

Donor effect on supramolecular structures of silver(I) perchlorate complexes of macrocycles with O₂S₂X (X=S, O and NH) donor sets†‡

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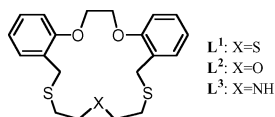
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Received 9th May 2005, Accepted 1st June 2005

First published as an Advance Article on the web 10th June 2005

By virtue of simple one donor variations of O₂S₂X-donor macrocycles (L¹: X=S, L²: X=O and L³: X=NH) towards silver(I) perchlorates, four supramolecular complexes (1–3) with different topologies have been isolated; L¹ afforded solvent- and anion-free sandwich complex (1), otherwise L² and L³ gave the dimeric (2a), 1-D polymeric (2b), and tetrameric bowl-type (3) complexes with solvent or anion coordination.

Besides the cavity size that varies to tune a binding selectivity for a given metal ion (*cavity-size effect*),¹ the introduction of hetero-donor atoms into the homoleptic macrocyclic ligands results in dramatic changes in both binding ability and geometry of the complexes (*donor effect*).² It is well established that macrocyclic thioethers favor the adoption of *exo*-coordination with S donors oriented out of the cavity.³ Our particular interest in this area has been the coordination of the hetromacrocycles such as thioaxa- or thioaxaaza-macrocycles with thiophilic metals to construct the supramolecular complexes.⁴ Recently we have realized that the only single donor atom variations in the parent S₃O₂ dibenzo macrocycle L¹ triggers a sudden change in coordination geometry for the resulting complexes. This approach has received less attention especially for the sulfur-rich macrocycles.^{2c} Herein we report the synthesis and crystal structures of silver(I) perchlorate complexes of the O₂S₂X macrocycles (L¹–L³) with emphasis on the influence of systematic donor atom variation on the respective supramolecular structures. The versatility of the results is highlighted by the formation of a tetrameric bowl-type complex with anion-linking.



The ligands L¹–L³ were prepared with the method reported by us previously.⁴ Their silver(I) perchlorate complexes **1**, **2a**, **2b** and **3** were prepared† and characterised by X-ray structure analysis.§ Reaction of L¹ with AgClO₄ in acetonitrile afforded the sandwich complex of formula [Ag(L¹)₂](ClO₄)₂ (**1**) (Fig. 1).

† Electronic supplementary information (ESI) available: X-ray crystallographic details for **1**, **2a**, **2b** and **3**, TGA diagram and isotope pattern (FAB mass) for **3**. See <http://dx.doi.org/10.1039/b506438d>

‡ Reaction of AgClO₄ with L¹ in methanol afforded colourless precipitate. The solid was filtered off, and dissolved in acetonitrile. X-ray quality crystals of **1** were obtained by slow evaporation of the solution. Equimolar amount of AgClO₄ was added to L² in acetonitrile and methanol, respectively and slow evaporation of the solution afforded colourless crystals of **2a** and **2b** suitable for X-ray analysis. Equimolar amount of AgClO₄ was added to L³ in acetonitrile and diffusion of diethyl ether into the solution afforded colourless crystals of **3** suitable for X-ray analysis.

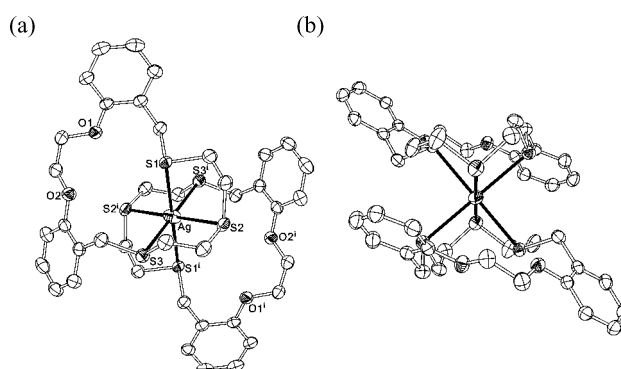


Fig. 1 Sandwich structure of **1**, [Ag(L¹)₂](ClO₄) (a) top view and (b) side view. Hydrogen atoms and noncoordinating anions are omitted.

The coordination of each L¹ to the silver(I) centre is via facial arrangement of its three sulfur donors, forming an approximate octahedral geometry with the ether oxygen donors remaining uncoordinated. Like other sandwich-type complexes with thiamacrocycles,⁵ the Ag centre in **1** is surrounded by a distorted octahedral array of six S atoms from two L¹. The S–Ag–S bite angles vary considerably from 76.00(2)° (intra-ligand) to 104.00(2)° (inter-ligand). Consequently, the metal centre is completely shielded by two L¹s and therefore is unable to contact the anion or solvent.

Reaction of L² with AgClO₄ afforded the two types of complexes (**2a** and **2b**), in which the binding behaviours vary with the solvents used. In acetonitrile **2a** crystallises in a cofacial dimeric form, with two [AgL²(CH₃CN)] units held together by an Ag–Ag contact⁶ of 3.329(1) Å (Fig. 2). The Ag(I) which lies outside the cavity is bonded to the two S atoms of L² as well as to the acetonitrile forming a distorted trigonal planar environment.

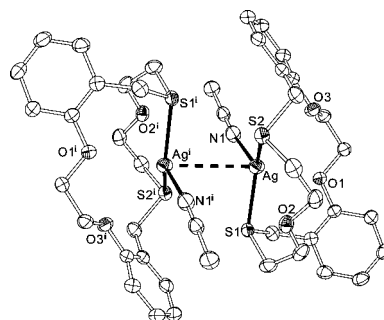


Fig. 2 Dimeric structure of **2a**, {[AgL²(CH₃CN)](ClO₄)₂}. Hydrogen atoms and noncoordinating anions are omitted.

In methanol **2b** crystallises in a 1-D coordination polymer consisting of [Ag₄(L²)₂(CH₃OH)₂](ClO₄)₄ units (Fig. 3).

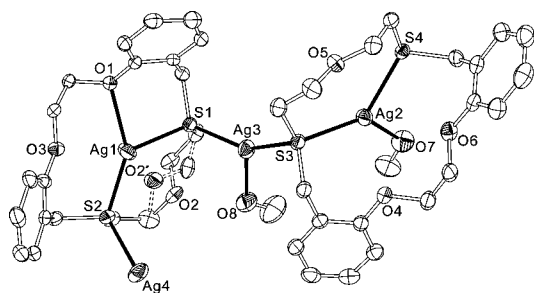


Fig. 3 1-D polymeric structure of **2b**, $\{[Ag_4(L^2)_2(CH_3OH)_2](ClO_4)_4\}_n$. Hydrogen atoms and noncoordinating anions are omitted.

Two independent L^2 s encircle Ag(1) and Ag(2) atoms in an *endo* manner. The Ag(3) and Ag(4) atoms bridge the *endo*-dentate Ag(1) and Ag(2) coordinating spheres resulting an $[Ag_4(L^2)_2(CH_3OH)_2]^{4+}$ repeating unit. The binding of solvent molecules are also observed at the coordination spheres of Ag(2) and Ag(3). The local coordination geometry of each Ag atom is distorted trigonal planar except Ag(4) which has two coordinates with highly bent conformation due to the anion interaction (ESI†). Consequently **2b** can be considered as an intermediate case of encapsulation and bridging coordination because it shows the unique conformation in which both the native *exo*-³ and *endo*-coordination are involved in the same complex. The solvent coordination behaviours of the respect L^2 complexes can be attributed to the relatively weaker coordinating O donor (than those of S or N) which led the coordination sphere of Ag(i) unsaturated. In fact, no solvent coordination was observed in the system of L^1 and L^3 complexes (see Figs. 2 and 4).

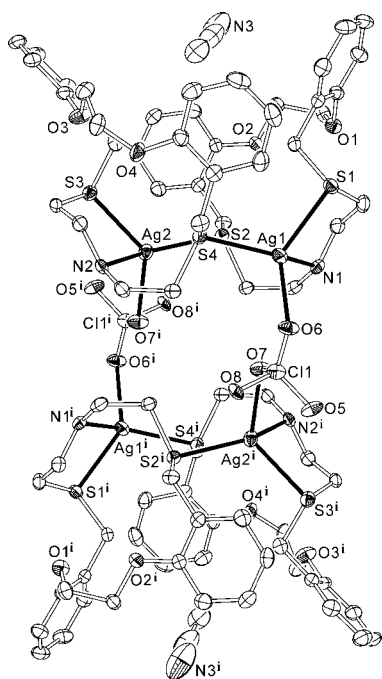


Fig. 4 Tetrameric bowl-type structure of **3**, $[Ag_4(L^3)_4(\mu-ClO_4)_2](ClO_4)_2(CH_3CN)_2$. Hydrogen atoms and noncoordinating anions are omitted.

Reaction of L^3 with $AgClO_4$ in acetonitrile afforded the unprecedented oligomeric complex of formula $[Ag_4(L^3)_4(\mu-ClO_4)_2](ClO_4)_2(CH_3CN)_2$ (**3**). Each Ag atom has essentially four coordinates. The Ag atom is bonded to one S and one N atom from one L^3 and to one S atom from another L^3 forming a bowl-type framework. Interestingly the array of four benzo-groups from two L^3 has a calix[4]arene or calix[4]crown conformations.⁷ Again, two bidentate ClO_4^- ions doubly bridge the metal centres via Ag–O(ClO_2)O–Ag as fourth coordinating sites. The overall geometry around each Ag atom can be described as a distorted

tetrahedral. The results also confirm the expected strong affinity of thioether sulfur for Ag(i): the affinity was observed to be comparable to that of a secondary amine. In this case, the binding of the SNS' donor set (S' means coordinating sulfur donors in neighboring L^3) to Ag centres allows not solvent coordination but anion coordination. Instead one acetonitrile molecule is captured by H-bonding in each three dimensional bowl cavity.

The high resolution mass spectrum for **3** showed a peak at m/z 1063.0249 (calculated value; 1063.0240) corresponding to $[Ag_4(L^3)_4(\mu-ClO_4)_2]^{2+}$. The relative abundance of its isotope pattern is in good agreement with that of simulated one (ESI†). As we understand, this is the first characterised coordination compound to possess bowl arrangement with anion-linkings. TGA analysis showed that **3** undergoes a gradual loss of 3.6% of total weight by 215 °C, corresponding to the loss of two H-bonded acetonitrile per formula unit (expected 3.4%) (ESI†).

It is interesting to compare the structures of the four complexes (**1–3**). In **1**, as mentioned, the complex has the related geometry without solvent or anion coordination. On going from **1** to **2a** or **2b**, and to **3**, we observed that the replacement of the S donor from parent system L^1 to O (L^2) or NH (L^3) induced the participation of the solvent and/or anion coordination because of the unsaturation of coordination sphere of Ag(i). This may serve the chance to prepare more interesting and sometimes unprecedented products.

In conclusion, an idea of the effect of donor atom variation of the macrocyclic system has been realized the self-assembly of a range of supramolecular complexes with different topologies. The donor effect in solid is believed to be more drastic than that observed in solution because the solvation is excluded or minimised. Thus the donor effect in the supramolecular construction is attractive and versatile tool, at least, for the soft-soft acid–base system. The extension of this approach to other soft metals is expected to open new avenues to the mixed donor macrocyclic complexes with supramolecular structures.

Acknowledgements

We gratefully acknowledge the support from Korea Science and Engineering Foundation (R01-2004-000-10321-0).

Notes and references

§ Crystal data for **1**: $C_{40}H_{48}AgClO_8S_6$, $M = 992.46$, triclinic, $a = 8.9985(7)$ Å, $b = 11.6633(9)$ Å, $c = 12.3578(9)$ Å, $\alpha = 116.7000(10)^\circ$, $\beta = 95.460(2)^\circ$, $\gamma = 106.721(2)^\circ$, $U = 1070.83(14)$ Å³, $T = 298(2)$ K, space group $P-1$ (no. 2), $Z = 1$, $\mu(Mo-K\alpha) = 0.876$ mm⁻¹, 7054 reflections measured, 4933 unique ($R_{int} = 0.0296$) which were used in all calculations. The final $wR(F_2)$ was 0.1093 (all data). Crystal data for **2a**: $C_{22}H_{27}AgClNO_7S_3$, $M = 624.89$, Monoclinic, $a = 10.6319(10)$ Å, $b = 21.039(2)$ Å, $c = 11.8585(11)$ Å, $\beta = 107.158(2)^\circ$, $U = 2534.5(4)$ Å³, $T = 298(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu(Mo-K\alpha) = 1.108$ mm⁻¹, 16246 reflections measured, 6159 unique ($R_{int} = 0.0426$) which were used in all calculations. The final $wR(F_2)$ was 0.1123 (all data). Crystal data for **2b**: $C_{42}H_{56}Ag_4Cl_4O_{24}S_4$, $M = 1646.39$, monoclinic, $a = 24.310(2)$ Å, $b = 12.6134(12)$ Å, $c = 18.2148(18)$ Å, $\beta = 92.659(2)^\circ$, $U = 5579.2(9)$ Å³, $T = 296(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu(Mo-K\alpha) = 1.805$ mm⁻¹, 36083 reflections measured, 13691 unique ($R_{int} = 0.1117$) which were used in all calculations. The final $wR(F_2)$ was 0.2212 (all data). Crystal data for **3**: $C_{64}H_{80}Ag_4Cl_4N_6O_{24}S_8$, $M = 2413.51$, Triclinic, $a = 11.5691(8)$ Å, $b = 13.3821(10)$ Å, $c = 16.2842(12)$ Å, $\alpha = 85.7870(10)^\circ$, $\beta = 75.2830(10)^\circ$, $\gamma = 82.8980(10)^\circ$, $U = 2417.4(3)$ Å³, $T = 173(2)$ K, space group $P-1$ (no. 2), $Z = 1$, $\mu(Mo-K\alpha) = 1.156$ mm⁻¹, 29151 reflections measured, 11330 unique ($R_{int} = 0.0612$) which were used in all calculations. The final $wR(F_2)$ was 0.1282 (all data). CCDC reference numbers 271048 (**1**), 271049 (**2a**), 271050 (**2b**) and 271051 (**3**). See <http://dx.doi.org/10.1039/b506438d> for crystallographic data in CIF or other electronic format.

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