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# Metal-ion Recognition. Donor-set Control of Silver(I)/Lead(II) Discrimination using Mixed-donor Macrocyclic Ligands

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The systematic variation of the donor atom set in a dibenzo-substituted, 17-membered ring structure on the ability of the resultant systems to discriminate between silver(I) and lead(II) has been performed; the compound containing a $S_2N_2S$-donor set yielded discrimination of the order of $10^9$ in favour of silver(I).

The metal-ion preferences of mixed-donor co-ordination sites are often difficult to predict, especially when transition and other heavy-metal ions are involved. Our research over recent years has involved the systematic design of mixed-donor macrocyclic ligands in order to investigate the co-ordination preferences of such sites.[1] Deliberate strategies have been developed for achieving discrimination between ions of the above type but, more importantly, for understanding the nature of such discrimination when it is achieved.[2]

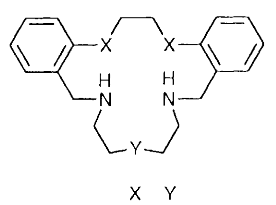
Although variation of the donor-atom set has long been employed to change the affinities of ligands towards individual metal ions, few systematic studies of this type involving heavy metals and macrocyclic ligands have been performed.[3,4] As an extension of our previous investigations we now report a study of the latter type in which the 17-membered rings $L^1$–$L^6$ (ref. 5) have been used to investigate the effect of stepwise donor-set variation on silver(I)/lead(II) discrimination.

Stability constants for the silver(I) and lead(II) complexes of $L^1$–$L^6$ in 95% methanol ($I = 0.1$ mol dm$^{-3}$, $NEt_4ClO_4$) were determined by potentiometric (pH) titration as described elsewhere.[6] The log $K$ values are summarised in Table 1. The interaction of silver(I) and lead(II) with the 'parent' (17-membered) $O_2N_3$-donor macrocycle $L^1$ was investigated initially; however, a stability difference of less than a factor of 10 was observed. Substitution of an ether oxygen for an NH donor in position Y (with X = O) to yield $L^2$ gave increased discrimination for silver over lead and it is evident that silver(I) shows a greater 'tolerance' for the $NHCH_2CH_2OCH_2CH_2NH$ string in $L^2$ than does lead(II).

Silver(I) is a b-class or 'soft' metal ion while lead(II) is borderline[7] and, in accordance with previous studies,[8] it was anticipated that the introduction of a sulfur donor in the donor set to yield $L^3$ would enhance the stability of the corresponding silver(I) complex relative to that of lead(II). A stability difference of approximately $10^4$ in favour of silver(I) was achieved in this case. Indeed, in an earlier calorimetric study (in acetonitrile) of the interaction of silver(I) with macrocycles of the present type it was shown that the affinity of a thioether for silver(I) is broadly similar to that of a secondary amine.[9]

Further donor variation to yield compound $L^4$, containing a $S_2N_3$-donor set, resulted in the expected increase in the absolute value of the stability of the silver(I) complex. However, in accordance with our previous observation, the restoration of the $N_3$-donor string in this compound leads to a rise in the stability of the lead(II) species relative to that of silver(I) such that lower discrimination occurs. The next ($S_2N_2O$-donor) macrocycle $L^5$ in the series results in increased discrimination towards silver(I) and, thus, further exemplifies the trends discussed so far.

The success of the above procedure is underlined by the exceptional discrimination achieved with the final member of the series $L^6$ which contains a $S_2N_2S$-donor set; for this system the discrimination is approximately $10^9$ in favour of silver!



| | X | Y |
|---|---|---|
| $L^1$ | O | NH |
| $L^2$ | O | O |
| $L^3$ | O | S |
| $L^4$ | S | NH |
| $L^5$ | S | O |
| $L^6$ | S | S |

**Table 1** Log $K$ data for formation of 1 : 1 complexes of silver(I) and lead(II)*

| | log $K$ | | |
|---|---|---|---|
| Ligand | $Ag^I$ | $Pb^{II}$ | $\Delta\log K$ |
| $L^1$ | 8.7 | 8.1 | 0.6 |
| $L^2$ | 7.1 | 5.5 | 1.6 |
| $L^3$ | ≈12.0 | 8.0 | ≈4.0 |
| $L^4$ | 8.6 | 4.5 | 4.1 |
| $L^5$ | 10.3 | ≈3 | ≈7.3 |
| $L^6$ | 12.4 | ≈3 | ≈9.4 |

* The values (at 25 °C, see text) are the mean of at least two individual determinations at different metal : ligand ratios.

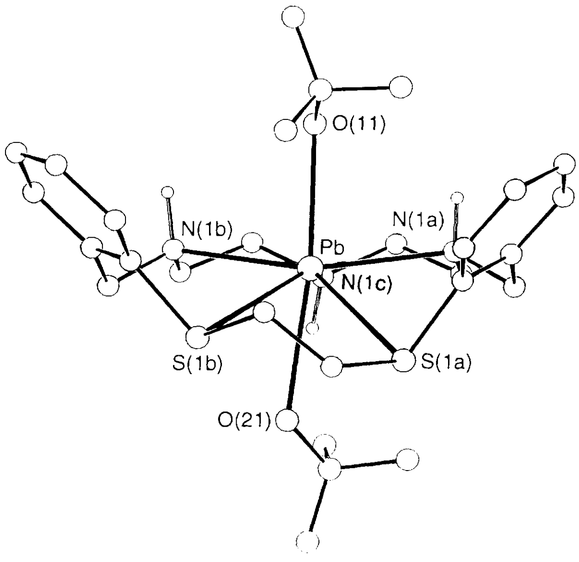


**Fig. 1** The structure of $[PbL^4(ClO_4)_2]$. Bond lengths (Å) to lead: S(1a), 3.175(4); S(1b), 3.141(3); N(1a), 2.577(9); N(1b), 2.630(10); N(1c), 2.488(10); O(11), 2.599(12); and O(21), 2.761(12)

In view of the above behaviour it was of interest to compare X-ray diffraction data for the silver(I) and lead(II) complexes of $L^4$. The structure of the silver complex has been reported previously.[10] This complex has an irregular five-co-ordinate geometry with all donor atoms of the macrocycle co-ordinated. The macrocycle wraps around the silver ion with the respective donor-to-metal bond lengths in each case being typical of those in a range of other five-co-ordinate silver complexes incorporating mixed donor macrocyclic ligands.[11] Clearly, the adoption of a 'tight' five-coordinate geometry (in which no long metal–donor bonds occur) is in accordance with a substantial silver(I)–macrocycle interaction being present. In contrast, the structure of the lead(II) complex of $L^4$, determined as part of the present study,* reveals that the metal is seven-co-ordinate being bound to the five donor atoms of the macrocycle and two perchlorate anions which occupy 'axial' positions (Fig. 1). The co-ordinated macrocycle adopts a flatter, more open, conformation (than occurs in the silver complex) with the metal situated above the macrocyclic cavity. This arrangement, together with the significantly longer metal to macrocyclic donor bond lengths found in this complex (and especially the longer Pb–S distances, see caption to Fig. 1), suggests that the affinity of $L^4$ for lead(II) is somewhat reduced relative to that for silver(I); in this context, it is noted that the Pauling ionic radii (six-co-ordinate) for silver(I) (1.26 Å) and lead(II) (1.21 Å) do not differ greatly.

In accordance with the above, a recent X-ray crystal structure of the silver(I) complex of $L^6$ [the ligand showing the highest silver(I)/lead(II) discrimination] confirms that a 'tight' five-co-ordinate geometry is maintained in this complex.[14]

While caution needs to be exercised in extrapolating from the solid state to solution, the results from the stability-constant determinations are nevertheless in broad accord with the inferences drawn from the above structural studies.

In summary, the present investigation provides an example of the successful achievement of an extremely large log *K* differential between corresponding complexes of silver and lead through careful 'tuning' of the donor set across otherwise similar ligands.

## Acknowledgements

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* Crystal data. $C_{20}H_{27}Cl_2N_3O_8PbS_2$, $M = 779.68$, monoclinic, space group $P2_1/n$, $a = 18.123(3)$, $b = 15.982(3)$, $c = 9.190(2)$ Å, $\beta = 95.88(2)°$, $U = 2647.79$ Å$^3$, $F(000) = 1528$, $\mu$(Mo-K$\alpha$) $= 67.20$ cm$^{-1}$, $Z = 4$, $D_c = 1.956$ g cm$^{-3}$. Data were collected with a Philips PW1100 diffractometer in the range $\theta$ 3–25° using a crystal of size 0.34 × 0.32 × 0.30 mm. The nitrogen-bonded hydrogens were directly located in a Fourier difference synthesis using data with $\sin\theta < 0.35$. Full-matrix refinement (SHELX 76 program[12]) with anisotropic thermal parameters assigned to all non-hydrogen atoms converged at $R = 0.0515$ [$R' = 0.0541$, reflections weighted as $1/\sigma^2(F_o)$ where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$] for 3218 absorption-corrected data (for details of method see ref. 13) with $I/\sigma(I) \geqslant 3.0$. The maximum residual peak in the final Fourier difference synthesis was 1.5 e Å$^{-3}$ in the vicinity of the lead atom. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.