

## Synthesis and X-Ray Crystal Structure of the First Pentanuclear Silver(I) Cluster of the Polyaza Cryptands

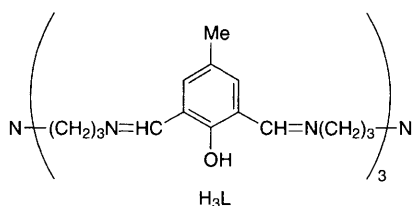
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A new silver(I) polyaza cryptate  $[\text{Ag}_5\text{L}][\text{BF}_4]_2 \cdot \text{H}_2\text{O}$  is synthesized and shown by X-ray crystallographic structure determination to consist of a pentanuclear silver(I) cluster incorporated in a polyaza cryptand.

The chemistry of cryptands and clusters is a very active research topic in inorganic, organic and physical chemistry due to its close relation to biomimetics, catalysis and material science.<sup>1,2</sup> Researches on silver(I) cryptates have been conducted by Lehn<sup>3</sup> and Nelson and coworkers,<sup>4-6</sup> most of which concentrated on binuclear silver(I) cryptates, and few silver(I) cryptates with more than two silver nuclei have been reported; de Mendoza and coworkers<sup>7</sup> obtained an interesting trinuclear silver(I) polyazacryptate which has been structurally characterised. We have synthesized a novel silver(I) cluster cryptate with five silver nuclei,  $[\text{Ag}_5\text{L}][\text{ClO}_4]_2 \cdot 4\text{MeOH}$ , through [2 + 3] condensation and obtained single crystals of the complex  $[\text{Ag}_5\text{L}][\text{BF}_4]_2 \cdot \text{H}_2\text{O}$ . The ligands in most reported silver(I) cluster complexes are noncyclic and contain sulfur atoms, while closed-shell silver(I) clusters containing a polyaza cryptand have not been reported previously.<sup>8-9</sup>



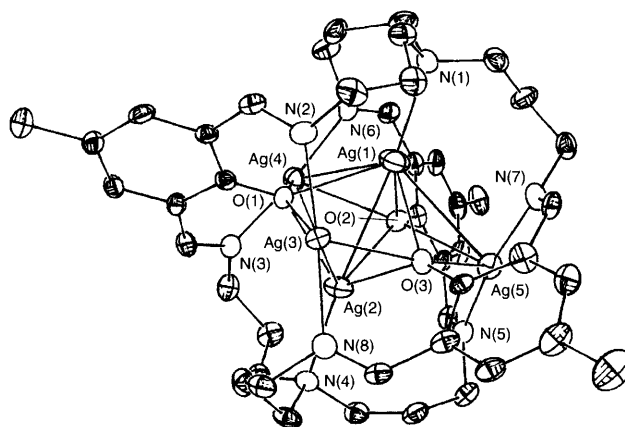
The cryptate  $[\text{Ag}_5\text{L}][\text{ClO}_4]_2 \cdot 4\text{MeOH}$  was obtained by [2 + 3] condensation of tris(2-aminopropyl)amine (trpn) with 2,6-diformyl-4-methylphenol in the presence of  $\text{Ag}^+$  as template. A solution of trpn (0.376 g, 2 mmol) in absolute methanol (60  $\text{cm}^3$ ) was added dropwise into a stirred solution of 2,6-diformyl-4-methylphenol (0.492 g, 3 mmol) and  $\text{AgNO}_3$  (0.425 g, 2.5 mmol) in absolute methanol (130  $\text{cm}^3$ ). After stirring for 3 h at 45 °C, the mixture was filtered and excess  $\text{NaClO}_4$  was added into the filtrate. The product  $[\text{Ag}_5\text{L}][\text{ClO}_4]_2 \cdot 4\text{MeOH}$  precipitated as yellow microcrystals, yield 43% (Found: C, 36.15; H, 4.52; N, 6.93.  $\text{C}_{49}\text{H}_{73}\text{Ag}_5\text{Cl}_2\text{N}_8\text{O}_{15}$  requires C, 36.20; H, 4.49; N, 6.89%).<sup>†</sup> To obtain high quality crystals,  $\text{NaBF}_4$  was used as precipitant instead of  $\text{NaClO}_4$ . Yellow crystals of the cryptate  $[\text{Ag}_5\text{L}][\text{BF}_4]_2 \cdot \text{H}_2\text{O}$  suitable for X-ray study were obtained<sup>‡</sup> by diffusion of diethyl ether into an acetonitrile solution of the complex.

The structures of  $[\text{Ag}_5\text{L}]^{2+}$  cation and its central core are shown in Figs. 1 and 2, respectively.

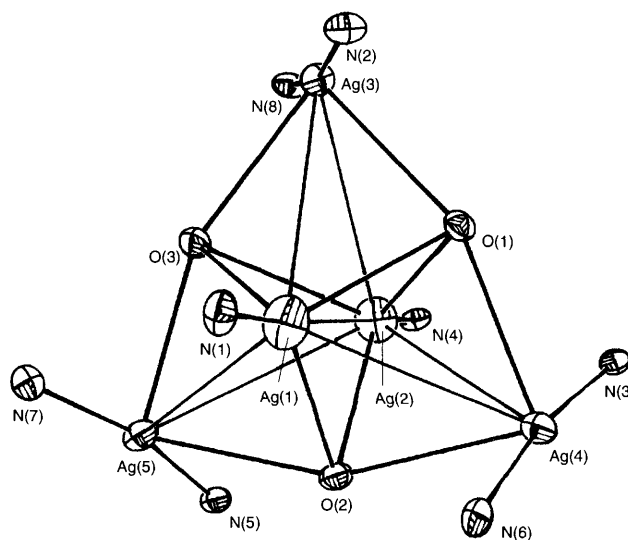
It can be seen from Fig. 1 that in  $[\text{Ag}_5\text{L}]^{2+}$  cation, the five silver(I) centres are enclosed within the polyaza cryptand and are coordinated by phenoxide oxygens and imine nitrogens. Fig. 2 shows that the central core  $\text{Ag}_5\text{O}_3$  exhibits a hexagonal-bipyramidal geometry with distorted  $D_{3h}$  symmetry. Three Ag atoms, Ag(3), Ag(4) and Ag(5), and three phenolic hydroxy oxygens, O(1), O(2) and O(3), are distributed evenly on the  $\sigma_h$  plane, while the other two silver ions Ag(1) and Ag(2) are located symmetrically on the principal axis. The  $\text{Ag} \cdots \text{Ag}$  distance  $\text{Ag}(1) \cdots \text{Ag}(2)$  is 3.083 Å and the non-bonding distances between Ag(1) or Ag(2) and the other three silver ions on the  $\sigma_h$  plane are in the range 3.146–3.389 Å. The three silver ions in this plane are well separated from one another and are bridged by phenoxide oxygen donors in the plane. All the  $\text{Ag}-\text{O}$

bond distances are ca. 2.55 Å and the  $\text{Ag}-\text{O}-\text{Ag}$  angles for this planar hexagonal structure are ca. 157°.

The coordination mode of the polyazacryptate to the silver(I) cluster is quite unusual, the macrocyclic phenol groups are all deprotonated and participate in coordination together with all the nitrogen atoms of the ligand which exerts a profound stabilizing effect to the cluster. The bridgehead nitrogens N(1)



**Fig. 1** A perspective view of cationic cryptate  $[\text{Ag}_5\text{L}]^{2+}$ . Relevant bond lengths (Å): Ag(1)–N(1) 2.286(8), Ag(1)–O(1) 2.535(6), Ag(1)–O(2) 2.455(7), Ag(1)–O(3) 2.524(7), Ag(2)–N(4) 2.265(7), Ag(2)–O(1) 2.445(6), Ag(2)–O(2) 2.472(6), Ag(2)–O(3) 2.623(7), Ag(3)–N(2) 2.139(8), Ag(3)–N(8) 2.161(8), Ag(3)–O(3) 2.553(6), Ag(3)–O(1) 2.561(7), Ag(4)–N(6) 2.129(8), Ag(4)–N(3) 2.129(7), Ag(4)–O(2) 2.581(6), Ag(4)–O(1) 2.599(6), Ag(5)–N(5) 2.126(9), Ag(5)–N(7) 2.167(9), Ag(5)–O(3) 2.552(6), Ag(5)–O(2) 2.599(7).§



**Fig. 2** Schematic representation of the geometry of the five silver centres of  $[\text{Ag}_5\text{L}]^{2+}$ . Bond lengths (Å) and angles (°): Ag(1)–Ag(2) 3.083(2), Ag(1)–Ag(5) 3.233(2), Ag(1)–Ag(4) 3.285(2), Ag(1)–Ag(3) 3.385(2), Ag(2)–Ag(3) 3.325(2), Ag(2)–Ag(4) 3.146(2), Ag(2)–Ag(5) 3.389(2), Ag(3)–O(1)–Ag(4) 156.4(3), Ag(4)–O(2)–Ag(5) 155.4(3), Ag(5)–O(3)–Ag(3) 157.8(3).

and N(4) coordinate with the axial Ag(1) and Ag(2) respectively [Ag(1)–N(1) 2.286, Ag(2)–N(4) 2.265 Å, Ag(1)–Ag(2)–N(4) and Ag(2)–Ag(1)–N(1) 174°], thus the two bridgehead nitrogens can be considered to be located approximately on the principal axis. The two imine nitrogens of each bridge chain originating from the bridgehead nitrogens bind to two in-plane silver atoms from opposite directions [e.g. N(2), N(3) coordinate to Ag(3) and Ag(4) respectively]. The coordination of six nitrogen atoms of the imine groups makes the three bridge chains *cis*-spiral up along the principal axis from the outside of the silver(I) cluster. The three bridge chains are located symmetrically in accord with the <sup>1</sup>H NMR spectra.

The coordination of oxygen atoms of phenolic hydroxy, the large cavity of cryptand and the spiral binding of the three highly flexible bridge chains are the key factors making the assembly of this silver(I) cluster within the cryptand possible, and leading to the high stability of this novel structure.

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### Footnotes

† *Spectroscopic data*: IR spectra (KBr): 1640s, ν(C=N), 1090, 625s, ν(ClO<sub>4</sub><sup>-</sup>), 3309br ν(MeOH)/cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, SiMe<sub>4</sub>): δ 8.26 (6 H, s, CH=N), 7.08 (6 H, s, aryl H), 3.65 (12 H, m, CH<sub>2</sub>N), 2.63 (12 H, m, CH<sub>2</sub>N=), 2.36 (12 H, s, CH<sub>2</sub>), 2.21 (9 H, s, CH<sub>3</sub>).

‡ *Crystal data*: C<sub>45</sub>H<sub>59</sub>Ag<sub>5</sub>B<sub>2</sub>F<sub>8</sub>O<sub>4</sub>N<sub>8</sub>, yellow crystal, *M* = 1488.96, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 12.563(7), *b* = 22.602(7), *c* = 19.621(7) Å, β = 90.57(3)°, *U* = 5581(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.77 g cm<sup>-3</sup>, *F*(000) = 2936. Crystal dimensions 0.38 × 0.22 × 0.22 mm. Data collected at 296 K on an Enraf-Nonius CAD4 diffractometer with ω–2θ scan technique (Δω = 0.50 + 0.35 tanθ°, scan rate 5.49° min<sup>-1</sup>). 10318 independent reflections were collected in the range 1.88 < 2θ < 50° of

which 6661 with *I* > 3σ(*I*) were used for the structure analysis. The structure was solved using MITHRIL direct methods and refined to *R* = 0.067, *R*<sub>w</sub> = 0.076. The hydrogen atoms were inserted at calculated positions by a direct method. All programs used in data reduction structure solution are contained in the TEXSAN package. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Relevant bond angles (°): N(1)–Ag(1)–O(2) 131.6(3), N(1)–Ag(1)–O(3) 127.9(3), N(1)–Ag(1)–O(1) 123.6(3), O(2)–Ag(1)–O(3) 87.2(2), O(2)–Ag(1)–O(1) 87.3(2), O(3)–Ag(1)–O(1) 84.4(2), N(4)–Ag(2)–O(1) 131.5, N(4)–Ag(2)–O(2) 128.3(2), O(1)–Ag(2)–O(2) 89.0(2), O(1)–Ag(2)–O(3) 84.2(2), O(2)–Ag(2)–O(3) 84.6(2), N(2)–Ag(3)–N(8) 166.5(3), N(2)–Ag(3)–O(3) 112.2(2), N(2)–Ag(3)–O(1) 76.9(3), N(8)–Ag(3)–O(3) 77.6(2), N(8)–Ag(3)–O(1) 114.5(3), O(3)–Ag(3)–O(1) 83.3(2), N(6)–Ag(4)–N(3) 171.2(3), N(6)–Ag(4)–O(2) 76.0(3), N(6)–Ag(4)–O(1) 109.0(3), N(3)–Ag(4)–O(2) 111.4(3), N(3)–Ag(4)–O(1) 77.2(2), O(2)–Ag(4)–O(1) 83.4(2), N(5)–Ag(5)–N(7) 169.1(3), N(5)–Ag(5)–O(3) 113.4(2), N(5)–Ag(5)–O(2) 77.6(3), N(7)–Ag(5)–O(2) 109.6(3), O(3)–Ag(5)–O(2) 83.6(2).

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