Letter

Synthesis and crystal structure of a luminescent infinite 2D brick-wall network with two- and three-coordinate silver(I) atoms and ligand-unsupported silver–silver interactions†

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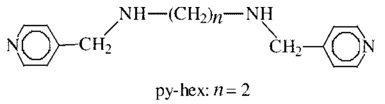
Assembly of a novel flexible tetradentate ligand 1,7-bis(4′-pyridyl)-2,6-diazaheptane (py-hep) with silver perchlorate hydrate provides an interesting two-dimensional (2D) brick-wall network: $[Ag_3(py\text{-}hep)_2](ClO_4)_3 \cdot 0.5CH_3CN$. The X-ray crystal structural analysis indicates that the framework consists of trigonal and linearly coordinated silver(I) atoms and ligand-unsupported metal–metal interactions. The complex shows photoluminescence in both the solid state and in acetonitrile solution.

The construction of transition metal complexes with specific network topologies is attracting extensive interest among chemists.[1] The primary reason for the interest in such compounds is their ability to afford functional solid materials with potentially controllable properties as well as fascinating molecular structures. The recent development of supramolecular chemistry has made it possible to select building units for assembly into structures with specific network topologies.[2] Crystal engineering of coordination polymeric networks based on multidentate ligands represents a growing area of coordination and supramolecular chemistry. We have focussed our attention on the assembly of metal ions with flexible ligands since they can adopt diverse coordination modes according to the different geometric needs of the metal ions.[3,4] As reported previously, the flexible tetradentate ligand 1,6-bis(4′-pyridyl)-2,5-diazahexane (py-hex) gives 1D or 2D frameworks depending on the metal ions and counter anions.[4] Now we have extended this work to a ligand with a propanediamine instead of an ethylenediamine unit, that is 1,7-bis(4′-pyridyl)-2,6-diazaheptane (py-hep). Surprisingly, reaction of py-hep with $AgClO_4 \cdot H_2O$ gives a 2D non-interpenetrating network that is entirely different from that found in the complex formed by py-hex and $AgClO_4 \cdot H_2O$.



py-hex: $n = 2$
py-hep: $n = 3$

The ligand py-hep was prepared according to a procedure similar to that used for py-hex.[4] Reaction between py-hep and $AgClO_4 \cdot H_2O$ in a 1 : 1 molar ratio in CH_3CN gave the compound $[Ag_3(py\text{-}hep)_2](ClO_4)_3 \cdot 0.5CH_3CN$.‡ The presence of CH_3CN was confirmed by electrospray mass spectral measurements in methanol with the appearance of $[Ag(py\text{-}hep)(CH_3CN)]^+$ at $m/z = 403.9$.

X-Ray crystal structural analysis indicates that the cationic part of the repeat unit contains three Ag(I) atoms and two ligands as shown in Fig. 1.§ It is interesting that the Ag(I) atoms have two different coordination environments. Fig. 2 shows the local coordination geometry around the three- and two-coordinate Ag(I) atoms. Both Ag(1) and Ag(2) are three-coordinate [Fig. 2(a)] by two NH groups of py-hep and one pyridine group of another py–hep with Ag–N distances in the range of 2.234(5)–2.374(5) Å. Ag(3) is twofold-coordinated by two nitrogen atoms of pyridine with an Ag–N distance of 2.108(6) Å [Fig. 2(b)]. It is clear that each Ag(I) atom is coordinated by two different py-hep and in turn each py-hep ligand connects three Ag(I) atoms. Such a coordination mode generates a polymeric network. The distance of 3.179(1) Å between Ag(3) and Ag(3B) [Fig. 2(b)] indicates the existence of weak ligand-unsupported metal–metal interactions.[5,6] Therefore, the framework is a wavy 2D brick-wall network structure,[5–8] as illustrated in Fig. 3.

There are also π–π and hydrogen bonding interactions in addition to the above weak Ag···Ag interactions in the title complex. The two parallel pyridine rings containing N(12) and N(12A) in Fig. 2(a) are separated by a centroid–centroid distance of 3.63 Å. The centroid–centroid distance between the two pyridine rings containing N(42) and N(32C) in Fig. 2(b), with a dihedral angle of 10.5°, is also 3.63 Å. Such short distances imply the presence of π–π interactions. The oxygen atoms of three perchlorate anions not only participate in the

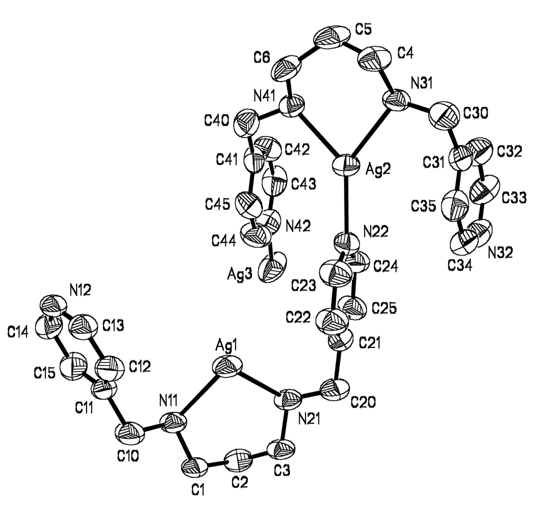


Fig. 1 Cationic structure of the repeat unit of $[Ag_3(py\text{-}hep)_2](ClO_4)_3 \cdot 0.5CH_3CN$; thermal ellipsoids are drawn at the 50% probability level.

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† Electronic supplementary information (ESI) available: figure showing the 2D network and weak interactions in the title compound. See http://www.rsc.org/suppdata/nj/b0/b008266j/

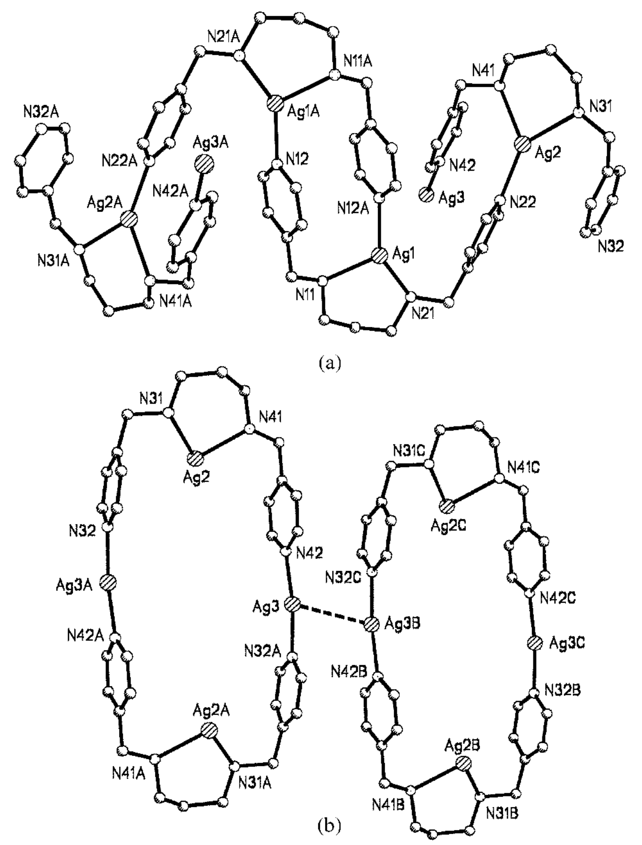

Fig. 2 Coordination environments of (a) three- and (b) two-coordinate Ag(I) atoms. Selected bond lengths (Å) and angles (°): Ag(1)–N(11) = 2.374(5), Ag(1)–N(12A) = 2.234(5), Ag(1)–N(21) = 2.284(5), Ag(2)–N(22) = 2.237(5), Ag(2)–N(31) = 2.368(5), Ag(2)–N(41) = 2.338(5), Ag(3)···Ag(3B) = 3.179(1), Ag(3)–N(32A) = 2.108(6), Ag(3)–N(42) = 2.108(6); N(11)–Ag(1)–N(12A) = 116.5(2), N(11)–Ag(1)–N(21) = 93.7(2), N(12A)–Ag(1)–N(21) = 145.3(2), N(22)–Ag(2)–N(31) = 41.1(2), N(22)–Ag(2)–N(41) = 134.7(2), N(31)–Ag(2)–N(41) = 84.1(2), Ag(3B)–Ag(3)–N(32A) = 74.6(2), Ag(3B)–Ag(3)–N(42) = 111.9(2), N(32A)–Ag(3)–N(42) = 173.0(3).

formation of a total of ten N–H···O and C–H···O hydrogen bonds but also weakly bind to the silver(I) atoms (see electronic supplementary information). The proximity of two perchlorate anions to the Ag(1) atom [Ag(1)···O(24A) = 2.93(1) and Ag(1)···O(33B) = 3.51(1) Å] implies a weak binding[6] and leads to the coordination geometry around Ag(1) being a distorted trigonal bipyramid [O(24A)–Ag(1)–O(33B) = 165.3°]. A similar situation occurs for Ag(2) [Ag(2)···O(21C) = 2.973(7) and Ag(2)···O(12D) = 3.017(8) Å; O(21C)–Ag(2)–O(12D) = 171.6°] with a distorted trigonal-bipyramidal geometry. In the case of Ag(3), the coordination geometry is a distorted square pyramid through weak coordination of oxygen atoms to Ag(3) [Ag(3)···O(31E) = 3.084(7) and Ag(3)···O(33F) = 3.20(1) Å; O(31E)–Ag(2)–O(33F) = 160.6, N(42)–Ag(3)–N(32A) = 173.0°]. This is a remarkable feature of the structure, meaning that the perchlorate anions are encapsulated in the vacancies of the 2D network through weak Ag···O and hydrogen bond interactions.[9] It is notable that neither weak Ag···O (perchlorate) nor Ag···Ag interactions was found in the 2D network of [Ag(py-hex)]ClO$_4$.[4] Thus, by inserting an additional CH$_2$ group in the flexible ligand of py-hex, a novel silver(I) complex network was obtained. This means that the self-assembly process is affected by subtle changes in the ligand.

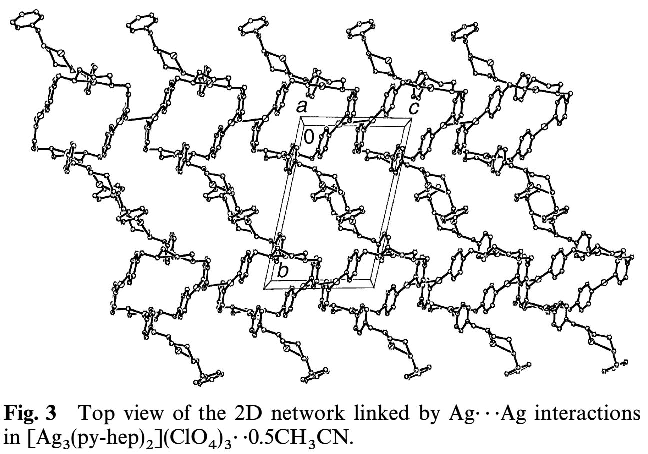

Fig. 3 Top view of the 2D network linked by Ag···Ag interactions in [Ag$_3$(py-hep)$_2$](ClO$_4$)$_3$·0.5CH$_3$CN.

Although Ag(I) complexes may emit weak photoluminescence at low temperature, such examples at room temperature are rare.[10,11] The title complex shows photoluminescence with an emission maximum at 398 nm upon excitation at 310 nm in the solid state, and displays photoluminescence with an emission maximum at 390 nm upon excitation at 290 nm in acetonitrile solution. Similar luminescent properties in the solid and solution states suggest that the polymeric structure might be maintained in acetonitrile solution at room temperature. The observed luminescence of the title complex is attributed to coordination of the silver(I) atom with the py-hep ligand, in particular with the terminal pyridine group.

In conclusion, the novel flexible ligand py-hep provides a new coordination mode to the metal ion for such a tetradentate ligand. The result reveals that a minor change of ligand can influence the self-assembly processes of supramolecular polymers.

Acknowledgement

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Notes and references

‡ Experimental: All procedures were carried out in the dark. A solution of AgClO$_4$·H$_2$O (22.5 mg, 0.1 mmol) in CH$_3$CN (10 ml) was added dropwise to a solution of the py-hep ligand (25.6 mg, 0.1 mmol) in CH$_3$CN (10 ml) with stirring to give a clear solution. Single crystals suitable for X-ray diffraction were obtained in 58% yield by slow diffusion of diethyl ether into the filtrate for several days. Anal. calc. for C$_{30}$H$_{40}$Ag$_2$Cl$_3$N$_8$O$_{12}$: C, 31.75; H, 3.55; N, 9.87%. Found: C, 31.61; H, 3.58; N, 9.49%. (The CH$_3$CN might be lost during the vacuum drying process.)

§ Crystal data for [Ag$_3$(py-hep)$_2$](ClO$_4$)$_3$·0.5CH$_3$CN: $M = 1155.18$, triclinic, space group $P\bar{1}$, $a = 13.612(2)$, $b = 15.789(4)$, $c = 10.172(4)$ Å, $\alpha = 100.50(3)$, $\beta = 102.23(2)$, $\gamma = 97.16(2)°$, $U = 2070$ (1) Å^3, $Z = 2$, μ(Mo-Kα) = 16.63 cm^{-1}, $T = 298(1)$ K. Data collection was carried out on a Rigaku AFC7R four-circle diffractometer by $\omega - 2\theta$ scan techniques using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). A total of 10049 reflections were collected of which 9511 were independent ($R_{\mathrm{int}} = 0.022$). The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-square calculations. The final $R_1 = 0.0421$ [$I > 2\sigma(I)$]. CCDC reference number 440/234. See http://www.rsc.org/suppdata/nj/b0/b008266j/ for crystallographic files in .cif format.

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