silver(I) over lead(II), metals which occur together in nature.



	X	Y	*m*	*n*	*p*
L^1	NH	NH	2	2	2
L^2	NH	O	2	2	2
L^3	NH	S	2	2	2
L^4	O	NH	2	2	1
L^5	O	NH	2	2	2
L^6	O	NH	2	3	2
L^7	O	NH	3	3	2
L^8	O	NH	2	2	4
L^9	O	O	2	2	2
L^{10}	O	O	2	2	4
L^{11}	O	S	2	2	1
L^{12}	O	S	2	2	2
L^{13}	O	S	3	3	2
L^{14}	O	S	2	2	4
L^{15}	S	NH	2	2	1
L^{16}	S	NH	2	2	2
L^{17}	S	O	2	2	2
L^{18}	S	S	2	2	1
L^{19}	S	S	2	2	2
L^{20}	S	S	2	2	3

Experimental

Physical measurements were performed as described previously.[4] Stability constants were determined potentiometrically in 95% methanol ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4) as described elsewhere[4] and the data processed using local versions of MINIQUAD[5] or SUPERQUAD.[6] Quoted log *K* values are the mean of at least two (and up to six) individual determinations at

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

different metal:macrocycle ratios. Macrocycle protonation constants for L^1–L^{20} have been reported previously.[7] The syntheses and characterisation of the macrocycles used in this study have also been described elsewhere.[8]

Synthesis of Metal Complexes.—All complexes were dried over P_4O_{10} before analysis. The silver complexes of the sulfur-containing macrocycles tended to be light sensitive and hence were prepared and stored in the near absence of light. **CAUTION**: the respective perchlorate and nitrate species are potentially explosive and appropriate precautions should be taken during their preparation, handling and storage.

$[AgL^5]ClO_4 \cdot 0.5H_2O$. Macrocycle L^5 (0.34 g) in hot ethanol (10 cm^3) was added to a stirred hot solution of silver(I) perchlorate hydrate (0.23 g) in hot ethanol (10 cm^3). The off-white solid which formed was isolated and washed with ethanol; yield 0.46 g (Found: C, 43.5; H, 5.5; N, 7.6. $C_{20}H_{28}AgClN_3O_{6.5}$ requires C, 43.1; H, 5.1; N, 7.5%). The complex $[AgL^6]ClO_4$ was prepared similarly, as a white solid; yield 0.2 g (Found: C, 44.8; H, 5.3; N, 7.4. $C_{21}H_{29}AgClN_3O_6$ requires C, 44.8; H, 5.2; N, 7.5%).

$[AgL^{12}]ClO_4 \cdot H_2O$. Silver nitrate (0.06 g) in acetonitrile (15 cm^3) and lithium perchlorate (0.05 g) were added to a boiling solution of L^{12} (0.10 g) in acetonitrile (15 cm^3). The volume of the solution was reduced to 10 cm^3; the solution was then cooled and filtered. On standing, crystals of the product separated; yield 0.06 g (Found: C, 41.2; H, 4.5; N, 5.0. $C_{20}H_{28}AgClN_2O_7S$ requires C, 41.2; H, 4.8; N, 4.8%).

Similarly prepared were: $[AgL^{15}]ClO_4 \cdot 0.67H_2O$, white translucent crystals, yield 0.07 g (Found: C, 39.3; H, 4.3; N, 7.3. $C_{19}H_{26.33}AgClN_3O_{4.67}S_2$ requires C, 39.4; H, 4.6; N, 7.3%), FAB mass spectrum *m/z* 466, $[AgL^{15}]^+$; $[AgL^{18}]ClO_4 \cdot 0.5H_2O$, crystalline flakes, yield 0.04 g (Found: C, 38.4; H, 4.1; N, 4.8. $C_{19}H_{25}AgClN_2O_{4.5}S_3$ requires C, 38.5; H, 4.3; N, 4.7%), FAB mass spectrum *m/z* 485, $[AgL^{18}]^+$; and $[AgL^{19}]ClO_4$, fine colourless needles, yield 0.06 g (Found: C, 40.1; H, 4.4; N, 5.3. $C_{20}H_{26}AgClN_2O_4S_3$ requires C, 40.3; H, 4.4; N, 4.7%), FAB mass spectrum *m/z* 497, $[AgL^{19}]^+$.

$[Pb(NO_3)L^5]NO_3 \cdot 2H_2O$. Lead(II) nitrate trihydrate (0.33 g) was suspended in methanol (30 cm^3). To this suspension was added L^5 (0.33 g) in hot methanol (30 cm^3) and, on heating the mixture to the boiling point, the lead(II) nitrate trihydrate dissolved. The solution was allowed to stand at room temperature and the product separated as an off-white solid which was filtered off and washed with methanol; yield 0.41 g (Found: C, 33.8; H, 4.0; N, 9.9. $C_{20}H_{31}N_5O_{10}Pb$ requires C, 33.9; H, 4.4; N, 9.9%). An excess of lithium perchlorate in hot methanol (10 cm^3) was added to the heated filtrate from the above preparation. On standing $[Pb(NO_3)L^5]ClO_4 \cdot H_2O$ separated as an off-white solid (Found: C, 32.6; H, 4.1; N, 7.4. $C_{20}H_{29}ClN_4O_{10}Pb$ requires C, 33.0; H, 4.0; N, 7.7%). The complex $[Pb(NO_3)L^6]NO_3$ was prepared similarly as an off-white solid; yield 0.5 g (Found: C, 36.9; H, 4.3; N, 10.0. $C_{21}H_{29}N_5O_8Pb$ requires C, 36.7; H, 4.3; N, 10.2%).

$[PbL^{16}][ClO_4]_2$. Lead perchlorate trihydrate (0.125 g) in ethanol (15 cm^3) was added to a stirred boiling solution of L^{16} (0.10 g) in ethanol (25 cm^3). The solution was filtered and cooled whereupon the product separated as a fine white powder which was recrystallised from ethanol; yield 0.03 g (Found: C, 31.0; H, 3.6; N, 5.4. $C_{20}H_{27}Cl_2N_3O_8PbS_2$ requires C, 30.8; H, 3.5; N, 5.4%). FAB mass spectrum: *m/z* 680, $[Pb(ClO_4)L^{16}]^+$.

Structure Solution and Refinement.—Crystals of $[AgL^{17}]ClO_4$, suitable for an X-ray study, were obtained by slow evaporation of an acetonitrile solution containing a stoichiometric mixture of L^{17} and silver perchlorate hydrate. The FAB mass spectrum (positive ion) of the product gave *m/z* 481, corresponding to $[AgL^{17}]^+$.

Crystal data. $C_{20}H_{26}AgClN_2O_5S_2$, $M = 581.68$, monoclinic, space group $P2_1/n$, $a = 19.410(4)$, $b = 9.602(2)$, $c = 12.747(3)$ Å, $\beta = 103.67(2)°$, $U = 2308.38$ Å^3, $F(000) = 1184$, μ(Mo-Kα) = 10.92 cm^{-1}, $Z = 4$, $D_c = 1.67$ g cm^{-3}. A crystal of size of 0.48 × 0.43 × 0.35 mm was employed.

Data were collected at room temperature on a Philips PW1100 diffractometer in the range θ 3–25°, with a scan width of 0.90° using the technique described previously.[9] Equivalent reflections were merged to give 2761 data with $I \geqslant 3\sigma(I)$. The coordinates of the metal atom were deduced from a Patterson synthesis[10] and the remaining non-hydrogen atoms located from subsequent Fourier-difference syntheses. The oxygen atoms of the perchlorate were resolved into two distinct sets corresponding to different orientations; these were assigned site-occupancy factors of 0.6 and 0.4. Neither perchlorate position is within bonding distance of the silver atom [the closest contact to the silver is O(11) at 3.236 Å]. All hydrogen atoms were located in a Fourier-difference synthesis calculated using data with $\sin\theta < 0.35$. These were included in the structure-factor calculations with fixed thermal parameters of 0.08 Å^2 but only the fractional coordinates of the *N*-bonded H atoms were refined. Empirical absorption corrections[11] were applied after initial refinement. All non-hydrogen atoms except the oxygens in the second orientation of the perchlorate ion were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement. The refinement converged at $R = 0.034$ and $R' = 0.37$ where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$ using a weighting scheme of $w = 1/[\sigma^2(F_o)]$. Atom positional parameters and selected bond lengths and angles are given in Tables 2 and 3 while a diagram of the structure is given in Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Isolation of Selected Metal Complexes.—In order to compare solid-state and solution stoichiometries and also to obtain crystalline products which might prove suitable for X-ray structural analysis, a selection of silver(I) and lead(II) complexes of the present macrocycles were synthesised. The perchlorate-containing compounds showed perchlorate stretching absorptions in their respective infrared spectra which were not always completely symmetrical. However, in no case was there firm evidence for perchlorate co-ordination. The spectra also showed the expected bands arising from the (co-ordinated) amine groups and water (when the latter was suggested to be present from the analytical data).

The conductance data for the silver complexes in methanol (where soluble) indicate the absence of co-ordination of the perchlorate ion in each case. All values fall in the expected range (80–115 S cm^2 mol^{-1})[14] for a 1:1 electrolyte in this solvent. In the case of lead, conductance data in methanol were obtainable for $[Pb(NO_3)L^6]NO_3$ (111 S cm^2 mol^{-1}) and $[PbL^{16}][ClO_4]_2$ (160 S cm^2 mol^{-1}). The values confirm that the former complex is a 1:1 electrolyte under the conditions of measurement while the value for the latter complex is at the lower end of the range for a 2:1 electrolyte (160–220 S cm^2 mol^{-1}).

Stability Constants.—The log *K* values determined as part of the present study are summarised in Table 1; the table also contains some stability constants for the complexes of particular 17-membered rings which were reported previously.[15] A number of structure–function relationships are evident from the data which not only serve to rationalise the present behaviour but which should also be useful as a guide for the design of new ligands for the recognition of these metals.

It is instructive to consider first the effect of variation of chelate-ring size (and concomitant macrocyclic ring size) within the systems investigated (Table 1). Although based on limited data, changing the number of methylene linkages in the NYN-donor string from *n* or *m* = 2 to *n* or *m* = 3, while the remainder of the ring remains unaltered, has only a relatively minor effect on the respective log *K* values for each metal ion.

Table 1 Stability constant data (ML^{n+}) for the silver(I) and lead(II) complexes of L^1–L^{20} [95% MeOH, I = 0.1 mol dm^{-3} (NEt_4ClO_4) at 25 °C][a]

			log *K*		
	Donor set	Ring size	AgL	PbL	Δ log *K*
L^1	N_5	17	10.3	9.4	0.9
L^2	N_4O	17	9.8	6.7	3.1
L^3	N_4S	17	10.8	5.9	4.9
L^4	O_2N_3	16	7.7	7.8(2)	−0.1
L^5	O_2N_3	17	8.7[b]	8.1[b]	0.6
L^6	O_2N_3	18	8.8	7.9	0.9
L^7	O_2N_3	19	*c*	7.6	—
L^8	O_2N_3	19	7.2	7.5	−0.3
L^9	O_2N_2O	17	7.1[b]	5.5(2)[b]	1.6
L^{10}	O_2N_2O	19	*c*	6.2	—
L^{11}	O_2N_2S	16	7.7	4.6	3.1
L^{12}	O_2N_2S	17	8.6	4.5	4.1
L^{13}	O_2N_2S	19	≈8.5	*c*	—
L^{14}	O_2N_2S	19	7.8	5.9	1.9
L^{15}	S_2N_3	16	10.9(2)	7.0(2)	3.9
L^{16}	S_2N_3	17	≈11.7	8.0	≈3.7
L^{17}	S_2N_2O	17	10.3(2)[b]	≈3[b]	≈7.3
L^{18}	S_2N_2S	16	11.0(2)	≈3.1	≈7.9
L^{19}	S_2N_2S	17	12.4[b]	≈3[b]	≈9.4
L^{20}	S_2N_2S	18	10.9	≈3.5	≈7.2

[a] All values ±0.1 unless otherwise indicated in parentheses; approximate values represent values obtained for a limited set of titration points. [b] From ref. 15. In this paper the log *K* values for L^{12} and L^{16} above were inadvertently interchanged. [c] Precipitation.

However, variation of the $(CH_2)_p$ (p = 1–4) chain linking the X donors, while maintaining the remainder of the ring unchanged, results in the following log *K* trends. First, those systems with $p = 1$ are in each case less stable than the corresponding complexes with $p = 2$ or 3. This is not unexpected since co-ordination of the X donors in the former complexes will give rise to four-membered chelate rings which are normally less favoured than five- or six-membered ones. Similarly, for silver(I), the systems with $p = 4$ are less stable than when $p = 2$ or 3, presumably reflecting the formation of less favoured seven-membered chelate rings in these cases. However, this latter trend is not observed for lead: compare the respective log *K* values for the lead complexes of L^8, L^{10} and L^{14} with those of the corresponding macrocycles (containing the same donor sets) with $p = 2$ or 3. In each of L^8, L^{10} and L^{14} the $X(CH_2)_pX$ bridge incorporates four carbons. For the complex of L^8 the stability is only marginally decreased (relative to the values for the complexes of L^5 or L^6), while, perhaps surprisingly, it is increased for the complex of L^{10} (relative to that of L^9) and L^{14} (relative to that of L^{12}). This trend, may largely reflect the presence of long Pb–X bonds in these complexes (relative to the equivalent bonds in the corresponding silver complexes); long Pb–X bonds should be more able to accommodate larger chelate rings since this will enable reasonable 'bite' angles to be maintained at the central metal. Although X-ray-quality crystals were not obtained for the lead complexes of L^8, L^{10} and L^{14}, the previously reported structure of the lead(II) complex of L^{16} does indeed show very long Pb–S bonds of 3.175(4) and 3.141(3) Å.[15]

Considering now the effect on stability of variation of the donor-atom set. The interaction of silver(I) and lead(II) with the N_5-donor ring (L^1) or any of the O_2N_3-donor rings (L^4–L^8) in every case led to a stability difference between the respective complexes of less than a factor of 10. It is noted that the N_5 macrocycle (incorporating two anilino and three aliphatic amines) yields the highest absolute values with each metal, undoubtedly reflecting the relatively poor co-ordinating power of ether oxygen donors towards both metals.

Overall, the most stable lead complexes are those formed by the macrocycles which contain a secondary amine in the Y position (to yield an aliphatic N_3 backbone). That is, incorporation of either a thioether sulfur or an ether oxygen at this position results in a decrease in the stability of the corresponding lead(II) complex, with complexes incorporating Y = O tending to be more stable than those with Y = S. For a given ring size, a similar dependence of stability on donor-atom type is evident on variation of X across the series.

In contrast to the above behaviour, substitution of an O donor for the 'centre' NH in the N_3 string in L^5 (to yield L^9) leads to increased discrimination for silver over lead and it is evident that silver(I) shows a greater 'tolerance' for an $NHCH_2CH_2OCH_2CH_2NH$ string than does lead(II).

Since silver(I) is a b-class or 'soft' metal ion while lead(II) is borderline,[16] it was anticipated that the introduction of sulfur into the donor set would enhance the stability of the corresponding silver(I) complex relative to that of lead(II). Indeed, in previous studies, thioether-containing macrocycles have been demonstrated to show particular affinity for Ag^I.[3,17,18] In the case of the 16- and 17-membered rings, L^{11} and L^{12}, stability-constant differences of approximately 10^3–10^4 in favour of silver(I) were achieved (although, for the 19-membered ring L^{14}, the difference is less at $10^{1.9}$). Indeed, in an earlier calorimetric study of the interaction of silver(I) with macrocycles of the present type it was shown that the affinity of a thioether for silver(I) in acetonitrile is broadly similar to that of a secondary amine.[19] Inspection of the data in Table 1 indicates that the stabilities of the silver(I) complexes of macrocycles with a thioether donor at the Y position are in all cases close to the values for the corresponding complexes incorporating a secondary amine in this position.

The presence of a S_2N_3-donor set, as occurs in L^{15} and L^{16}, results in the expected increase in the absolute stability values of the corresponding silver(I) complexes. However, in accordance with our previous observation, the restoration of the N_3-donor string in these macrocycles also results in a rise in stability of the lead(II) species resulting in reduced discrimination for silver relative to the corresponding S_2N_2S-donor ligands L^{18}–L^{20} (see below). As expected the 17-membered, S_2N_2O-donor ring L^{17} gives rise to significantly increased discrimination for silver(I), further exemplifying the trends discussed so far.

Finally, very high discrimination is achieved by the final members of the series L^{18}–L^{20}, containing S_2N_2S-donor sets. Of these the 17-membered ring L^{19} yields maximum discrimination, in this case approximately 10^9 in favour of silver.

X-Ray Diffraction Studies.—The crystal structure determination of [AgL^{17}]ClO$_4$ confirms that the silver atom is bonded to all five donor atoms of the macrocycle which define a very irregular co-ordination polyhedron approximating to a trigonal bipyramid (Fig. 1) with N(1b) and S(1a) occupying axial sites [N(1b)–Ag–S(1a) 143.9(1)°], and the remaining donor atoms in equatorial sites [N(1a)–Ag–S(1b) 148.2(1), N(1a)–Ag–O(1c) 73.3(1) and O(1c)–Ag–S(1b) 137.5(1)°]. The three atoms defining the equatorial sites and the silver atom are coplanar to within 0.095 Å. The 'axial' Ag–S(1a) length of 2.691(1) Å is significantly longer than the Ag–S(1b) length of 2.664(1) Å and both are quite close to the mean of 2.675 Å (with a standard deviation of 0.015 Å) for 51 such bonds taken from the Cambridge Crystallographic Data Base. The axial Ag–N(1b) length of 2.369(4) Å appears marginally longer than the equatorial Ag–N(1a) length of 2.353(4) Å; both agree well with literature values.[20] The silver to ether oxygen distance at 2.631(4) Å is in accord with the mean of 2.562 Å (standard deviation 0.120 Å) for 47 such silver to aliphatic ether bonds taken from the Cambridge Crystallographic Data Base. Clearly, the adoption of a 'tight' five-co-ordinate geometry is in accordance with a substantial silver(I)–macrocycle interaction being present in [AgL^{17}]ClO$_4$. The co-ordination sphere and the configuration of the cyclic ligand in this complex are both quite similar to those in the corresponding silver perchlorate complexes of the related 17-membered S$_2$N$_3$–[12] and S$_2$N$_2$S–[13] donor ligands, L^{16} and L^{19}. Corresponding bond distances are very similar (Table 2); in all three complexes the torsion angles in the inner great rings of the macrocycles are similar (Table 4) and in general show only relatively minor deviations from 'ideal' values, in keeping with the presence of low-strain, macrocyclic ligand co-ordination in these complexes. Interestingly, in the case of [AgL^{17}]ClO$_4$ and [AgL^{19}]ClO$_4$,[13] the NHCH$_2$CH$_2$YCH$_2$CH$_2$NH fragment does not co-ordinate such that the amine groups fall opposite each other in the respective co-ordination spheres. The situation hence does not mimic that found for the classical silver(I) diammine complex in which linear ammine co-ordination is present.

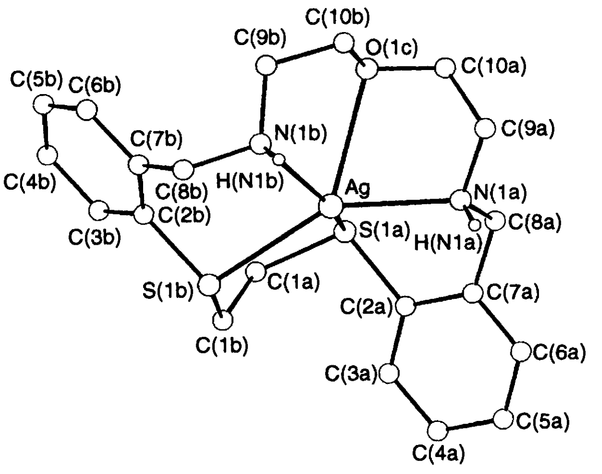

Fig. 1 Crystal structure of [AgL^{17}]$^+$

Table 2 Bond lengths (Å) and angles (°) in the co-ordination spheres of [AgL^{17}]ClO$_4$, [AgL^{16}]ClO$_4$ [12] and [AgL^{19}]ClO$_4$ [13]

	[AgL^{17}]ClO$_4$ Y = O(1c)	[AgL^{16}]ClO$_4$ Y = N(1c)	[AgL^{19}]ClO$_4$ Y = S(1c)
Ag–S(1a)	2.692(1)	2.652(3)	2.706(4)
Ag–S(1b)	2.664(1)	2.713(2)	2.668(4)
Ag–N(1a)	2.353(4)	2.367(5)	2.373(6)
Ag–N(1b)	2.369(4)	2.392(6)	2.455(7)
Ag–Y	2.631(4)	2.552(6)	2.695(4)
S(1a)–Ag–S(1b)	82.5(1)	82.3(1)	81.5(1)
S(1a)–Ag–N(1a)	85.0(1)	86.4(1)	84.7(2)
S(1a)–Ag–N(1b)	143.9(1)	145.0(1)	152.9(2)
S(1a)–Ag–Y	98.6(1)	100.8(1)	102.7(1)
S(1b)–Ag–N(1a)	148.2(1)	142.1(1)	140.0(2)
S(1b)–Ag–N(1b)	84.4(1)	82.4(1)	81.9(2)
S(1b)–Ag–Y	137.5(1)	145.0(1)	138.7(1)
N(1a)–Ag–N(1b)	121.2(1)	123.6(1)	121.6*
N(1a)–Ag–Y	73.3(1)	75.4(2)	81.0(2)
N(1b)–Ag–Y	69.8(2)	73.8(2)	76.3*

* Generated from atom coordinates in the Cambridge Crystallographic Data Base, not available in ref. 13.

Another feature of the above complexes is that the co-ordination requirements of the central silver ion are met solely by binding to all five donor atoms of the respective macrocycles; in our earlier studies of metal complexation by L^1–L^{20} no other example where this occurred was documented.[2,4,7,21]

In contrast to the situation for silver, L^{16} provides only part of the co-ordination sphere of lead(II) in [PbL^{16}(ClO$_4$)$_2$].[15] The latter has a seven-co-ordinate structure with an approximate equatorial arrangement of the S$_2$N$_3$-donor set and axial perchlorate oxygens, giving an overall distorted pentagonal-bipyramidal geometry. The lead atom lies above the equatorial donor plane, being displaced 0.44 Å towards O(11) of the co-ordinated perchlorate group. Relative to the corresponding silver complex, metal to donor bond lengths tend to be elongated in this structure (and especially the Pb–S distances). The respective bond lengths (Å) from L^{16} to lead are: S(1a) 3.175(4), S(1b) 3.141(3), N(1a) 2.577(9), N(1b) 2.630(10) and N(1c) 2.488(10). The covalent radius for lead is greater than for silver by about the amount indicated in the

Table 3 Fractional atomic coordinates with estimated standard deviation in parentheses for [AgL^{17}]ClO$_4$

Atom	*x*	*y*	*z*
Ag	0.144 95(2)	0.253 32(4)	−0.196 76(3)
S(1a)	0.240 27(6)	0.066 69(13)	0.767 17(10)
S(1b)	0.253 61(7)	0.334 22(12)	−0.038 82(10)
N(1a)	0.094 9(2)	0.234 6(4)	−0.383 3(3)
N(1b)	0.075 2(2)	0.317 8(5)	−0.075 2(4)
O(1c)	0.034 9(2)	0.086 5(4)	−0.219 1(3)
C(1a)	0.311 8(3)	0.092 3(5)	−0.114 1(4)
C(2a)	0.265 7(3)	0.166 6(5)	−0.335 7(4)
C(3a)	0.333 9(3)	0.208 5(6)	−0.327 8(4)
C(4a)	0.351 8(3)	0.286 7(7)	−0.410 1(5)
C(5a)	0.300 9(4)	0.319 4(7)	−0.499 5(5)
C(6a)	0.232 1(3)	0.276 5(6)	−0.508 8(4)
C(7a)	0.212 3(3)	0.199 6(5)	−0.427 5(4)
C(8a)	0.137 6(3)	0.151 1(6)	−0.442 3(5)
C(9a)	0.021 3(3)	0.184 0(6)	−0.401 2(5)
C(10a)	0.013 0(4)	0.061 2(7)	−0.332 9(6)
C(10b)	−0.015 0(4)	0.160 9(10)	−0.175 2(7)
C(9b)	0.021 3(4)	0.214 2(9)	−0.066 6(6)
C(8b)	0.115 5(3)	0.371 1(6)	0.031 6(4)
C(7b)	0.167 3(3)	0.264 9(5)	0.092 6(4)
C(6b)	0.151 5(4)	0.191 3(7)	0.179 3(5)
C(5b)	0.197 5(4)	0.097 8(6)	0.238 8(4)
C(4b)	0.262 8(3)	0.076 8(6)	0.217 6(4)
C(3b)	0.281 0(3)	0.147 3(6)	0.132 3(4)
C(2b)	0.233 2(3)	0.238 8(5)	0.070 5(4)
C(1b)	0.325 7(3)	0.239 6(6)	−0.072 5(5)
Cl	−0.023 48(7)	0.575 45(14)	−0.322 84(11)
O(11)	0.040 3(3)	0.499 6(6)	−0.312 3(6)
O(12)	−0.017 8(3)	0.720 2(5)	−0.313 8(6)
O(13)	−0.074 3(3)	0.534 6(7)	−0.419 4(5)
O(14)	−0.049 6(5)	0.517 8(8)	−0.237 9(6)
O(21)	0.028 7(11)	0.546 8(23)	−0.377 1(17)
O(22)	−0.005 6(15)	0.586 0(31)	−0.205 3(24)
O(23)	−0.087 2(14)	0.538 8(29)	−0.352 0(23)
O(24)	0.006 4(14)	0.701 7(29)	−0.362 6(22)
H(N1b)	0.006 0(3)	0.386(7)	−0.104(5)
H(N1a)	0.090(3)	0.313(7)	−0.406(5)

Table 4 Torsional angles (°) within the inner great rings of the macrocycles in $[AgL^{17}]ClO_4$, $[AgL^{16}]ClO_4$[12] and $[AgL^{19}]ClO_4$[13]

	$[AgL^{17}]ClO_4$ Y = O(1c)	$[AgL^{16}]ClO_4$ Y = N(1c)	$[AgL^{19}]ClO_4$ Y = S(1c)
C(1b)–C(1a)–S(1a)–C(2a)	−61.0	−61.4	−61.0
C(1a)–S(1a)–C(2a)–C(7a)	162.2	161.8	163.1
S(1a)–C(2a)–C(7a)–C(8a)	1.8	1.4	1.3
C(2a)–C(7a)–C(8a)–N(1a)	−80.2	−81.0	−80.6
C(7a)–C(8a)–N(1a)–C(9a)	−179.4	−177.0	−173.3
C(8a)–N(1a)–C(9a)–C(10a)	−80.8	−73.3	−75.9
N(1a)–C(9a)–C(10a)–Y	−59.7	−60.6	−58.3
C(9a)–C(10a)–Y–C(10b)	−78.9	−81.1	−65.3
C(10a)–Y–C(10b)–C(9b)	−164.2	−162.4	−150.4
Y–C(10b)–C(9b)–N(1b)	−65.5	−67.2	−69.8
C(10b)–C(9b)–N(1b)–C(8b)	177.7	179.8	171.8
C(9b)–N(1b)–C(8b)–C(7b)	−73.2	−70.8	−78.3
N(1b)–C(8b)–C(7b)–C(2b)	−79.2	−78.8	−80.5
C(8b)–C(7b)–C(2b)–S(1b)	2.1	1.9	3.8
C(7b)–C(2b)–S(1b)–C(1b)	162.4	162.8	168.2
C(2b)–S(1b)–C(1b)–C(1a)	−63.6	−62.9	−65.2
S(1b)–C(1b)–C(1a)–S(1a)	−56.5	−58.1	−54.3

respective mean M–N bonds. Hence Pb–S bonds with a similar lengthening of about 0.2 Å might be expected; that is, lengths of the order of 2.8–2.9 Å. Thus the extremely long values observed in the lead compound are consistent with the presence of relatively weak covalent bonding.

While caution needs to be exercised in extrapolating from the solid state to solution, the inferences from the above structural studies are nevertheless in broad accord with the results from the stability-constant determinations. That is, the affinity of L^{16} for lead(II) is reduced relative to its affinity for silver(I). More generally, the structural data for $[AgL^{16}]ClO_4$, $[AgL^{17}]ClO_4$ and $[AgL^{19}]ClO_4$[13] are consistent with the high discrimination shown by L^{16}, L^{17} and L^{19} for silver(I) over lead(II).

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