SHORT PAPER

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A novel two-dimensional non-interpenetrating coordination polymer $[Ag_{2.5}L(NO_3)_{2.5}]_\infty$ with three different coordination modes of Ag^I (L = diquinoxalino[2,3-a:2′,3′-c]phenazine)[†]

Miao Du[a], Xian-He Bu[a]*, Kumar Biradha[b] and Mitsuhiko Shionoya[c]

[a]*Department of Chemistry, Nankai University, Tianjin 300071, P.R. China*

[b]*Department of Applied Chemistry, School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan*

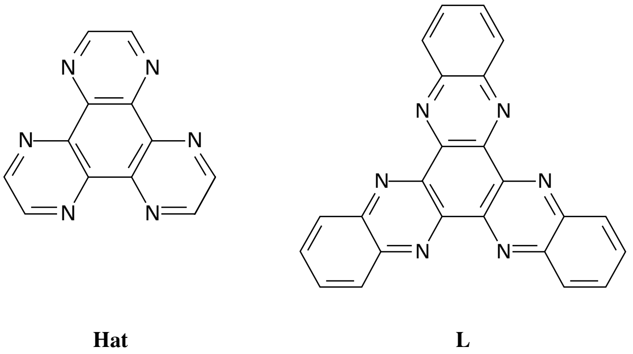
[c]*Department of Chemistry, Graduate School of Science, the University of Tokyo, Hongo, Tokyo 113-0033, Japan*

A novel 2-D Ag^I neutral infinite framework of a large delocalised system diquinoxalino[2,3-a:2′,3′-c]phenazine (L), $[Ag_{2.5}L(NO_3)_{2.5}]_\infty$ (1), has been synthesised and structurally determined, in which three kinds of different coordination modes are found for the Ag^I centers.

Keywords: two-dimensional non-interpenetrating coordination polymer of Ag

Construction of coordination polymer networks based upon bridging ligands and metal centres represents a fast growing area in coordination and supramolecular chemistry. Interest in such investigation has been driven by the aim of rational design and developing new materials with unique electronic, magnetic, catalytic and optical properties.[1–5] One of the key points to obtain robust network structures is to employ bridging ligands with powerful chelate effects that bind metal centers strongly at the sites. Bridging ligands providing three bidentate metal-binding sites, such as 1,4,5,8,9,12-hexaazatriphenylene (Hat, Scheme 1),[6] are particularly promising as building blocks for the construction of coordination polymers because they produce robust networks with good electronic communication between metal centres.[7,8]

In our effort to construct novel extended coordination networks, the ligand diquinoxalino[2,3-a:2′,3′-c]phenazine (**L**, Scheme 1) has attracted our attention, and a fascinating Ag^I complex of it consisting of two 3-D networks which are enantiomeric and interpenetrating has been obtained.[9] This ligand has a very similar backbone and coordination sites to Hat but has extended aromatic rings. Also, **L** has a more delocalised π-electron system than Hat, which may provide more facile electronic communication. Therefore, **L** forms quite different networks from those of Hat. In this contribution, we report a novel 2-D Ag^I coordination polymer (**1**) of **L**, in which three different coordination modes were found for the independent Ag^I centers.



Scheme 1

Reaction of $AgNO_3$ with **L** in the dark afforded the orange crystals of the title complex **1**. The IR spectrum of **1** shows absorption bands resulting from the skeletal vibrations of the aromatic rings system of the ligand in the 1400–1600 cm^{-1} region. The peak at 1345 cm^{-1} is attributed to the characteristic band of the nitrate anions.

In the crystal structure of the title complex, the ligand **L** coordinates to three independent Ag^I centres as shown in Fig. 1. It is quite interesting that the coordination modes of three Ag^I centres are different from each other. As depicted in Fig. 2, the Ag(1) centre acts as an expected two-connecting node by connecting two ligands (A′ and B) and the dihedral angle between the two large delocalised planes is 36.0°. The Ag(1) is four-coordinated to form a distorted tetrahedral geometry with four nitrogen donors of two ligands. The two Ag–N bond distances are 2.274(3) and 2.285(3) Å, being within the normal range observed in relevant Ag^I complexes.[6] However, the Ag(2) and Ag(3) centres are bridged by two nitrate anions to form a binuclear unit. Ag(2) is penta-coordinated to two nitrogen atoms of the ligand (A) and three oxygen donors of three nitrate anions. The coordination environment of Ag(2) can be described as a distorted square-pyramid with O(2B) occupying the axial position, which is reflected by the τ value (0.25 here) defined by Addison *et al.* ($\tau = 0$ for an ideal square-pyramid, and $\tau = 1$ for an ideal trigonal bipyramid).[10,11] Ag(2) deviates from the mean equatorial plane N(21)–N(31)–O(2A)–O(3C) of the square pyramid by *ca* 0.33 Å. The Ag(3) ion is also penta-coordinated and takes an approximately ideal square-pyramid geometry with a τ value of 0.002. However, the AgN_2O_3 coordination sphere consists of two nitrogen atoms of the ligand (A′) and three oxygen donors of two bridging nitrate anions. The Ag(3) ion deviates from the mean equatorial plane N(12)–N(32)–O(2B)–O(3B) of the square pyramid by *ca* 0.21 Å toward the apical O(3C) atom. It should be noted that the nitrate anions also have three coordination forms when bound to Ag^I: monodentate (η^1), monodentate bridging (μ, η^1) and bidentate bridging (μ, η^2). Thus, the nitrate anions and the ligands (A and A′) connect the Ag(2) and Ag(3) centres to form a one-dimensional arrangement, which links ligand B through the two-connecting node Ag(1) ion to form a two-dimensional infinite network along the *xy* plane as shown in Fig. 3.

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* To receive any correspondence. E-mail: buxh@nankai.edu.cn.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

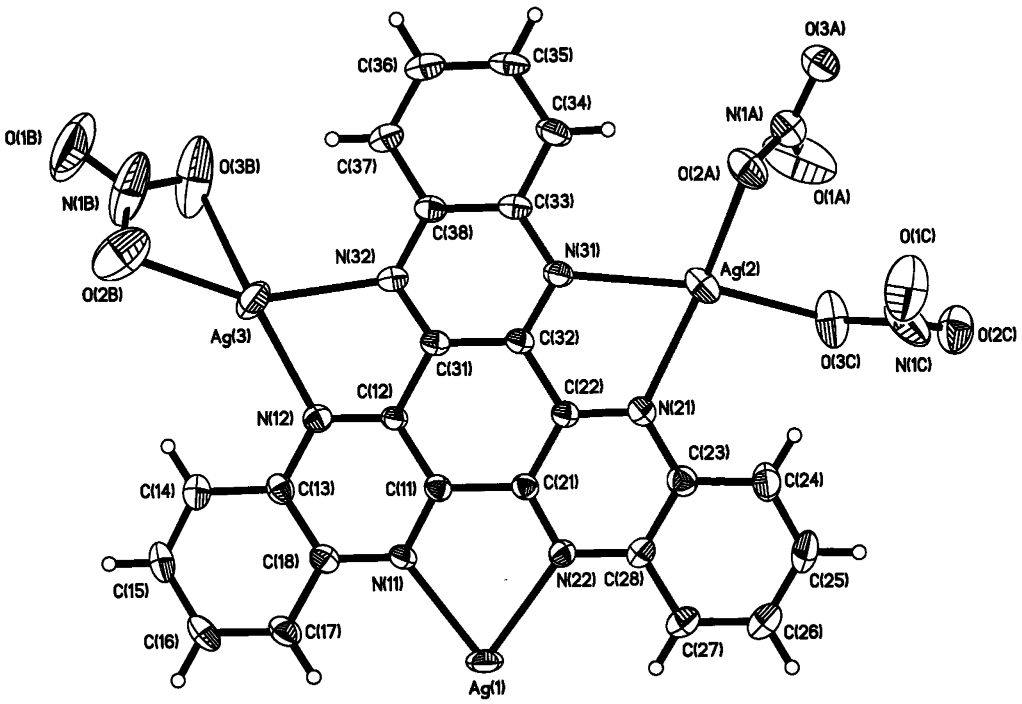

Fig. 1 ORTEP view of the $[Ag_{2.5}\mathbf{L}(NO_3)_{2.5}]$ asymmetric unit in **1** with 50% thermal ellipsoid probability.

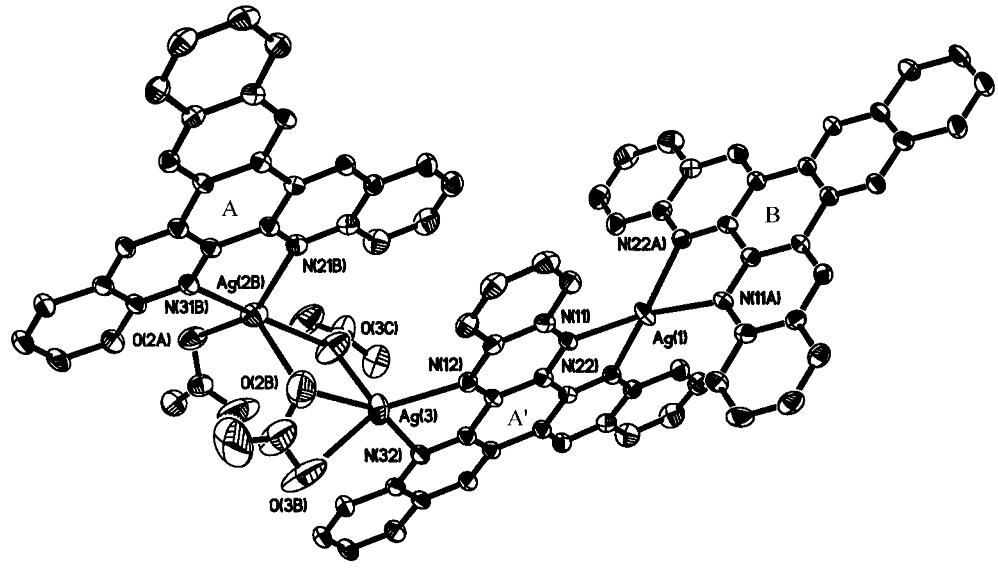

Fig. 2 Coordination environments of the three independent Ag^I centres.

Comparing this structure with $[Ag_3\mathbf{L}_2](NO_3)_3$ obtained from the same procedure,[9] which consists of two independent enantiometric and interpenetrating 3D networks, we can see that the coordination effect of the nitrate anion is crucial to the type of architecture observed.

The non-bond separation of the two Ag^I centres bridged by NO_3^- is 3.823 Å. For the three Ag^I centres coordinated to one ligand (Fig. 1), the distances of Ag(1)···Ag(2), Ag(1)···Ag(3) and Ag(1)···Ag(3) are 7.449, 7.597 and 7.327 Å, respectively. For the ligand, in the central C_6 ring, the maximum deviation of any atom from the best-fit plane is 0.0154 Å, while the average deviation is 0.0096 Å (the corresponding values of the free ligand are 0.0106 and 0.0068 Å).[12] Furthermore, all non-H atoms of the ligand in the title complex lie in a plane and the mean deviation of any non-H atoms from the best-fit plane describing them is only 0.0479 Å, forming a dihedral angle of 0.8° with the central C_6 ring. However, the corresponding values in the free ligand are 0.1282 Å and 2.30°, respectively, which indicates that the planar feature of the ligand has been improved when coordinated to the Ag^I ions. The distortions from planarity should have a noticeable effect on the electronic communication provided by this bridging ligand.

In summary, the title two-dimensional coordination polymer can be assembled by means of the reaction of $AgNO_3$ and the nitrogeneous heterocyclic bridging ligand **L**. **L** has a large delocalised π-electron system which may allow facile d–π

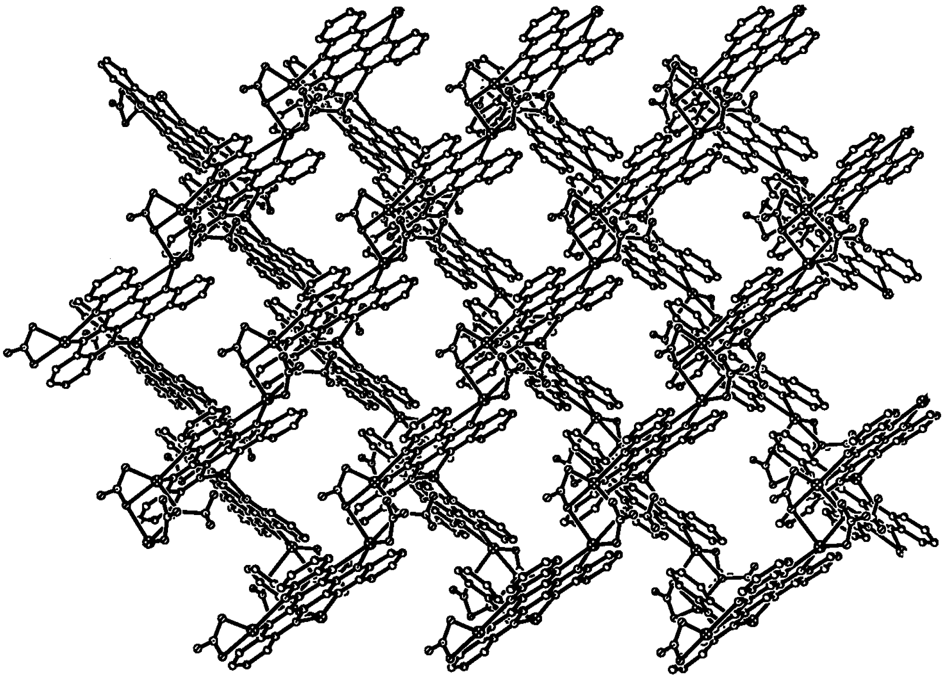

Fig. 3 The two-dimensional extended architecture along (1 1 0) plane.

interactions between ligands and remote metal centres throughout the extended network. It will provide interesting experimental data for supramolecular chemistry and crystal engineering.

Experimental

All reagents for syntheses and analyses were of analytical grade and used without further purification. FT-IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer and elemental analyses were performed on a Perkin-Elmer 240C analyzer.

Preparation of **1**: Slow diffusion of a CH_3CN solution of $AgNO_3$ onto a $CHCl_3$ solution of **L** with 2: 1 molar ratio in a tube in the dark resulted in the orange crystals of the title complex $[Ag_{2.5}L(NO_3)_{2.5}]_\infty$, suitable for single-crystal X-ray diffraction, within two weeks. Elemental analyses results are in good agreement with the stoichiometries. Anal. Calcd for $C_{24}H_{12}Ag_{2.5}N_{8.5}O_{7.5}$: C, 35.62; H, 1.48; N, 14.7. Found: C, 35.44; H, 1.74; N, 14.6.

X-ray analysis: Single-crystal X-ray diffraction measurements were carried out with a Bruker Smart CCD diffractometer equipped with a graphite monochromator for data collection at 203(2) K. The determination of unit cell parameters and data collections was performed with MoKα radiation (λ = 0.71073 Å) and unit cell dimensions were obtained with least-squares refinements. The structure was solved by direct methods and semi-empirical absorption corrections were applied. Ag^I atoms were located from E-maps and all the other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was carried out by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically and riding on the concerned atoms and refined with fixed thermal factors. Crystal data for **1**: $C_{24}H_{12}Ag_{2.5}N_{8.5}O_{7.5}$, Mr = 809.1, monoclinic, space group *C2c*, a = 17.1211(10), b = 11.8518(6), c = 24.1557(13) Å, β = 97.222(2)°, V = 4862.7(5) Å^3, Z = 8, D_c = 2.210 g/cm^3, μ (Mo–Kα) = 2.072 mm^{-1}, F(000) = 3144. A total of 20575 reflections were collected and the independent reflection number is 5831 with 399 refined parameters. Final convergent [$I \geq 2\sigma(I)$] R = 0.0341, wR = 0.0876 and Goodness-of-fit = 1.036. Full crystallographic details have been deposited at the Cambridge Crystallographic data Center as supplementary materials (no. CCDC-138230).

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