LETTER

NJC
www.rsc.org/njc

Synthesis and helical polymeric structure of a luminescent pendant-armed macrocyclic silver(I) complex with Ag–Ag interactions

Laura Valencia,*[a] Rufina Bastida,*[a] Alejandro Macías,[a] Manuel Vicente[a] and Paulo Pérez-Lourido[b]

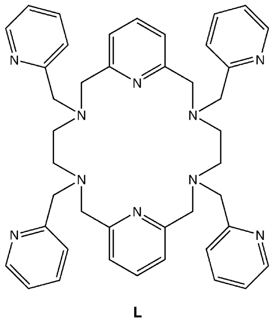
[a] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Avda. de las Ciencias s/n., 15782 Santiago de Compostela, La Coruña, Spain.*
E-mail: qibastid@usc.es;qilaura@usc.es; Fax: 00 34 981597525; Tel: 00 34 981 528073
[b] *Departamento de Química Inorgánica, Facultad de Ciencias, Universidade de Vigo, 36310 Vigo Pontevedra, Spain*

Received (in Durham, UK) 25th October 2004, Accepted 12th January 2005
First published as an Advance Article on the web 1st February 2005

DOI: 10.1039/b416342g

An interesting 1D helical chain complex has been obtained with silver(I) nitrate and a tetrapyridyl pendant-armed macrocyclic ligand (L) in acetonitrile. The X-ray crystal structure of the complex, which has the formula ($[Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$, presents silver–silver interactions in an infinite spiral chain structure that is unprecedented in such pyridyl macrocyclic complexes. The structure forms a large cavity or channel that contains the silver(I) ions and presents face-to-face π,π-stacking between the pyridyl rings. The complex shows fluorescence in the solid state and acetonitrile solution at room temperature.

Over the last three decades there has been extensive research into the coordination chemistry of macrocyclic ligands. Such species have shown considerable potential in such areas as catalysis, modelling of metalloenzyme activity, molecular recognition *etc.*[1] In recent years pendant-armed macrocyclic ligands and their metal complexes have attracted a great deal of interest owing to the fact that the incorporation of functionalised pendant arms provides additional coordinating functions, enhances complex stability or promotes the formation of supramolecular structures with different properties and applications.[2] Several examples of macrocyclic ligands bearing pyridyl pendant groups have been described in the literature.[3] We recently investigated the coordination capability of a new pyridyl pendant-armed macrocyclic ligand (L, Scheme 1).[4] As reported previously, the flexibility of these pendant groups makes this a more versatile molecule, which allows coordination of the encapsulated metal or promotes the formation of polymeric complexes, depending on the steric requirements of the metal ion employed and the coordinative behaviour of the counterions. Although diverse metal ions have been used for the design of polymeric structures, Ag(I) complexes are well known due to the fact that this ion presents a variety of coordination environments, including linear, T-shaped, tetrahedral and octahedral.[5]



Scheme 1

On the other hand, a great deal of attention has been paid to d^{10} metal compounds due to their photophysical and photochemical properties.[6] However, luminescent properties of Ag(I) complexes have been less widely studied—in contrast to Cu(I) and Au(I) complexes—and examples that emit fluorescence at room temperature are rare.[7]

We report here the synthesis and characterisation of a 1D macrocyclic Ag(I) complex with silver–silver interactions that exhibits fluorescence in the solid and solution states at room temperature.

The ligand (L) was prepared from the hexaaza macrocycle precursor[8] by alkylation with picolyl chloride using a previously reported method.[3] The reaction between $AgNO_3$ and L in a 2 : 1 molar ratio in acetonitrile gave the complex ($[Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$. The crystal structure, which is shown in Fig. 1 together with the atomic numbering scheme adopted and selected bond distances and angles, can be described as a 1D shallow helical polymer. A crystallographically imposed symmetry is present in the unit cell and three different silver(I) ions are found in the asymmetric unit. Two of these, Ag(2) and Ag(3), are endomacrocyclically coordinated with a similar {AgN4} core, with each metal bonded by one pyridinic nitrogen of the macrocyclic backbone, two tertiary amine nitrogen atoms and one pyridine pendant group. The geometry cannot be described as a regular polyhedron; Ag(2) is in the plane formed by N(4)–N(6)–N(10) (rms 0.0110) and N(5) is 1.9781(0.0033) Å away from this plane. In the same way, N(2) is 1.9646 Å away from the Ag(3)–N(1)–N(3)–N(8) plane (rms 0.0086). The distance between the metal centres [Ag(2)···Ag(3), 2.9749 (5) Å] is slightly longer than in metallic silver (2.888 Å) but significantly less than twice the van der Waals radius for silver (3.44 Å), thus indicating a certain degree of intermetallic interaction.[9]

The remaining two pyridyl pendant groups are almost normal to the cavity of the ligand and are directed towards opposite sides, with the N atoms coordinated to two different Ag(1) atoms. This arrangement gives rise to a helical polymeric chain. The Ag(1) atom is linked by two nitrogen atoms of the

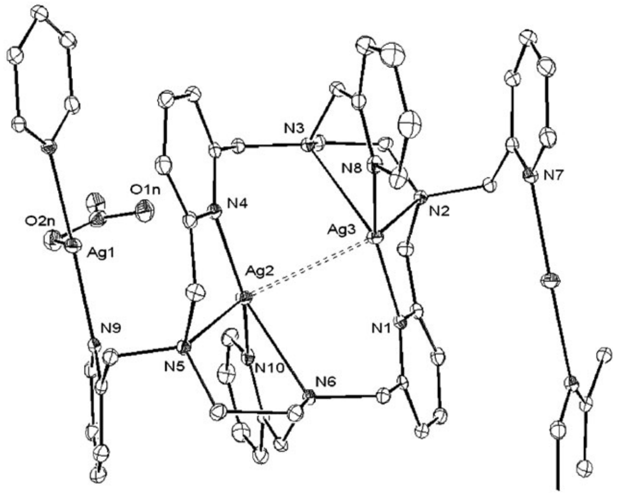


Fig. 1 Partial view of the crystal structure of ($[Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$. Hydrogen atoms, water molecules and ionic nitrate counterions have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–Ag(3) 2.218(2), N(2)–Ag(3) 2.540(3), N(3)–Ag(3) 2.498(2), N(4)–Ag(2) 2.199(2), N(5)–Ag(2) 2.531(3), N(6)–Ag(2) 2.494(2), N(7)–Ag(1)#1 2.169(3), N(8)–Ag(3) 2.228(3), N(9)–Ag(1) 2.171(3), N(10)–Ag(2) 2.204(3), Ag(1)–N(7)#2 2.169(3), Ag(2)–Ag(3) 2.9749(5), N(7)#2–Ag(1)–N(9) 169.13(10), N(4)–Ag(2)–N(10) 156.56(9), N(4)–Ag(2)–N(6) 128.86(9), N(10)–Ag(2)–N(6) 74.52(9), N(4)–Ag(2)–N(5) 74.55(9), N(10)–Ag(2)–N(5) 116.60(9), N(6)–Ag(2)–N(5) 73.70(8), N(4)–Ag(2)–Ag(3) 85.95(7), N(10)–Ag(2)–Ag(3) 100.47(7), N(6)–Ag(2)–Ag(3) 82.83(6), N(5)–Ag(2)–Ag(3) 127.56(6), N(1)–Ag(3)–N(8) 158.35(9), N(1)–Ag(3)–N(3) 128.33(9), N(8)–Ag(3)–N(3) 73.27(9), N(1)–Ag(3)–N(2) 74.28(9), N(8)–Ag(3)–N(2) 116.57(9), N(3)–Ag(3)–N(2) 73.25(8), N(1)–Ag(3)–Ag(2) 85.92(7), N(8)–Ag(3)–Ag(2) 100.14(7), N(3)–Ag(3)–Ag(2) 81.95(6), N(2)–Ag(3)–Ag(2) 126.00(6).

pyridyl pendant groups from two different ligand molecules, as well as to the oxygen atom of the nitrate counterion [Ag(1)–O(2N), 2.611 Å].[10] This gives rise, as previously observed in a number of polymeric silver(I) complexes,[11] to a distorted T-shaped coordination [N(9)–Ag(1)–N(7#), 169.13(10)°, N–Ag–O(2N), 97.57(9)° for N(7#) and 92.86(9)° for N(9); $\Sigma_{Ag} = 359.56°$]; the distortion is believed to be caused by the proximity of another nitrate oxygen atom [Ag(1)···O(1N), 3.009 Å] that is involved in a long weak interaction.[12]

The polymeric complex displays interesting structural features. Analysis of the short inter- and intramolecular interactions reveals that all aromatic units are packed in such a way that two columnar pyridyl stacks form along the *c*-axis and show some π,π-interactions (Fig. 2). Thus, the majority of the pyridine rings form dihedral angles of around 10° with distances between centroids of aromatic groups around 3.8 Å, which can be considered as face-to-face π,π-interactions.[13] In the other cases the dihedral angles are *ca.* 37°. The silver atoms are located within the large cavity or channel formed by the macrocyclic ligands and are coordinated to the nitrogen donor atoms, which are directed toward this cavity.

The chains are packed together in a grid surrounded by anions and solvent molecules. There is no evidence for interactions between adjacent polymeric chains to form a type of high-dimensional polymeric structure.

The IR spectrum of the complex (KBr disc) shows, as in the free ligand, split bands associated with ν(C=N) and ν(C=C) vibrations from the pyridine rings. These bands are shifted to higher wavenumbers on complexation and this is due to the interaction between the silver(I) ions and the pyridinic nitrogen atoms.[14] Several bands are present in the region associated with nitrate vibrations and these clearly indicate a species containing coordinated nitrate groups, although an intense absorption band at 1380 cm^{-1} also indicates the presence of free ionic nitrate.[15] The FAB mass spectrum shows the characteristic fragmentation pattern resulting from stepwise loss of counterions and metal atoms from the neutral parent ion, which is consistent with the polymeric nature of the complex ($[Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$. Raman spectroscopy studies show an active band at 85 cm^{-1}, which can be assigned to the Ag–Ag vibration.[16] The molar conductance was measured in acetonitrile at 25 °C and lies in the range reported for 3 : 1 electrolytes, suggesting that the nitrate anions are not coordinated to the silver(I) ions in solution.[17]

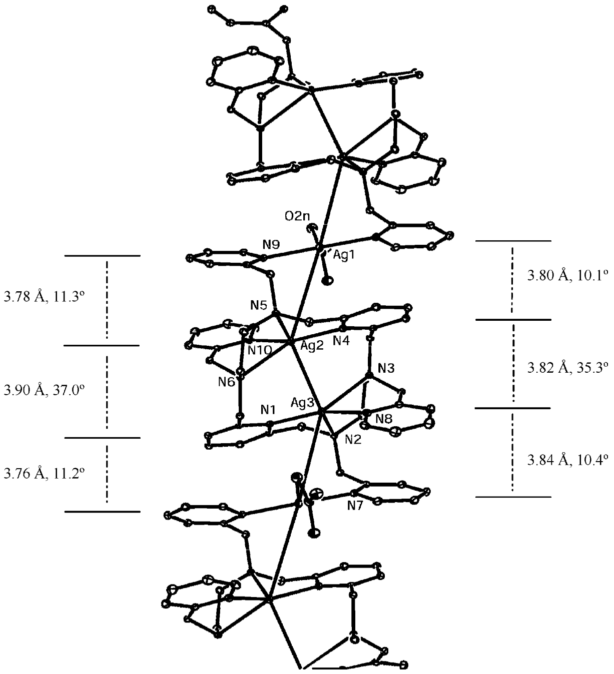


Fig. 2 The columnar pyridyl stacks along the *c*-axis maintained by π,π-interactions present in ($[Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$. The distance between centroids of pyridine rings and the dihedral angle are shown.

The ^{1}H NMR spectrum of the silver complex was recorded in CD_3CN at 298 and 258 K. The room temperature spectrum is quite complicated and two groups of unresolved broad multiplets can be observed: one multiplet between 2.5 and 4.0 ppm belonging to the aliphatic protons of the molecule and the other multiplet, between 6.8 and 8.0 ppm, belonging to the aromatic protons. The 258 K spectrum, although quite complicated and difficult to assign completely, shows that the ligand has lost its four-fold symmetry. Indeed, one signal is observed for each of the protons of the molecule, as reported previously for the complex $[Ag_2L](ClO_4)_2 \cdot 2CH_3CN$.[4]

The absorption spectrum of the complex at room temperature shows a broad band centered at 450 and at 435 nm in the solid state and in acetonitrile solution, respectively. Emission measurements at room temperature show that the complex exhibits fluorescence at 565 nm in the solid sate and at 532 nm in acetonitrile solution upon excitation at 430 nm. These results could be indicative of disaggregation of the polymer in solution, as described previously.[18] The absorption band is not observed in the spectrum of the free ligand and the fluorescence behaviour of the complex can be attributed to Ag–N coordination and the presence of Ag···Ag interactions.[19]

In summary, we have described the synthesis and characterisation of a novel one-dimensional Ag(I) helical polymer complex with a pyridyl pendant-armed macrocyclic ligand. The structure presents Ag···Ag interactions and face-to-face π,π-stacking interactions between the pyridyl groups. The absorption and emission studies reveal that the complex shows luminescence in the solid and solution states at room temperature, and this is believed to be due to the existence of intermetallic interactions.

Experimental

The silver(I) complex was obtained by direct reaction between $AgNO_3$ (0.5 mmol) in acetonitrile (10 mL) and L (0.25 mmol) in refluxing acetonitrile (30 mL). The reaction mixture was heated under reflux for 2 h and concentrated using a rotary evaporator to give a total volume of *ca.* 5–6 mL. The resulting white crystalline product was filtered off, dried and recrystallised from water (yield: 67%). The microanalytical data reveal the presence of a trinuclear Ag(I) complex $[Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O$. Anal. Calc. for $C_{42}H_{62}N_{13}O_{17}Ag_3$: C, 37.5; H, 4.7, N, 13.5. Found: C, 37.6, H, 4.9; N, 13.4%. IR (KBr, cm^{-1}): 1437, 1462, 1571, 1582, 1600 [ν(C=C) and $\nu(C{=}N)_{py}$], 1304, 1380, 1500 [$\nu(NO_3^-)$]. MS (FAB, *m*/*z*): 797 $[AgL]^+$, 986 $[Ag_2L(NO_3)]^+$, 1185 $[Ag_4L(NO_3)]^+$, 1137 $[Ag_3L(NO_3)_2]^+$, 1307 $[Ag_4L(NO_3)_3]^+$. $\Lambda_M/\Omega^{-1}\ cm^2\ mol^{-1}$(in CH_3CN): 347 (3 : 1).

X-Ray crystallography

Data collection for $([Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$ was performed at 293 K on a BRUKER Smart-CCD-1000 diffractometer (Mo-K_α, $\lambda = 0.710\,73$ Å). Reflections were corrected for Lorentz and polarisation effects and for absorption by an empirical method.[20] The structure was solved by direct methods and refined with the full-matrix least-squares technique (SHELXL-97)[21] to give a final R_1 value of 0.0315 for 677 parameters and 12638 unique reflections with $I \geq 2\sigma(I)$ and wR_2 of 0.0980 for all 47797 reflections. Molecular graphics: ORTEP-3.[22]

X-Ray crystal data for $([Ag_3L(NO_3)](NO_3)_2 \cdot 8H_2O)_\infty$: $C_{42}H_{62}N_{13}O_{17}Ag_3$ ($M = 1344.66$), monoclinic, $P2_1/c$, $a = 14.991(3)$, $b = 17.852(4)$, $c = 19.543(4)$ Å, $\beta = 100.154(3)°$, $V = 5148.3(17)$ Å^3, $Z = 4$, $T = 239$ K, $\rho_{calcd.} = 1.735$ g cm^{-3}, $F(000) = 2728$, $\mu = 1.213$ mm^{-1}. CCDC reference number 241779. See http://www.rsc.org/suppdata/nj/b4/b416342g/ for crystallographic data in .cif or other electronic format.

Acknowledgements

We thank the Xunta de Galicia (PGIDT04PXIB20901PR) for financial support. Intensity measurements were performed at the Unidade de Rayos X, RIAIDT, University of Santiago de Compostela, Spain.

References

1 P. Guerriero, S. Tamburini and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17, and references therein.

2 (*a*) E. V. Rybak-Akimova, A. Y. Nazarenko and S. S. Silchenco, *Inorg. Chem.*, 1999, **38**, 2974; (*b*) M. Botta, *Eur. J. Inorg. Chem.*, 2000, 399; (*c*) K. P. Wainwright, *Adv. Inorg. Chem.*, 2001, **52**, 293.

3 (*a*) I. M. Atkinson, J. D. Chartres, G. W. Everett, X.-K. Ji, L. F. Lindoy, O. A. Matthews, G. V. Meehan, B. W. Skelton, G. Wei and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 1191; (*b*) P. Xue, Q. Yuan, E. Fu and C. Wu, *J. Organomet. Chem.*, 2001, **637–639**, 327; (*c*) W. S. Szulbinski and R. S. Czernuszewicz, *Inorg. Chim. Acta*, 1996, **247**, 11; (*d*) S. J. Brudenell, L. Spiccia and E. R. T. Tiekink, *Inorg. Chem.*, 1996, **35**, 1974; (*e*) S. J. Brudenell, L. Spiccia, A. M. Bond, P. Comba and D. C. R. Hockless, *Inorg. Chem.*, 1998, **37**, 3705.

4 R. Bastida, D. E. Fenton, M. López-Deber, A. Macías, L. Valencia and M. Vicente, *Inorg. Chim. Acta*, 2003, **355**, 292.

5 M. Munakata, L.-P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173, and references therein.

6 (*a*) D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum, New York, 1994, ch. 2–4, and references therein; (*b*) V. W. W. Yam, K. K.-W. Lo, W. K.-M. Fung and C.-R. Wang, *Coord. Chem. Rev.*, 1998, **171**, 17; (*c*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (*d*) R. J. Puddephatt, *Chem. Commun.*, 1998, 1055.

7 (*a*) M.-L. Tong, J.-X. Shi and X.-M. Chen, *New J. Chem.*, 2002, **26**, 814, and references therein; (*b*) C.-C. Wang, C.-H. Yang, S.-M. Tseng, S.-Y. Lin, T.-Y. Wu, M.-R. Fuh, G.-H. Lee, K.-T. Wong, R.-T. Chen, Y.-M. Cheng and P.-T. Chou, *Inorg. Chem.*, 2004, **43**, 4781.

8 G. L. Rothermel, Jr, L. Miao, A. L. Hill and S. C. Jackels, *Inorg. Chem.*, 1992, **31**, 4854.

9 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

10 (*a*) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6837; (*b*) P. W. Miller, M. Nieuwenhuyzen, X. Xu and S. L. James, *Chem. Commun.*, 2002, 2008.

11 (*a*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; (*b*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1997, **119**, 4562.

12 S. Silong, Effendy, J. D. Kildea, B. W. Skelton, U. Tooptakong and A. H. White, *Aust. J. Chem.*, 2003, **56**, 35.

13 (*a*) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525; (*b*) R.-F. Song, Y.-B. Xie, J.-R. Li and X.-H. Bu, *Dalton Trans.*, 2003, 4742.

14 N. S. Gill, R. H. Nuttall, D. E. Scaife and D. W. Sharp, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.

15 (*a*) J. C. G. Bünzli and D. Wessner, *Coord. Chem. Rev.*, 1984, **191**, 253; (*b*) I. A. Kahwa, J. Selbin, T. C. Y. Hasieh and R. A. Lane, *Inorg. Chim. Acta*, 1986, **118**, 179.

16 M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle and H. H. Patterson, *Inorg. Chem.*, 1998, **37**, 1380, and references therein.

17 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 181.

18 M.-L. Tong, X.-M. Chen, B.-H. Ye and L.-N. Ji, *Angew. Chem., Int. Ed.*, 1999, **38**, 2237.

19 (*a*) R.-H. Uang, C.-K. Chan, S.-M. Peng and C.-M. Che, *J. Chem. Soc., Chem. Commun.*, 1994, 2561; (*b*) V. J. Catalano, H. M. Kar and B. L. Bennett, *Inorg. Chem.*, 2000, **39**, 121.

20 G. M. Sheldrick and Sadabs, *Program for Empirical Absoption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.

21 G. M. Sheldrick, *SHELX-97*, An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.

22 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.