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Note

Syntheses, spectroscopy and crystal structure of several binuclear silver(I) cryptates

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Abstract

Three binuclear silver(I) cryptates were synthesized by template condensation of tris(3-aminopropyl)amine with 5-R-2-methoxy-1,3-phenylenedialdehyde (R = CH_3O, CH_3 or Br) and characterized by physical measurements (solution electrical conductivity, ^1H NMR, IR and electronic spectra). The crystal structure of the cryptate of L^1 (R = CH_3O) was determined by X-ray diffraction and presents a novel basket structure for the cation $[Ag_2L^1]^{2+}$ in which both silver(I) centres possess three coordinate environments. The crystal is monoclinic, space group *Cc*, $C_{48}H_{68}Cl_2N_8O_{15}Ag_2$, $M_r = 1283.75$, $a = 11.349(2)$, $b = 29.16(1)$, $c = 17.506(6)$ Å, $\beta = 102.38(2)°$, $Z = 4$, $R = 0.063$ and $R_w = 0.071$ for 3693 reflections. Each Ag atom locates at the top of a trigonal pyramid distorted from a planar triangle composed of one bridgehead tertiary nitrogen and two imino nitrogens. Only two bridging chains of the cryptand coordinate to the metals, another does not. The internuclear distance Ag(1)···Ag(2) is 7.468(12) Å. All cryptates possess similar spectroscopic features.

Keywords: Crystal structures; Silver complexes; Cryptate complexes

1. Introduction

Polyaza cryptands have strong coordination ability and special recognition function towards transition metal ions, with regard to biomimetic, catalytic, photo, electric and magnetic chemistry [1–6]. Therefore, considerable attention has focussed on the design and synthesis of polyaza cryptands and their complexes with special structures. More recently, an efficient synthetic alternative, based on one-step, high yield, without high dilution conditions, Schiff base condensation of tris(2-aminoethyl)amine (tren) with aryl dialdehydes, has been developed [7–17]. However, little work about the cryptands or cryptates condensed by tris(3-aminopropyl)-amine (trpn), an analogue of tren, with the corresponding dialdehydes has been reported [18]. It is predicated that the resulting cryptands derived from trpn may exhibit novel configurations and host–guest properties owing to their high flexibilities and large cavities. We have synthesized three binuclear silver(I) cryptates by condensation of trpn with 5-R-2-methoxy-1,3-phenylenedialdehyde (R = CH_3O, L = L^1; CH_3, L^2; Br, L^3) (Fig. 1) in the presence of $AgNO_3$ and obtained single crystals of cryptate of L^1. Both the physical measurements and X-ray structure analysis show a novel basket configuration and three-coordinate structure present in the cationic complex $[Ag_2L^1]^{2+}$. To our knowledge, very few three-coordinate binuclear Ag(I) cryptates have been presented, although some Ag(I) complexes of related macrobicyclic ligands were reported earlier [19–21].

2. Experimental

2.1. Materials

All starting materials were of chemical purity. Tris(3-aminopropyl)amine was prepared by a modified literature method [22] with a purity of over 99%, identified

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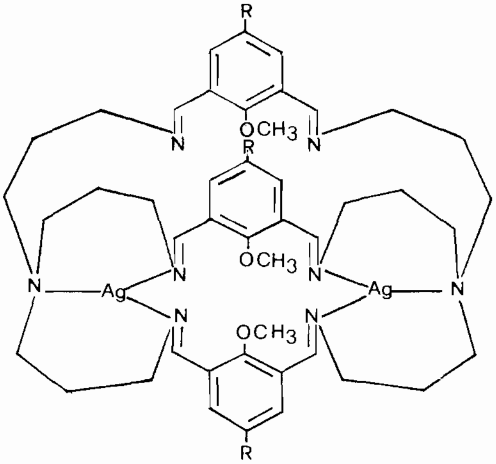

Fig. 1. The cationic complexes of binuclear Ag(I); R = CH_3O, CH_3 and Br (L^1, L^2 and L^3).

by IR spectra and conductimetric titration. The derivatives of isophthalaldehyde were prepared by literature [23] methods. Their physical constants and spectral data were in agreement with literature data [23].

2.2. Physical measurements

Solution electrical conductivity was measured by a BSD-A numerical conductometer (Jiangsu, China) with solute concentrations of $\sim 10^{-4}$ mol dm^{-3} in acetonitrile. IR spectra were measured as KBr discs using a Nicolet 5DX FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV 260 spectrophotometer. ^1H NMR was performed on a Varian FT-80 NMR spectrometer (TMS as the internal reference).

2.3. Syntheses

2.3.1. $[Ag_2L^1](ClO_4)_2\cdot H_2O$ (1)

To a stirred solution of $AgNO_3$ (0.425 g, 2.5 mmol) and 2,5-dimethoxy-1,3-phenylenedialdehyde (0.582 g, 3 mmol) in 100 cm^3 absolute ethanol was added dropwise a solution of trpn (0.376 g, 2 mmol) in 50 cm^3 absolute ethanol. After stirring for 3–4 h, the mixture was filtered and then an excess of $NaClO_4\cdot H_2O$ (0.7 g, ~5 mmol) in 20 cm^3 ethanol was added. Yellowish microcrystals were precipitated and refiltered. By slow evaporation of the filtrate at room temperature, yellowish plate crystals suitable for X-ray structure determination were obtained (0.1 g, 8%). *Anal.* Calc. for $C_{48}H_{68}N_8O_{15}Cl_2Ag_2$: C, 44.87; H, 5.30; N, 8.72; Ag, 16.8 Found: C, 44.82; H, 5.35; N, 8.87; Ag, 16.6%. IR (cm^{-1}): 3535 (w, ν(OH)(H_2O)); 1637 (s, ν(C=N)). UV–Vis (λ_{max} (nm), CH_3CN): 325 (9700 M^{-1} cm^{-1}); 270 (10 750); 265 (9560); 230 (11 500). ^1H NMR (ppm, CD_3CN): 8.60 (s, 2H, CH=N); 8.51 (s, 4H, CH=N); 7.13 (s, 4H, ph-H); 6.54 (s, 2H, ph-H); 4.10 (m, 24H, $CH_2N{=}+CH_2N\langle$); 3.77 (s, 9H, 2-OCH_3); 3.41 (s, 9H, 5-OCH_3); 2.99 (m, 12H, CH_2. Λ_M (CH_3CN, 290 K): 340 S cm^2 mol^{-1}.

2.3.2. $[Ag_2L^2](ClO_4)_2\cdot 4H_2O$ (2)

A similar procedure to the above afforded the complex with L^2 obtained as a yellowish crystalline product (1.0 g, 85%). *Anal.* Calc. for $C_{48}H_{70}N_8O_{15}Ag_{12}Cl_2$: C, 44.69; H, 5.74; N, 8.69; Ag, 16.7. Found: C, 44.39; H, 5.27; N, 8.69; Ag, 16.8%. IR (cm^{-1}): 3528 (w, ν(OH)(H_2O)); 1635 (s, ν(C=N)). UV–Vis (λ_{max} (nm), CH_3CN): 318 (6600 M^{-1} cm^{-1}): 275 (9000); 270 (7300); 230 (8900). ^1H NMR (ppm, CD_3CN): 8.50 (s, 6H, CH=N); 7.35 (s, 4H, Ph-H); 6.75 (s, 2H, ph-H); 4.10 (m, 24H, $CH_2N{=}+CH_2N\langle$); 3.78 (s, 9H, OCH_3); 2.75 (m, 12H, CH_2); 1.79 (s, 9H, CH_3). Λ_M (CH_3CN, 290 K): 332 S cm^2 mol^{-1}.

2.3.3. $[Ag_2L^3][ClO_4)_2$ (3)

Yellow microcrystals (1.1 g, 80%). *Anal.* Calc. for $C_{45}H_{57}N_8O_{11}Br_3Ag_2Cl_2$: C, 38.24; H, 4.03; N, 7.93; Ag, 14.9. Found: C, 38.49; H, 4.04; N, 8.13; Ag, 15.1%. IR (cm^{-1}): 1635 (s, ν(C=N)). UV–Vis (λ_{max} (nm), CH_3CN): 325 (7300 M^{-1} cm^{-1}), 275 (8370), 265 (7800), 230 (9500). ^1H NMR (ppm, CD_3CN): 8.65 (s, 2H, CH=N); 8.52 (s, 4H, CH=N); 7.66 (s, 4H, ph-H), 7.00 (s, 2H, ph-H), 4.07 (m, 24H, $CH_2N{=}+CH_2N\langle$); 3.84 (s, 9H, OCH_3); 3.50 (m, 12H, CH_2). Λ_M (CH_3CN, 290 K): 286 S cm^2 mol^{-1}.

Caution. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. The complexes described in this report have, so far, been found to be safe when used in small quantities.

2.4. X-ray crystal structure determination of $[Ag_2L^1](ClO_4)_2\cdot H_2O$

2.4.1. Crystal data

$C_{48}H_{68}N_8O_{15}Cl_2Ag_2$, $M = 1283.75$, crystallizes from ethanol as yellowish plates, monoclinic, space group Cc, $a = 11.349(2)$, $b = 29.16(1)$, $c = 17.506(6)$ Å, $\beta = 102.38(2)°$, $U = 5659(3)$ Å^3, $F(000) = 2640$, $Z = 4$, $D_c = 1.51$ g cm^{-3}, $D_m = 1.53$ g cm^{-3}, graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), $T = 296$ K, μ(Mo Kα) = 8.47 cm^{-1}, MSC/RIGAKU AFC 5R diffractometer.

2.4.2. Data collection and processing

A single crystal having approximate dimensions $0.70 \times 0.40 \times 0.10$ mm was mounted on a glass fibre and used for structure determination. The unit cell parameters were determined from least-squares refinement of the setting angles ($5 < \theta < 10°$) for 25 reflections. The ω–2θ technique ($\Delta\omega = 1.365 + 0.35 \tan\theta$) was used to measure 5378 reflections (5099 unique) in the range $3 < 2\theta < 50°$, of which 3693 with $I > 2\sigma(I)$ were used

Table 1
The contribution of coordination effects to the proton chemical shifts of benzene rings in disilver(I) cryptates (ppm)

Cryptate	5-Substituent	δ_c	δ_f	S_c	S_f	δ_c–δ_f
1	OCH_3	7.13	6.54	0.44	−0.15	0.59
2	CH_3	7.35	6.75	0.38	−0.22	0.60
3	Br	7.66	7.00	0.22	−0.44	0.66

in the structure analysis. Corrections for Lorentz–polarization, anisotropic decay and an empirical absorption were applied, using the DIFABS procedure [24], which resulted in transmission factors ranging from 0.8168 t 1.1927. The data were considered likely to be of rather poor quality due to weak diffraction.

2.4.3. Structure analysis and refinement

The structure was solved by direct methods. Approximate positions of Ag atoms were obtained from direct methods. The remaining non-hydrogen atoms were located from a difference Fourier map. Hydrogen atoms were introduced in calculated positions and isotropically joined only in F_c calculations. The final least-squares cycle gave $R=0.063$ and $R_w=0.071$. The weighting scheme was $w=1/\sigma^2(F_o)$. The maximum and minimum peaks on the final difference Fourier map corresponded to +0.72 and −0.83 e Å^{-3}, respectively. All calculations were performed on a Micro VAX II computer with the MSC/RIGAKU TEXSAN V2.1 package [25].

3. Results and discussion

3.1. Spectroscopic characterization of cryptates

The three cryptates possess similar spectroscopic features. Based on their molar conductivities, they are attributed as 1:2 electrolytes [26]. The π–π^* transitions of the K band of the benzene rings and C=N groups are observed in the UV range of their electronic spectra. In the IR spectra of **1** and **2**, the wide bands appearing at about 3530 cm^{-1} imply the existence of crystalline water. The strong peaks at about 1635 cm^{-1} in all the cryptates are attributed to the vibration of C=N.

Giving as an example the ^{1}H NMR data of **1**, two types of chemical shifts appearing at 8.60, 8.51 and 7.13, 6.54 ppm are suggested to be due to CH=N and ph–H, respectively. The proton number ratio of a pair of C=N peaks at 8.60 and 8.51 is 1:2, so is that of a pair of ph–H peaks at 6.54 and 7.13. This means that the protons of both CH=N and ph–H have different chemical environments. The crystal structure also reveals that only two bridging chains, one of which includes N(2) and N(3) and one N(5) and N(6), in the cryptand coordinate to the metals, the other which includes N(7) and N(8) does not. Therefore, the protons of both CH=N and ph–H have different chemical shifts.

Since there are two coordinated bridging chains and one non-coordinated in the cryptand ligand, the effects of substitution and coordination upon the chemical shifts of benzene ring protons may be estimated by the following modified empirical equations [27].

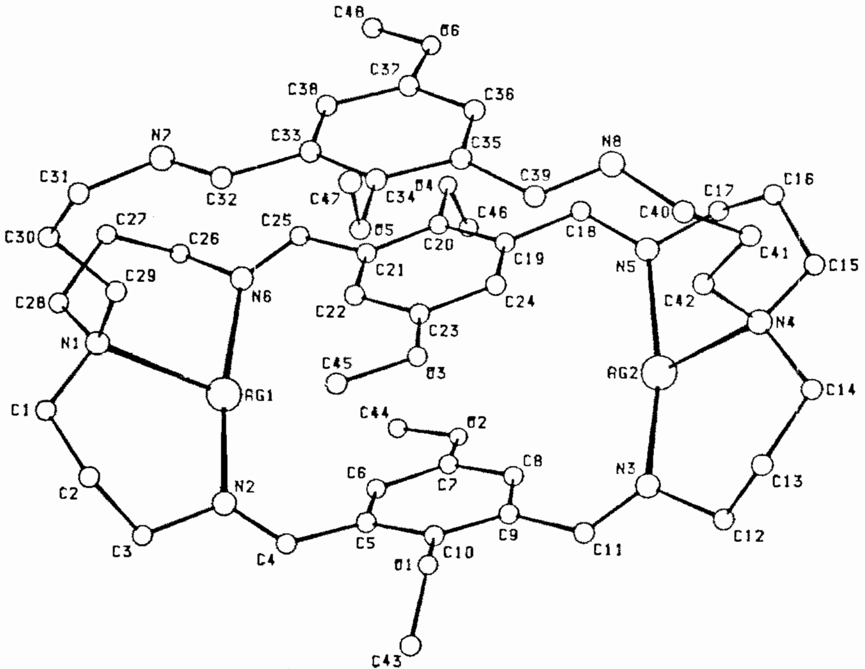

Fig. 2. A perspective view of cationic cryptate $[Ag_2L^1]^{2+}$.

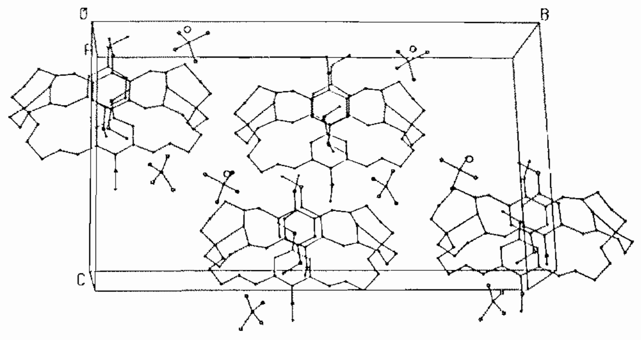

Fig. 3. A packing diagram for cryptate $[Ag_2L^1](ClO_4)_2 \cdot H_2O$.

$$\delta_c = 7.26 + \sum s + S_c \qquad (1)$$

$$\delta_f = 7.26 + \sum s + S_f \qquad (2)$$

where Σs denotes the contributions of substituents quoted from the literature [27], δ_c and δ_f denote the proton chemical shift values of benzene rings in the coordinated and non-coordinated bridging chains, respectively. S_c and S_f are the contributions of coordination effect which can be obtained from Eqs. (1) and (2), respectively. Their values are given in Table 1.

As shown in Table 1, the values of S_c are positive, indicating that coordination causes deshielding effects. It results in downfield shifts. The negative values of S_f indicate that there are high shielding effects in the benzene protons of uncoordinated bridging chains, resulting in upfield shifts. The proton shifts may be attributed to the total contributions of effects of both coordination and substitution. The value of $\delta_f - \delta_c$ represents the total contribution in this type of cryptate. These cryptates have a sequence of $\delta_f - \delta_c$ value as follows: **1** ($R = CH_3O$) $\leqslant$ **2** ($R = CH_3$) < **3** ($R = Br$).

3.2. Description of the structure of $[Ag_2L^1](ClO_4)_2 \cdot H_2O$

A perspective view of the cation $[Ag_2L^1]^{2+}$ and a packing diagram are shown in Figs. 2 and 3, respectively. Coordinates of non-hydrogen atoms, and selected interatomic distances and bond angles are given in Tables 2 and 3, respectively.

It may be seen from Fig. 2 that in the cation $[Ag_2L^1]^{2+}$ each Ag(I) atom lies in the three-coordinate environment composed of one tertiary nitrogen N(1) or N(4) and two imino nitrogens N(2) and N(6) or N(3) and N(5). The imino nitrogens of only two bridging chains (one includes N(2) and N(3), the other includes N(5) and N(6)) coordinate to the silver(I) atoms. The distances Ag(1)–N(1) and Ag(2)–N(2) are 2.48(1) and 2.47(1) Å, respectively, i.e. longer than normal. This indicates a weaker interaction between silver(I) and the more strongly basic tertiary nitrogen. The distances between Ag(I) and imino nitrogens N(2) and N(6) or

Table 2
Coordinates of the non-hydrogen atoms of cryptate $[Ag_2L^1](ClO_4)_2 \cdot H_2O$ ($\times 10^4$)

Atom	*x*	*y*	*z*
Ag(1)	9949	16491(4)	2757
Ag(2)	10376(2)	−904.9(4)	2654(1)
N(1)	11220(10)	2286(4)	3426(8)
N(2)	8910(10)	1552(5)	3639(8)
N(3)	9270(2)	−881(5)	3520(10)
N(4)	11720(10)	−1498(4)	3378(8)
N(5)	11840(10)	−809(5)	2014(8)
N(6)	11250(10)	1618(5)	1984(9)
N(7)	14690(10)	1711(5)	4415(9)
N(8)	14840(10)	−759(5)	4659(9)
C(1)	10530(20)	2523(6)	3940(10)
C(2)	9910(20)	2208(6)	4440(10)
C(3)	8710(20)	1981(6)	4050(10)
C(4)	8460(20)	1174(6)	3820(10)
C(5)	8480(10)	752(6)	3400(8)
C(6)	8380(20)	770(6)	2620(10)
C(7)	0.842(1)	377(6)	2140(10)
C(8)	8550(20)	−41(6)	2520(10)
C(9)	8620(20)	−75(6)	3340(10)
C(10)	8610(10)	319(6)	3770(8)
C(11)	8670(20)	−530(7)	3700(10)
C(12)	9080(20)	−1321(6)	3880(10)
C(13)	10280(20)	−1544(6)	4330(10)
C(14)	11040(20)	−1796(6)	3820(10)
C(15)	12220(20)	−1786(6)	2850(10)
C(16)	12920(20)	−1543(7)	2320(10)
C(17)	12250(20)	−1208(7)	1690(10)
C(18)	12340(20)	−414(6)	1870(10)
C(19)	12070(10)	5(5)	2256(8)
C(20)	12100(10)	428(6)	1872(9)
C(21)	11870(10)	827(6)	2260(10)
C(22)	11770(10)	818(6)	3044(8)
C(23)	11770(10)	408(5)	3400(10)
C(24)	11950(10)	1(5)	3020(10)
C(25)	11850(20)	1276(7)	1830(10)
C(26)	11360(20)	2045(7)	1600(10)
C(27)	12090(20)	2390(7)	2240(10)
C(28)	11400(20)	2607(6)	2830(10)
C(29)	12350(20)	2088(6)	3880(10)
C(30)	13380(20)	2401(6)	4230(10)
C(31)	14410(20)	2122(7)	4800(10)
C(32)	14650(10)	1334(6)	4770(10)
C(33)	14830(10)	886(6)	4430(10)
C(34)	14700(20)	486(6)	4850(10)
C(35)	14780(10)	59(6)	4473(9)
C(36)	15010(20)	47(6)	3710(10)
C(37)	15110(20)	447(7)	3320(10)
C(38)	15020(10)	876(6)	3660(10)
C(39)	14520(20)	−364(6)	4870(10)
C(40)	14440(20)	−1153(6)	5050(10)
C(41)	13710(20)	−1478(6)	4450(10)
C(42)	12630(20)	−1209(6)	3900(10)
O(1)	8830(10)	283(5)	4559(7)
C(43)	7920(20)	354(8)	4960(10)
O(2)	8260(10)	383(4)	1354(7)
C(44)	8070(20)	802(7)	960(10)
O(3)	11660(10)	352(3)	4154(6)
C(45)	11560(20)	760(6)	4600(10)
O(4)	12220(10)	439(4)	1107(7)
C(46)	11170(20)	365(7)	560(10)

(continued)

Table 2 (*continued*)

O(5)	14480(10)	499(4)	5572(6)
C(47)	15520(20)	480(10)	6170(10)
O(6)	15290(20)	384(5)	2580(8)
C(48)	15290(20)	770(9)	2130(10)
Cl(1)	7568(6)	2120(2)	1298(4)
Cl(2)	8430(7)	1515(2)	6290(4)
O(11)	7010(20)	2531(8)	980(10)
O(12)	8480(20)	2260(8)	1930(10)
O(13)	8220(20)	1911(7)	780(10)
O(14)	6950(30)	1820(10)	1670(20)
O(15)	7480(30)	1650(10)	5780(20)
O(16)	9160(20)	1770(10)	6910(20)
O(17)	9200(40)	1270(10)	5910(30)
O(18)	7900(40)	1330(10)	6760(20)
O(19)	4280(30)	2080(10)	1280(20)

Table 3
Selected interatomic distances (Å) and bond angles (°)

Ag(1)–N(2)	2.16(1)	Ag(1)–N(6)	2.20(2)
Ag(1)–N(1)	2.48(1)	Ag(2)–N(3)	2.16(2)
Ag(2)–N(5)	2.21(2)	Ag(2)–N(4)	2.47(1)
N(1)–C(28)	1.45(2)	N(1)–C(29)	1.48(2)
N(1)–C(1)	1.48(2)	N(2)–C(4)	1.28(2)
N(2)–C(3)	1.48(2)	N(3)–C(11)	1.31(2)
N(3)–C(12)	1.47(2)	N(4)–C(15)	1.45(2)
N(4)–C(14)	1.48(3)	N(4)–C(42)	1.48(2)
N(5)–C(18)	1.33(2)	N(5)–C(17)	1.42(2)
N(6)–C(25)	1.27(2)	N(6)–C(26)	1.43(2)
N(7)–C(32)	1.27(2)	N(7)–C(31)	1.44(2)
N(8)–C(39)	1.29(2)	N(8)–C(40)	1.47(2)
Ag(1)···Ag(2)	7.468(12)	Ag(1)···N(7)	5.545(15)
Ag(2)···N(8)	5.528(16)		
N(2)–Ag(1)–N(6)	167.2(5)	N(2)–Ag(1)–N(1)	96.4(5)
N(6)–Ag(1)–N(1)	85.7(5)	N(3)–Ag(2)–N(5)	164.0(5)
N(3)–Ag(2)–N(4)	93.0(6)	N(5)–Ag(2)–N(4)	84.3(5)
C(1)–N(1)–Ag(1)	108(1)	C(28)–N(1)–Ag(1)	107(1)
C(29)–N(1)–Ag(1)	108(1)	C(3)–N(2)–Ag(1)	114(1)
C(4)–N(2)–Ag(1)	127(1)	C(25)–N(6)–Ag(1)	128(1)
C(11)–N(3)–Ag(2)	128(1)	C(12)–N(3)–Ag(2)	116(1)
C(14)–N(4)–Ag(2)	110(1)	C(15)–N(4)–Ag(2)	111(1)
C(17)–N(5)–Ag(2)	116(1)	C(18)–N(5)–Ag(2)	127(1)
C(42)–N(4)–Ag(2)	101(1)		

N(3) and N(5) average 2.20 Å. However, there are no chemical bonds formed between the Ag(I) atoms and the imino nitrogens in the other bridging chain which includes N(7) and N(8), because the distances Ag(1)···N(7) and Ag(2)···N(8) are 5.545(15) and 5.528(16) Å, respectively. The distance Ag(1)···Ag(2) is 7.468(12) Å; apparently, there is no interaction between the two metals.

As shown in Table 4, the coordinated nitrogens locate over the plane 1 or 2 with maximum deviations of 0.25 or 0.35 Å, the Ag(1) or Ag(2) atom being near the corresponding plane. Thus, the coordination environment about Ag(I) would be considered as a trigonal pyramid distorted slightly from a planar triangle. The Ag(I) atom locates at the top of the trigonal pyramid.

Table 4
Selected least-squares planes

Plane	Atoms	Distance (Å)
1	Ag(1)	−0.0003(3)
	N(1)	0.0078(132)
	N(2)	0.2238(131)
	N(6)	0.2536(143)
2	Ag(2)	−0.0040(15)
	N(3)	0.3463(163)
	N(4)	−0.0088(135)
	N(5)	0.2429(137)
3	N(2)	0.0445(131)
	N(3)	−0.1244(163)
	N(5)	0.0664(137)
	N(6)	−0.0969(143)

Least-squares plane 3 is composed of N(2), N(3), N(5) and N(6). Ag(1) and Ag(2) are situated under plane 3 by 0.1694(140) and 0.2847(138) Å, respectively. The dihedral angles between plane 3 and plane 1 and between plane 3 and plane 2 are 43.93(53) and 42.92(64)°, respectively. The cationic complex [Ag_2L^1] appears as a basket structure. Two metal atoms lie in the bottom of the 'basket' composed of two coordinate bridging chains and two bridgehead nitrogens, while the non-coordinate bridging chain looks like the handle of the 'basket'. In addition, neither the water molecule nor anion coordinates to Ag(I), and no hydrogen bond is formed.

4. Supplementary material

Tables of crystal data, positional and anisotropic thermal parameters, selected bond lengths and angles, torsion angles and *U* values (11 pages), and structure factors (25 pages) are available from the authors on request.

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References

[1] J.-M. Lehn, *Angew. Chem., Int. Ed. Engl., 27* (1988) 90.
[2] J.-M. Lehn, *Pure Appl. Chem., 52* (1980) 2411.
[3] F. Barigelletti, L. de Cola, V. Balzani, P. Belser, A. von Zelewsky, F. Vogtle, F. Ebmeyer and S. Grammenudi, *J. Am. Chem. Soc., 111* (1989) 4662.

[4] M. Gubelmann, J.-M. Lehn, J.L. Sessler and A. Harriman, *J. Chem. Soc., Chem. Commun.,* (1988) 77.

[5] J.-M. Lehn, in K.J. Laidler (ed.), *IUPAC Frontiers of Chemistry,* Pergamon, Oxford, 1982, p. 265.

[6] M.D. Timken, W.A. Marritt, D.N. Hendrickson and R.A. Gagne, *Inorg. Chem., 24* (1985) 4202.

[7] J. Jazwinski, J.-M. Lehn, D. Lilienbaunm, R. Ziessel, J. Guilhem and C. Pascard, *J. Chem. Soc., Chem. Commun.,* (1987) 1691.

[8] D. McDowell and J. Nelson, *Tetrahedron Lett., 29* (1988) 385.

[9] D. McDowell, J. Nelson and V. McKee, *Polyhedron, 8* (1989) 1143.

[10] O. Kocian, R.J. Mortimer and P.D. Beer, *Tetrahedron Lett., 31* (1990) 5069.

[11] J.-M. Lehn, R. Meric, J.-P. Vigneron, I. Bkouche-Waksman and C. Pascard, *J. Chem. Soc., Chem. Commun.,* (1991) 62.

[12] R. Menif, J. Reibenspies and A.E. Martell, *Inorg. Chem., 30* (1991) 3446.

[13] J. Hunter, J. Nelson, C. Harding, M. McCann and V. McKee, *J. Chem. Soc., Chem. Commun.,* (1990) 1148.

[14] M.G.B. Drew, J. Hunter, D.J. Marrs, J. Nelson and C. Harding, *J. Chem. Soc., Dalton Trans.,* (1992) 3235.

[15] P.D. Beer, O. Kocian, R.J. Mortimer and P. Spencer, *J. Chem. Soc., Chem. Commun.,* (1992) 602.

[16] J.-M. Lehn, J.-P. Vigneron, I. Bkouche-Waksman, J. Guilhem and C. Pascard, *Helv. Chim. Acta, 75* (1992) 1069.

[17] M.-T. Youinou, J. Suffert and R. Ziessel, *Angew. Chem., Int. Ed. Engl., 31* (1992) 775.

[18] M.P. Ngwenya, A.E. Martell and J. Reibenspies, *J. Chem. Soc., Chem. Commun.,* (1990) 1207.

[19] J. de Mendoza, E. Mesa, J.C. Rodriguez-Ubis, P. Vazquez, F. Vögtle, P.M. Windscheif, K. Rissanen, J.-M. Lehn, D. Lilienbaum and R. Ziessel, *Angew. Chem., Int. Ed. Engl., 30* (1991) 1331.

[20] M.G.B. Drew, D. McDowell and J. Nelson, *Polyhedron, 7* (1988) 2229.

[21] J.C. Rodriguez-Ubis, B. Alpha, D. Plancherel and J.-M. Lehn, *Helv. Chim. Acta, 67* (1984) 2264.

[22] J. Chin, M. Banaszczyk, V. Jubian and X. Zou, *J. Am. Chem. Soc., 111* (1989) 186.

[23] Hu Yaofei and Hu Hongwen, *Chem. J. Chin. Univ., 7* (1986) 132.

[24] N. Walker and D. Stuart, *Acta Crystallogr., Sect A, 39* (1983) 158.

[25] (a) Molecular Structure Corporation, *CONTROL*, an automatic package for Rigaku AFC single crystal diffractometers, College Station, TX, USA, 1988; (b) Molecular Structure Corporation, *TEXSAN*, TEXRAY structure analysis package, The Woodlands, TX, USA, 1989.

[26] W.J. Geary, *Coord. Chem. Rev., 7* (1971) 81.

[27] R.J. Abraham and P. Loftus, *Proton and Carbon-13 NMR Spectroscopy,* Wiley Heyden, New York, 1978, p. 28.