# Syntheses and Structures of Silver and Copper Coordination Polymers with 4,4′-Azopyridine − Effect of Counter Anions and π−π Interactions on the Network Systems

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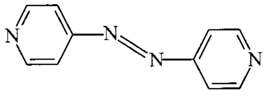
The syntheses and structures of $[Ag(azpy)](NO_3)(H_2O)(CH_3OH)$ (**1**), $[Cu(azpy)_2](ClO_4)$ (**2**), $[Cu(azpy)_2(H_2O)_2](NO_3)_2(H_2O)_2$ (**3**) and $[Cu(azpy)_2(H_2O)_2](ClO_4)_2(C_2H_5OH)_2$ (**4**), where azpy = trans-4,4′-azopyridine, are reported to test the dependence of network topology on counter anions and π–π interactions. Complex **1** contains pairs of linear chains of alternating $Ag^I$ ions and azpy ligands, resembling a ladder structure in which the ligands form π–π interactions (with a distance of 3.53 Å) and AgAg interactions (with a distance of 3.30 Å). Complex **2** exists as a 3D adamantoid polymer in which each $Cu^I$ center is coordinated to four azpy ligands in a tetrahedral geometry, the ligands are in turn coordinated to four other $Cu^I$ centers. The cavities are filled with four other adamantoid units forming five interpenetrating networks. Complexes **3** and **4** are composed of two-dimensional sheets in which the $Cu^{II}$ atom is coordinated in an octahedral geometry to two water molecules and four ligands. The ligands are in turn coordinated to four other $Cu^{II}$ centers. While the sheets in complex **3** display inclined 2D interpenetration, the sheets in complex **4** are all parallel and isolated, with an intersheet separation of ca. 4.7 Å.

## Introduction

Much interest at present is focused on the deliberate construction of coordination polymers by self-assembly of the component metal complexes. These solid materials with well-defined, discrete network topologies are attractive to chemists not only for aesthetic reasons, but also for their potential applications in many areas.[1−3] A large amount of these research works have used the 4,4′-bipyridine (4,4′-bipy) ligand and its analogues.[4−5] The coordination polymers observed can be predicted to a certain extent and this led to the development of a wide variety of architectures related to common models such as the honeycomb,[6] ladder,[7] grid,[8] and adamantoid network,[9] or to less common ones exhibiting different degrees of interpenetrations.[1b,10] Although the overall structure is predominantly controlled by the coordination preferences of the transition metal and the ligand building blocks, more subtle effects such as anion control[11] and π−π stacking interactions[12] have been seen to have a profound effect upon network topology. Here we report on the syntheses of some silver and copper complexes, by reaction of the potentially bridging ligand 4,4′-azopyridine (Scheme 1) and metal salts with different anions. A few compounds which exhibit quite novel structures with this ligand have been reported.[13−15] As a result of the different conformations exhibited by this type of ligand, its capability of forming hydrogen bonds with the anions and solvent molecules, as well as the potential π−π stacking interactions between ligands, it was anticipated that the products would present interesting structural features.



Scheme 1. 4,4′-Azopyridine

## Results and Discussion

### Structure of $[Ag(azpy)](NO_3)\cdot(CH_3OH)\cdot(H_2O)$

The structure contains pairs of linear chains (Figure 1) of alternating $Ag^I$ ions and azpy ligands, resembling a ladder structure in which the ligands form π−π interactions (with a distance of 3.53 Å) and weak AgAg interaction (with a distance of 3.30 Å). Each $Ag^I$ ion coordinates to two azpy ligands in a linear arrangement [Ag(1)−N(1) 2.147(8) Å, Ag(1)−N(4A) (A: 1 + *x*, *y*, 1 + *z*) 2.180(9) Å, N(1)−Ag(1)−N(4A) 173.0(3)°], giving an infinite chain of alternating $Ag^I$ separated by 14.65 Å, and azpy ligands which align themselves along the (101) direction. The pairs of chains are linked together by π−π interactions between the azpy ligands and in which the ligands lie parallel to each other at a distance of 3.36 Å forming a two-dimensional sheet. Chains, ladders and sheets of (bipyridine)silver(I) complexes have been reviewed by A. J. Blake et. al.[2a] It is said that the π−π stacking interaction had a profound effect upon the solid-state packing of Ag−bipyridine chains. From the simple linear chains of $[Ag(4,4'\text{-bipy})](BF_4)$, to the ladders of $[Ag(pybut)](PO_2F_2)$ [pybut = 1,4-bis(4-pyridyl)butadiyne],[2a] and to the 2D sheets of $[Ag(diaz)](BF_4)$ (diaz = 2,7-diazapyrene[10b]), it can be seen

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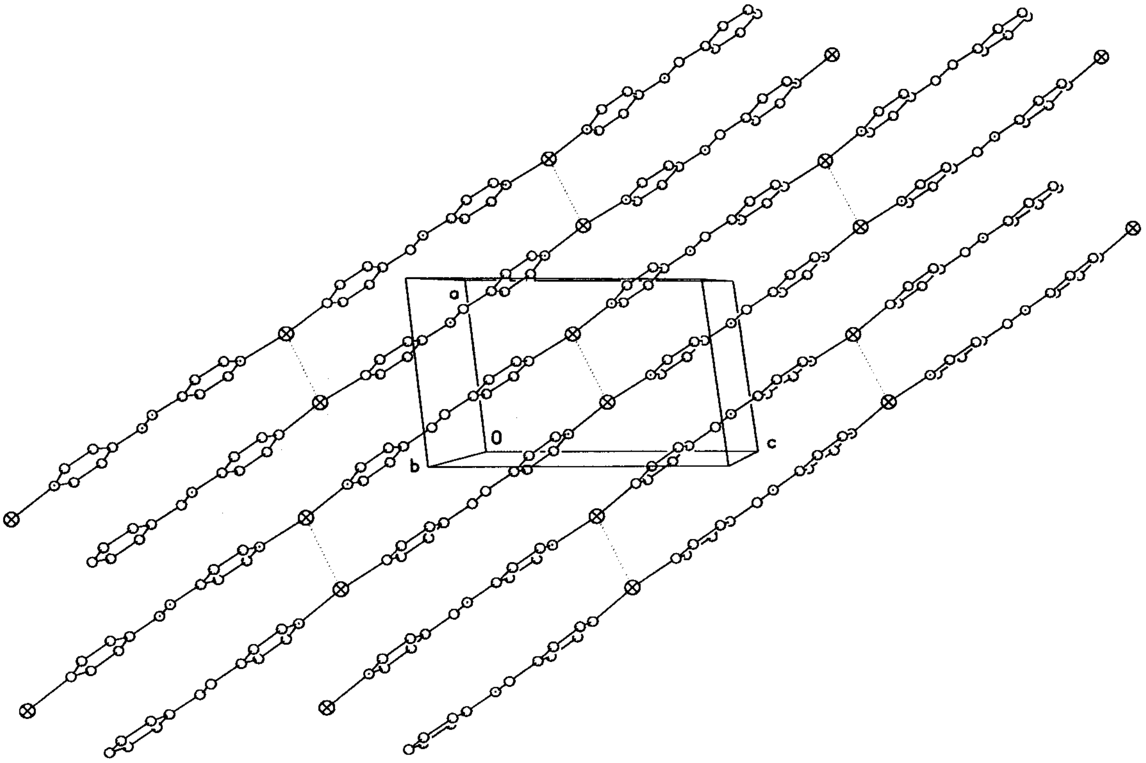

Figure 1. View of the pairs of linear chains observed in complex **1**, in which the ligands form π−π interactions (with a distance of 3.53 Å) and AgAg interactions (with a distance of 3.30 Å)

that by increasing the ability of the ligand to form π−π interactions, the construction of long-range arrays is be encouraged. The increased ability of azpy to form π−π interactions compared with 4,4′-bipy and pybut, encourages not only the formation of pairs of chains, or ladders, but also the formation of a sheet structure with extended π−π stacking interactions.

### Structure of [Cu(azpy)$_2$]ClO$_4$

The reaction of [Cu(MeCN)$_4$]ClO$_4$ with azpy in MeCN/CH$_2$Cl$_2$ affords black crystal suitable for X-ray analysis. The crystal structure shows that the complex exists as a three-dimensional adamantoid polymer in which each Cu$^I$ is coordinated in a tetrahedral geometry to four azpy ligands, which are in turn coordinated to four other Cu$^I$ centers, Cu(1)-N, 2.054(7) Å, Cu(2)-N, 2.025(10) Å. The 3D structure is built through the formation of edge-sharing adamantoid units. The CuCu separation is 12.98 Å creating large cavities within this first 3D lattice. These cavities are filled with four other [Cu(azpy)$_2$]$^+$ lattices so that a total of five independent adamantoid lattices, related by translation symmetry, interpenetrate throughout the 3D structure, as illustrated in a simplified form by the five adamantoid units (Figure 2).

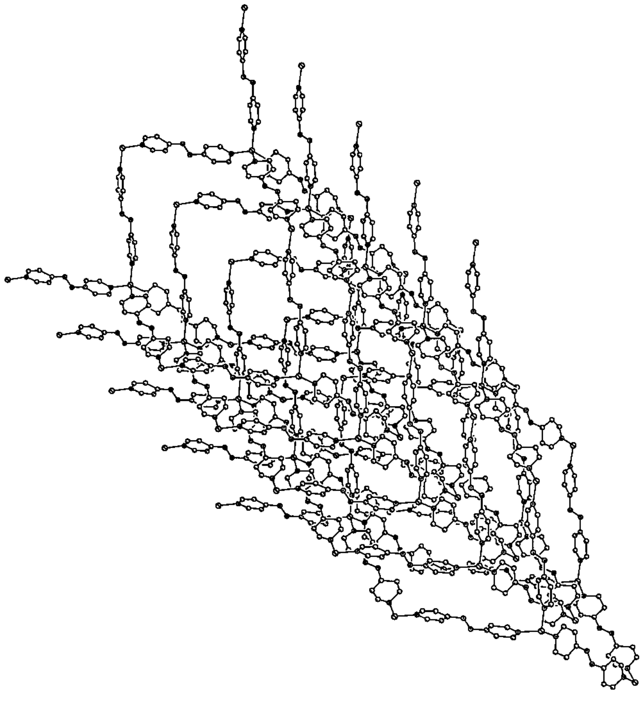

Figure 2. The five independent interpenetrating adamantoid lattices of complex **2**

The channels running through the structure are parallel to the translation vector relating the five networks and accommodate the ClO$_4^-$ counter anions (Figure 3).

Adamantoid networks based on bifunctional linear ligands have been studied for some Cu$^I$ and Ag$^I$ complexes. In general, the lengths of the bridging ligands and the lateral bulk of the ligands are possible factors in controlling the degree and type of interpenetration in adamantoid lattices. Comparing this structure with two other isomorphous structures [Cu(bpe)$_2$](BF$_4$)·0.5CH$_2$Cl$_2$[9b] and [Cu(bpe)$_2$]-(BF$_4$)(CH$_3$CN)[16] [bpe = *trans*-1,2-bis(4-pyridyl)ethene], it

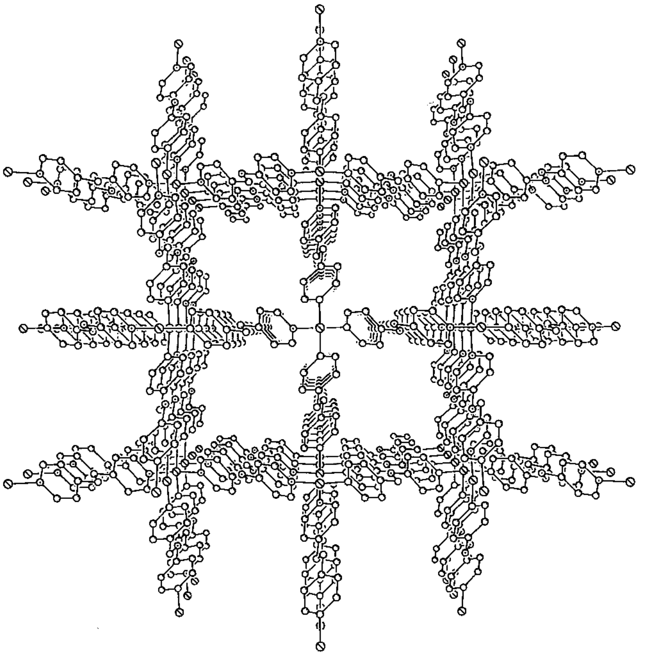

Figure 3. View of the complex **2** network illustrating the channels that run through the accommodating counter ions

is interesting to find that the structure remains essentially the same with different ligands and anions. The implications of this are that the solvent and the counter anion have little or no templating effects.

### Structures of $[Cu(azpy)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ and $[Cu(azpy)_2(H_2O)_2](ClO_4)_2 \cdot 2EtOH$

The Cu$^{II}$ complexes **3** and **4** are obtained as large black crystals by treating $Cu(NO_3)_2$ or $Cu(ClO_4)_2$ in water with the azpy ligand in an ethanol solution in a 1:2 molar ratio. One of the aims of this research was to compare the behavior of azpy with that of the shorter 4,4′-bipyridine ligand. These ligands give both interpenetrated[17] and noninterpenetrated structures when treated with $ZnSiF_6$.[8a] Another aim was to assess the effect of the counter anion on the crystal packing of the sheets.

The structure of **3** contains two-dimensional layers of squares (Figure 4). The Cu$^{II}$ atoms are octahedrally coordinated to four equatorial azpy ligands (Cu−N distance ca. 2.02 Å) and two axial water molecules (Cu−O distance ca. 2.50 Å). Each azpy unit is attached to two copper centers to form an infinite sheet. The Cu$^{II}$ cations within a sheet are coplanar and form a grid of edge-shared squares, the average CuCu distance along the edge is ca. 12.95 Å. Parallel sheets, stacked on top of each other, are laterally displaced so that the copper centers of the first sheet, viewed in the horizontal plane, are vertically above those of the 3rd, 5th, 7th etc. sheets, and are vertically above the midpoints of the $Cu_4$ squares of the 2nd, 4th, 6th etc. sheets. An equivalent stack of sheets is found in planes perpendicular to the first, giving rise to the interpenetrating pattern represented in Figure 5. Hydrogen bonds are apparent between the coordinated water molecules and the disordered $NO_3^-$ anions.

The structure of **3** is isomorphous with the structure of $[Zn(azpy)_2(H_2O)_2]$ $SiF_6 \cdot H_2O$,[13b] the size of the cavity is almost equivalent (166 vs. 165 Å$^2$). An interesting feature of this structure is the fact that the structure remains essentially unchanged whether the metal center is Cu$^{II}$ or Zn$^{II}$ and the anion is $SiF_6^{2-}$ or $NO_3^-$. The implications of this are that either $SiF_6^{2-}$ and $NO_3^-$ behave similarly as templates for the interpenetrating structure, or they have little or no template effect. In both structures the counter anions and water molecules are contained in the tetrahedral channels, although there is twice as much $NO_3^-$ included as there is $SiF_6^{2-}$. It was anticipated that when the perchlorate counter anion was used instead of the nitrate counter anion, the expected structure would be similar to that proposed for **3** and $[Zn(azpy)_2(H_2O)_2]SiF_6 \cdot H_2O$. However, after synthesizing and studying the crystal structure of the perchlorate salt of **3** (i.e. **4**), it was surprising to find that the structure of **4** is quite different.

Compound **4** crystallizes in the tetragonal space group *P*4$_2$/*mnm* with $Z = 2$. The skeleton structure of the two-dimensional sheet 2 (in **4**) is the same as that in **3** (CuCu distance along the edge is 13.06 Å, and the Cu−N, Cu−O distances ca. 2.02 Å, 2.68 Å, respectively). However, the sheets subsequently stack along *c* in a close-packed staggered manner, as described above, with interplane separations 4.7 Å. Such short inter-plane separations certainly

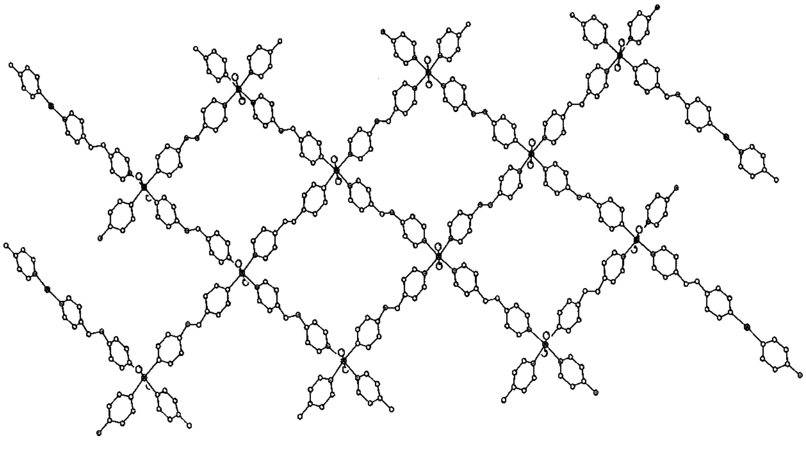

Figure 4. View of the two-dimensional sheets of complex **3**

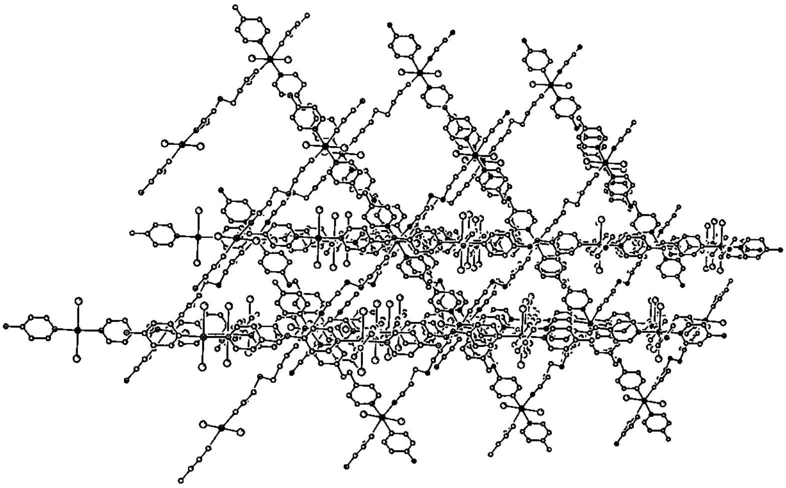

Figure 5. A schematic view of the interpenetration of the layers, showing its inclined nature, and the channels of complex **3**; the anions and the solvent molecules are omitted for clarity

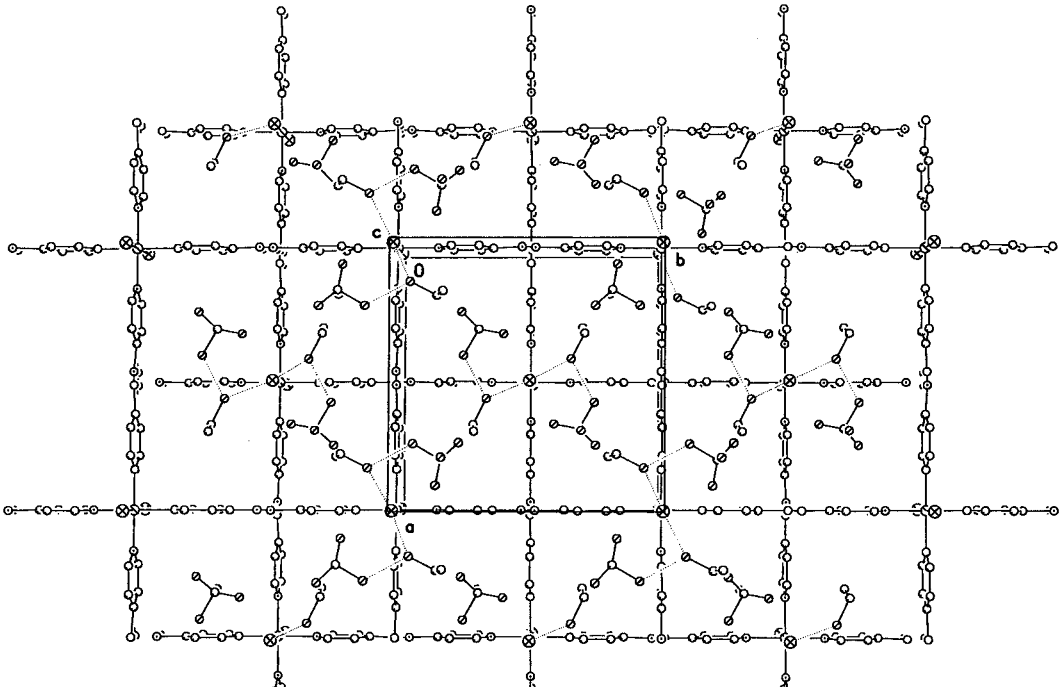

Figure 6. View of the square cavities of a single sheet in complex **4**, showing the $ClO_4^-$ anions and ethanol molecules in the clathrates

preclude the possibility of interpenetration. The square cavities are enclosed by the azpy ligands. Two $ClO_4^-$ anions and two ethanol molecules occupy the square cavity within the clathrate (Figure 6). There is significant hydrogen bonding between the ethanol molecules and the $ClO_4^-$ anions.

It is interesting to find that the water molecules coordinated to the $Cu^{II}$ atom extend to the center of the cavity on the adjacent layer and interact with the two ethanol molecules in the clathrate by hydrogen bonding, to form one-dimensional chains along the *c* axis (Figure 7).

The fact that the counter anions can influence the final structure of coordinated complexes has been noted. It is clearly indicated that noncoordinating counter anions can play an important role in the crystal engineering of coordination complexes. The result of this study illustrates the fine balance between interpenetrated and noninterpenet-

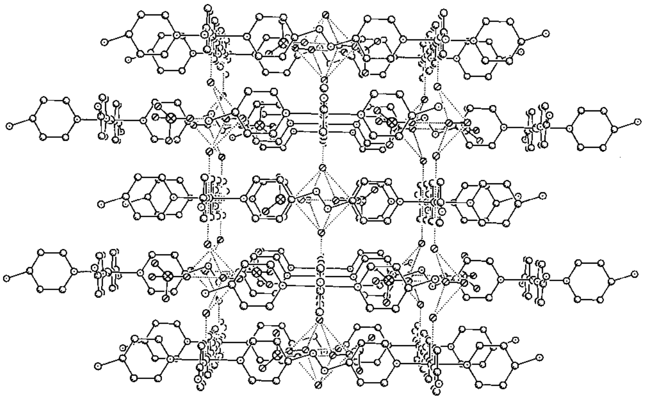

Figure 7. View through the *ac* plane in complex **4**, showing the one-dimensional hydrogen-bonding chains on the *c* axis

rated structures. Although the mechanism of the structural change is unpredictable, understanding the features may be a clue to the design of self-assembly network compounds.

## Experimental Section

**General:** All starting materials were purchased from Aldrich and used as received. The ligand 4,4′-azopyridine[18] and Cu(-MeCN)$_4$ClO$_4$[19] were prepared by literature procedures. − The IR spectra were recorded with a Nicolet 170SX FT-IR spectrophotometer with KBr pellet in the 4000−400cm$^{-1}$ region. − $^1$H NMR spectra were recorded with Am5600 Bruker spectrometers at 298 K using TMS as an internal standard.

**[Ag(azpy)](NO$_3$)(CH$_3$OH):** A solution of AgNO$_3$ (0.10 g, 0.59 mmol) in water (5 mL) was added to a stirred solution of azpy (0.11 g, 0.60 mmol) in methanol (10 mL ). A pale red precipitate formed and was filtered off and dried under vacuum( 0.16 g, yield 69%). − $C_{11}H_{12}AgN_5O_4$ (386.1133): calcd. C 34.2, H 3.1, N 18.1; found C 34.7, H 2.7, N 18.2. − $^1$H NMR [(CD$_3$)$_2$SO]: δ = 8.88 (d, $J$ = 5.0 Hz, 4 H, py], 7.84 [d, $J$ = 5.6 Hz, 4 H, py]. − IR (KBr): ṽ = 1594 cm$^{-1}$ (m), 1587 (m), 1565 (m), 1486 (w), 1414 (s), 1384 (s), 1317 (m), 1238 (w), 1222 (m), 1051 (w), 1006 (w), 989 (w) and 836 (s). Crystals were obtained by slow concentration of an acetonitrile/ethanol solution at ambient temperature.

**[Cu(azpy)$_2$](ClO$_4$):** Solutions of Cu(CH$_3$CN)$_4$ClO$_4$ (0.10 g, 0.31 mmol) in CH$_2$Cl$_2$ (10 mL) and azpy (0.12 g, 0.65 mmol) in CH$_3$CN (10 mL) were mixed. After concentrating the solution to a small volume, black crystals of **2** were obtained and were filtered off (0.09 g, yield 55%). − $C_{20}H_{16}ClCuN_8O_4$ (531.3950): calcd. C 45.2, H 3.0, N 21.1; found C 45.6, H 3.2, N 21.3. − IR (KBr): ṽ = 1595 (s), 1563 (m), 1486 (m), 1467 (w), 1416 (s), 1324 (w), 1241 (w), 1224 (m), 1101 (s), 1083 (s), 1051 (s), 1010 (m), 962 (m), 932 (w), 867 (w), 846 (s), 831 (s).

**[Cu(azpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$2H$_2$O:** Solutions of Cu(NO$_3$)$_2$6H$_2$O (0.10 g, 0.33 mmol) in water (10 mL ) and azpy (0.12 g, 0.65 mmol) in ethanol (10 mL). After slow concentration of the solution to a small volume, black crystals were formed and were filtered off. − IR (KBr): ṽ = 3431 (w), 3102 (w), 1608 (s), 1570 (w), 1513 (m), 1480 (s), 1424 (s), 1384 (s), 1352 (s), 1327 (m), 1293 (s), 1274 (s), 1231 (m), 1194 (m), 1094 (w), 1051 (m), 1034 (w), 1013 (m), 995 (m), 850 (s), 803 (m) .

**[Cu(azpy)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$2CH$_3$CH$_2$OH:** Solutions of Cu(-ClO$_4$)$_2$6H$_2$O (0.10 g, 0.27 mmol) in water (10 mL ) and azpy (0.10 g, 0.54 mmol) in ethanol (10 mL ) were mixed. Black crystals were obtained by slowly concentrating the solution in air. They were filtered off. − IR (KBr): ṽ = 3449 (w), 3111 (w), 1609 (s), 1568 (w), 1494 (w), 1423 (s), 1229 (m), 1184 (s), 1043 (s), 989 (m), 928 (m), 846 (s), 621 (s).

**X-ray Crystallography:** Parameters for data collection and refinement of the crystals are summarized in Table 1. Intensities were collected with a Siemens P4 four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation (λ = 0.71073 Å) using the ω-2θ scan mode. Data were corrected for Lorentz polarization effects during data reduction using XSCANS,[20] and a semi-empirical absorption correction from ψ scans was applied. The structures were solved by direct methods and refined on $F^2$ by full-matrix least-squares methods using SHELXTL version 5.0.[21] Anisotropic thermal parameters were refined for the non-hydrogen atoms. For complex **1**, the nitrate anion, and the H$_2$O and CH$_3$OH molecules were found to be disordered into two occupied sites. The site occupancy factor (SOF) of the atoms of the NO$_3$$^-$ anion were refined using

Table 1. X-ray crystal data of compounds **1−4**

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Molecular formula | $C_{11}H_{14}AgN_5O_5$ | $C_{20}H_{16}ClCuN_8O_4$ | $C_{20}H_{24}CuN_{10}O_{10}$ | $C_{24}H_{32}Cl_2CuN_8O_{12}$ |
| $M$ | 404.14 | 531.40 | 628.03 | 759.02 |
| Crystal system | triclinic | tetragonal | orthorhombic | tetragonal |
| Space group | $P\bar{1}$ | $I\bar{4}$ | $Pbcm$ | $P4_2/mnm$ |
| $a$ [Å] | 7.691(2) | 17.765(9) | 12.314(6) | 13.063(1) |
| $b$ [Å] | 9.176(3) | 17.765(9) | 11.134(7) | 13.063(1) |
| $c$ [Å] | 11.601(3) | 7.567(6) | 19.875(7) | 9.401(2) |
| α [°] | 105.18(2) | | | |
| β [°] | 96.53(2) | | | |
| γ [°] | 100.41(3) | | | |
| $V$/Å$^3$ | 792.7(4) | 2388(2) | 2725(2) | 1604.2(3) |
| Z | 2 | 4 | 4 | 2 |
| $T$ [K] | 293(2) | 293(2) | 293(2) | 293(2) |
| μ [mm$^{-1}$] | 1.301 | 1.069 | 0.873 | 0.920 |
| No. reflections measured | 2970 | 1553 | 5854 | 2017 |
| No. unique reflections | 2752 ($R_{int}$ = 0.035) | 1447 ($R_{int}$ = 0.058) | 2485 ($R_{int}$ = 0.075) | 799 ($\mathrm{R}_{int}$ = 0.046) |
| $R1$ | 0.069 | 0.074 | 0.0670 | 0.0779 |
| $wR2$(all data) | 0.180 (0.202) | 0.170 (0.221) | 0.174 (0.209) | 0.216 (0.257) |
| Goodness of fit | 1.037 | 1.039 | 1.108 | 1.044 |

free variables, the SOF of the atoms in the methanol molecules, however, were fixed at 0.5. To assist in the refinement, several restraints were applied for the nitrate anion: 1) all N-O bonded and all OO nonbonded distances were restrained to be similar; 2) thermal parameters on adjacent atoms were restrained to be similar for the disordered pairs. For complex **2**, the perchlorate anion was disordered with the SOF of the atoms fixed at 0.5. The $ClO_4^-$ was refined to the idealized tetrahedron with Cl−O distance fixed at 1.43(1) Å, and OO separation fixed at 2.32(2) Å. For complex **3**, hydrogen atoms of the water molecules were found from the difference Fourier maps, however, they were refined using the riding model. The ligands were disordered along the direction of the Cu−azpy−Cu chains, the ligands and the nitrate anions were also affected. The SOF was fixed at 0.5 for each ligand. In order to make the refinement stable, many restrains such as distance restrains on the atoms in the ligands and thermal parameter restrains were used in the refinement of the nitrate anions. For complex **4** the oxygen atoms of the perchlorate anion were found to be disordered, the site occupancy factors for them were fixed at 0.25. The atoms of the ethanol molecules were also found to be disordered, the SOF for them were also fixed at 0.25, the C−O and C−C distances were fixed at 1.45(1) Å. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC-145343 (**1**), CCDC-145344 (**2**), CCDC-145346 (**3**), CCDC-145345 (**4**). Copies of the data can be obtained free of charge and by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] R. Robson, in *Comprehensive Supramolecular Chemistry* (Eds.: J. L Atwood, J. E. D. Davies, D. D. MacNicol, F. Vortle, J. M. Lehn), Pergamon, Oxford, **1997**, vol. 6, ch. 22, pp. 733−755. − [1b] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, 37, 1460−1494.

[2] [2a] A. J. Blake, N. R. Champness, P. Hubberstey, W-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117−138. − [2b] N. R. Champness, M. Schröder, *Curr. Opin. Solid. State Mater. Sci.* **1998**, *3*, 419−424.

[3] [3a] L. Carlucci, G. Ciani, P. Macchi, D. M. Proserpoo, S. Rizzato, *Chem. Eur J.* **1999**, *5*, 237−243. − [3b] M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1998**, *46*, 173−303.

[4] [4a] M. Fujata, K. Ogura, *Coord. Chem. Rev.* **1996**, *148*, 249. − [4b] P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* **1999**, *38*, 2638−2684.

[5] [5a] B. Olcnyuk, A. Fechtenkotter, P. J. Stang, *J. Chem. Soc., Dalton Trans.* **1998**, 1707−1728. − [5b] P. J. Stang, *Chem. Eur J.* **1998**, *4*, 19−27.

[6] [6a] G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **1995**, *374*, 792−795. − [6b] L. R. MacGillivray, S. Subramanan, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.* **1994**, 1325−1326.

[7] [7a] M. Fujita, O. Sasaki, K. Watanabe, K. Ogura, K. Yamaguchi, *New. J. Chem.* **1998**, 189−191. − [7b] A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W-S. Li, M. Schroder, *Chem. Commun.* **1997**, 2027−2028.

[8] [8a] S. Subramanian, M. J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2127−2129. − [8b] M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am Chem. Soc.* **1994**, *226*, 1151−1152.

[9] [9a] M. J. Zaworotko, *Chem. Soc. Rev.* **1994**, 283−288. − [9b] A. J. Blake, N. R. Champness, S. S. M. Chung, W-S. Li, M. Schroder, *Chem. Commun.* **1997**, 1005−1006.

[10] [10a] K. A. Hirsch, S. R. Wilson, J. S. Moore, *Chem. Eur. J.* **1997**, *3*, 765−771. − [10b] A. J. Blake, N. R. Champness, A. N. Khlobystov, D. A. Lemenovski, W-S. Li, M. Schroder, *Chem. Commun.* **1997**, 1339−1340.

[11] [11a] D. M. P. Mingos, A. L. Rohl, *Inorg. Chem.* **1991**, *30*, 3769−3771. − [11b] K. A. Hirsch, S. R. Wilson, J. S. Moore, *Inorg. Chem.* **1997**, *36*, 2960−2968.

[12] [12a] K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward, M. J. Zaworotko, *Chem Commun.* **1999**, 1327−1328. − [12b] M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W −S. Li, M. Schroder, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2327−2329.

[13] [13a] L. Carlucci, G. Ciani, D. M. Proserpio, *J. Chem. Soc., Dalton Trans.* **1999**, 1799−1804. − [13b] L. Carlucci, G. Ciani, D. M. Proserpio, *New. J. Chem.* **1998**, 1319−1321.

[14] [14a] S. Noro, M. Kondo, T. Ishii, S. Kitagawa, H. Matsuzaka, *J. Chem. Soc., Dalton Trans.* **1999**, 1569−1574. − [14b] M. Kondo, M. Shimamura, S. Noro. T. Yoshitomi, S. Minakoshi, S. Kitagawa, *Chem Lett.* **1999**, 285−286.

[15] [15a] N. Molinear, M. C. Munoz, J. A. Real, *Inorg. Chem. Commun.* **1999**, *2*, 25−27. − [15b] M. A. Withersby, P. A. Cooke, A. J. Blake, N. R. Champness, P. Hubberstey, M. Schroder, *New. J. Chem.* **1999**, 573−576.

[16] S. R. Batten, J. C. Jeffery, M. D. Ward, *Inorg. Chem. Acta* **1999**, *292*, 231−237.

[17] R. W. Gable, B. F. Hoskins, R. Robson, *J. Chem. Soc., Chem. Commun.* **1990**, 1677−1678.

[18] J.-P. Launay, M. Tourrel-Pagis, J.-F. Lipskier, V. Marvaud, C. Joachim, *Inorg. Chem.***1991**, *30*, 1033−1038.

[19] B. J. Hathaway, D.G. Holah, J. D. Postlethwaite, *J. Chem. Soc.* **1961**, 3215−3218.

[20] *XSCANS, Version 2.1*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, **1994**.

[21] Siemens, *SHELXTL, Version 5.0*, Siemens Industrial Automation, Inc. Analytical Instrumentation, Madison, WI, **1995**.

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