Synthesis and Characterisation of Two Supramolecular Polymers $[CuAg_4(CN)_6(tacn)]_n$ and $[CuAu_2(CN)_4(tacn)]_n$ Containing Metal−Metal Interactions

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Two novel heterobimetallic supramolecular polymers, $[CuAg_4(CN)_6(tacn)]_n$ (**1**) and $[CuAu_2(CN)_4(tacn)]_n$ (**2**) (tacn = 1,4,7-triazacyclononane), have been synthesised from the building block $[Cu(tacn)]^{2+}$, together with $[Ag(CN)_2]^-$ (for **1**) and $[Au(CN)_2]^-$ (for **2**). The large difference in structural type between **1** and **2** is probably due to the fact that the Ag^I centre is three-coordinate and trigonal whereas the Au^I centre is linear. Metal–metal interactions play an important role in the formation of the supramolecular framework of **1** and the novel topology of **2**.

Introduction

The construction of supramolecular arrays by coordination has developed into a central theme of supramolecular chemistry.[1] Many novel supramolecular complexes have been produced with single metal centres linked by bi- or multifunctional ligands.[2] Cyanometalate anions, because of their ability to form strong bonds with transition metal cations, have been extensively used as building blocks in supramolecular coordination polymers.[3] Compared to the higher-coordination counterparts of various transition metals, there has been less investigation of two-coordinate, linear cyanometalate building blocks in the construction of coordination polymers.[3] Therefore, we chose the linear units $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ in order to construct multi-dimensional structures and novel topologies. At the same time, investigations into the attractive interactions between closed-shell metal atoms and ions continue to generate much interest.[4] As well as being able to use their cyano groups as bridging ligands, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ can also produce polymeric structures through Ag···Ag and Au···Au interactions. It is now well-established that Ag^I and Au^I complexes aggregate with a metal−metal interaction that is shorter than the sum of their van der Waals radii (3.44 Å for Ag and 3.6 Å for Au).[4,5] Although crystal engineering of supramolecular structures by Ag···Ag and Au···Au interactions is well-documented,[6] most of the reported structures contain only gold or silver without other metals, and there are few reports on heterobimetallic M−Ag or M−Au supramolecular compounds.[7] Leznoff has reported some Cu−Ag and Cu−Au complexes with capping amine ligands,[7] however, to the best of our knowledge, the use of the tacn ligand in a such system has not been reported.

Our interest has focused especially on the field of the d^{10}-d^{10} interactions of Ag^I and Au^I complexes. The energy of these interactions is similar to that of hydrogen bonds,[7] and they have been employed in the construction of multidimensional structures and novel topologies. We would therefore like to report the structural properties of two novel supramolecular polymers **1** and **2**, containing the tacn ligand and the linear units $[Ag(CN)_2]^-$ (in **1**) and $[Au(CN)_2]^-$ (in **2**). The differences between the structural properties, novel topologies and metal−metal interactions of both complexes form the subject of this contribution.

Results and Discussion

The coordination environment of **1** is shown in Figure 1; selected bond lengths and angles are listed in Table 1. Each of the $[Cu(tacn)]^{2+}$ cations is connected to two cyano groups; each copper(II) ion is therefore five-coordinate. The copper centre adopts a distorted square-pyramidal coordination, such that one nitrogen atom of the tacn ligand is coordinated apically, and the four equatorial positions are occupied by the two nitrogen atoms of the tacn ligand and the two cyano groups. The apical Cu−N bond length [Cu1−N1 = 2.171(8) Å] is slightly shorter than those of the previously reported distorted copper complexes (apical

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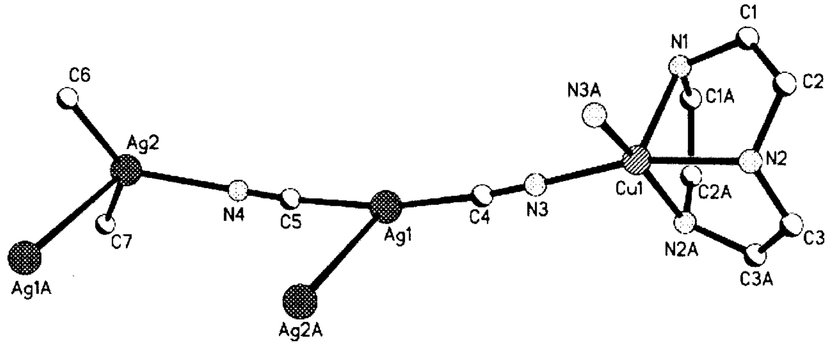

Figure 1. Perspective view of $[CuAg_4(CN)_6(tacn)]_n$ (**1**) showing the atom numbering; hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**

Ag(1)−C(5)	2.062(7)	Cu(1)−N(3)	1.967(6)
Ag(1)−C(4)	2.066(8)	Cu(1)−N(2)	2.039(5)
Ag(1)−Ag(2)#1	3.2940(13)	Cu(1)−N(1)	2.171(8)
Ag(2)−C(7)	2.138(6)	Ag(2)−C(6)	2.112(6)
Ag(2)−N(4)	2.279(7)	N(2)−Cu(1)−N(2)#2	82.3(3)
C(5)−Ag(1)−C(4)	168.9(3)	N(3)−Cu(1)−N(1)	107.5(2)
C(5)−Ag(1)−Ag(2)#1	87.42(19)	N(2)−Cu(1)−N(1)	83.1(2)
C(4)−Ag(1)−Ag(2)#1	92.8(2)	C(1)−N(1)−Cu(1)	105.1(5)
C(6)−Ag(2)−C(7)	134.7(2)	C(3)−N(2)−Cu(1)	109.5(5)
C(6)−Ag(2)−N(4)	115.8(3)	C(2)−N(2)−Cu(1)	108.4(5)
C(7)−Ag(2)−N(4)	109.4(2)	C(4)−N(3)−Cu(1)	174.9(6)
C(6)−Ag(2)−Ag(1)#1	68.4(2)	N(3)−C(4)−Ag(1)	175.2(6)
C(7)−Ag(2)−Ag(1)#1	102.27(19)	C(5)−N(4)−Ag(2)	166.4(6)
N(4)−Ag(2)−Ag(1)#1	104.40(16)	N(4)−C(5)−Ag(1)	174.2(6)
N(3)−Cu(1)−N(3)#2	93.5(3)	N(5)#3−C(6)−Ag(2)	174.5(7)
N(3)−Cu(1)−N(2)	166.7(3)	N(6)#4−C(7)−Ag(2)	172.08(18)
N(3)#2−Cu(1)−N(2)	90.9(2)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+3, -y+1, -z+1$; #2: $x, y, -z+1/2$; #3: $x, -y+3/2, -z+1$; #4: $x, y, -z+3/2$.

Cu−N bond length = 2.2−2.7 Å).[8] It should be noted that the coordination numbers of the Ag centres for Ag1 and Ag2 are 3 and 4, respectively.

The X-ray crystal analysis of **1** revealed a one-dimensional structure constructed from necklace-shaped rings. Each ring contains one copper, six silver and seven cyano groups, as shown in Figure 2. These necklaces-shaped rings are linked by shared edges up and down in the [011] direction. To the best of our knowledge, this structure is the first example of a necklace-shaped topology. The 1D structures in **1** are alternately linked via Ag···Ag interactions of 3.2940(13) Å [which is significantly less than the sum of the van der Waals radii of the two Ag(I) centres], and creates a 2D array in the *a* direction. Figure 3 shows the Ag···Ag metallic bonds that exist between the planes of the 2D array. As a result, the silver−silver interactions have increased the dimensionality of **1** from one to two, and can thus be viewed as a tool with which to increase structural dimensionality.[3]

The 2D arrays are connected into a weakly bonded supramolecule through further weak interactions between silver ladders (Figure 4). Within each silver ladder, there are

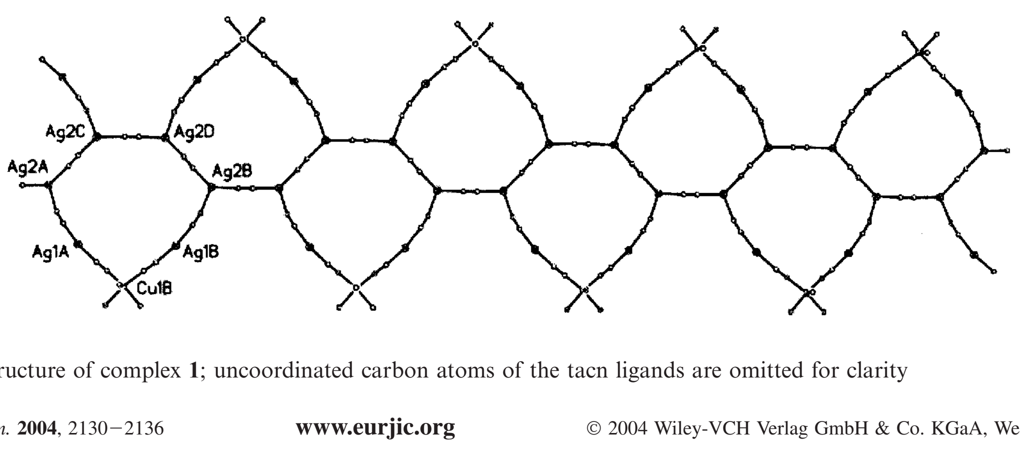

Figure 2. 1D structure of complex **1**; uncoordinated carbon atoms of the tacn ligands are omitted for clarity

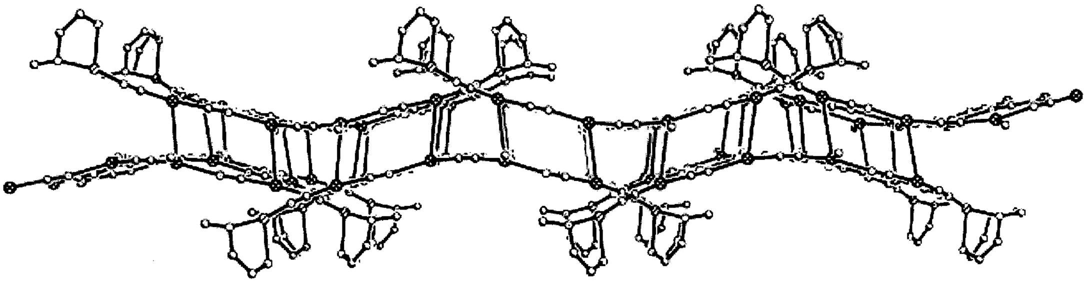

Figure 3. View of the double two-dimensional structure of **1**, showing metal−metal interactions between the two planes

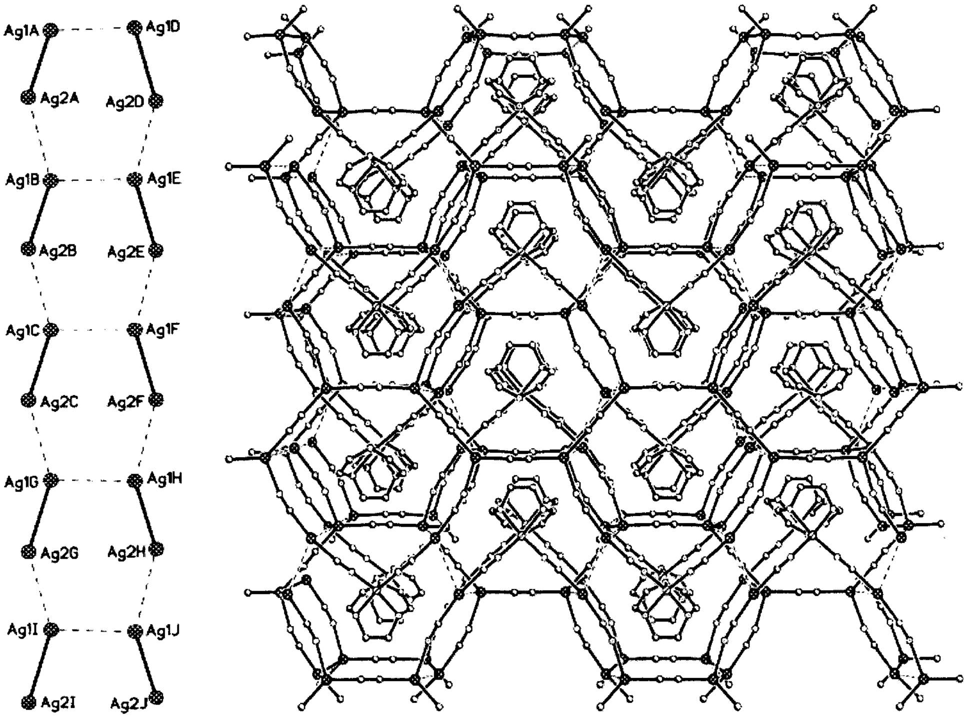

Figure 4. The silver ladder (left) and supramolecular structure (right) of complex **1**

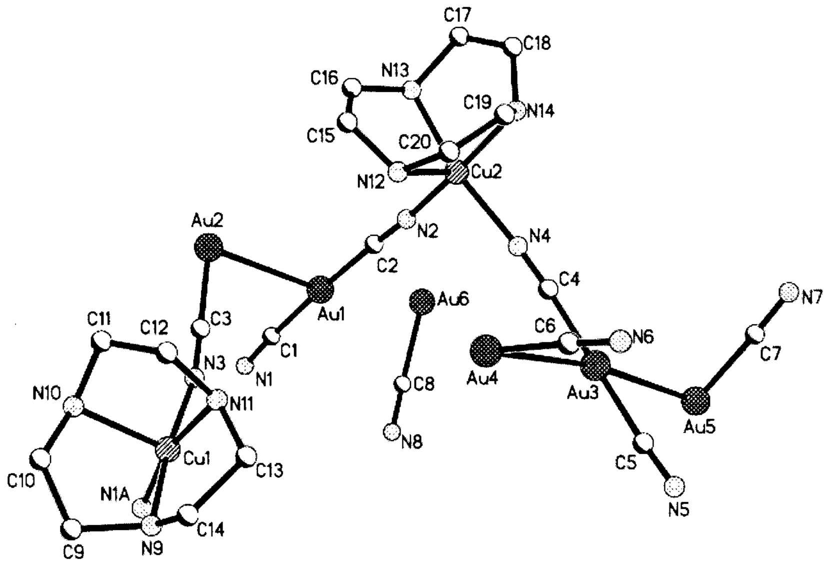

Figure 5. Perspective view of $[CuAu_2(CN)_4(tacn)]_n$ (**2**) showing the atom numbering; hydrogen atoms are omitted for clarity

no significant silver−silver interactions. The sum of the van der Waals radii of the two Ag^I centres is 3.44 Å, and is thus at the upper limit of a distance for a viable aurophilic interaction.[5] The Ag1B···Ag1E distance of 3.486 Å is beyond this threshold, and the Ag1B···Ag2A distance of 3.748 Å is even larger. As shown in Figure 4, the frameworks of AgCN exhibit a hexagon-like supramolecular structure. The siting of copper ions within these hexagons is an example of a rather rare topology.

Complex **2** was obtained by repeating the same procedure as for the preparation of **1**, but by using $[Au(CN)_2]^-$ instead of $[Ag(CN)_2]^-$. The coordination environment of **2** is shown in Figure 5; selected bond lengths and angles are listed in Table 2. Each of the $[Cu(tacn)]^{2+}$ cations is five-coordinate and adopts a distorted square-pyramidal coordination, similar to the Cu^{II} ions of **1**. The apical Cu1−N10 and Cu2−N12 bond lengths are 2.176(13) Å and 2.159(15) Å, respectively.

The packing structure of **2** reveals that there are two kinds of gold chains (see Figure 6), and that the copper ions act as bridges to link these gold chains together to form a 3D polymer. The zigzag chain is formed from gold ions in four kinds of coordination environment, in an **ABCDABCD** pattern. The distances of Au3A···Au4A and Au3A···Au5A are 3.2295(12) and 3.2614(12) Å, respectively; much shorter than the van der Waals separation of Au···Au. Chain b shows two kinds of centrosymmetric trinuclear units and two kinds of free $[Au(CN)_2]^-$ units, which are connected alternately with Au1A···Au2A and Au1A···Au6A interactions of 3.1321(11) and 3.33(8) Å, respectively. The axis of these gold chains is in the *a* direction, and they alternate along the *b* direction. As in **1**, the copper centre is five-

Table 2. Selected bond lengths [Å] and angles [°] for complex **2**

Au(1)−C(2)	1.941(19)	Au(6)−C(8)	1.99(2)
Au(1)−C(1)	1.967(16)	Cu(1)−N(1)#5	1.950(14)
Au(1)−Au(2)	3.1321(11)	Cu(1)−N(3)	1.975(14)
Au(2)−C(3)	1.959(18)	Cu(1)−N(9)	2.016(13)
Au(2)−Au(1)#1	3.1321(11)	Cu(1)−N(11)	2.044(14)
Au(3)−C(5)	1.960(17)	Cu(1)−N(10)	2.176(13)
Au(3)−C(4)	1.964(16)	Cu(2)−N(2)	1.967(15)
Au(3)−Au(4)	3.2295(12)	Cu(2)−N(13)	1.973(17)
Au(3)−Au(5)	3.2614(12)	Cu(2)−N(14)	1.996(14)
Au(4)−C(6)	1.94(2)	Cu(2)−N(4)	1.999(16)
Au(4)−Au(3)#2	3.2295(12)	Cu(2)−N(12)	2.159(15)
Au(5)−C(7)	1.93(2)	N(1)−Cu(1)#5	1.950(14)
Au(5)−Au(3)#3	3.2614(12)		
C(2)−Au(1)−C(1)	177.0(7)	N(9)−Cu(1)−N(10)	83.0(6)
C(2)−Au(1)−Au(2)	87.8(5)	N(11)−Cu(1)−N(10)	83.9(6)
C(1)−Au(1)−Au(2)	94.0(5)	N(2)−Cu(2)−N(13)	90.5(8)
C(3)−Au(2)−C(3)#1	180.000(1)	N(2)−Cu(2)−N(14)	167.3(7)
C(3)−Au(2)−Au(1)#1	86.3(5)	N(13)−Cu(2)−N(14)	83.4(8)
C(3)−Au(2)−Au(1)	93.7(5)	N(2)−Cu(2)−N(4)	92.2(6)
Au(1)#1−Au(2)−Au(1)	180.000(3)	N(13)−Cu(2)−N(4)	172.0(7)
C(5)−Au(3)−C(4)	176.4(7)	N(14)−Cu(2)−N(4)	92.5(7)
C(5)−Au(3)−Au(4)	92.7(5)	N(2)−Cu(2)−N(12)	107.7(7)
C(4)−Au(3)−Au(4)	84.1(5)	N(13)−Cu(2)−N(12)	83.6(8)
C(5)−Au(3)−Au(5)	79.8(5)	N(14)−Cu(2)−N(12)	82.8(7)
C(4)−Au(3)−Au(5)	103.5(5)	N(4)−Cu(2)−N(12)	102.7(7)
Au(4)−Au(3)−Au(5)	171.49(2)	C(1)−N(1)−Cu(1)#5	166.4(14)
C(6)−Au(4)−C(6)#2	180.000(4)	C(2)−N(2)−Cu(2)	174.3(15)
C(6)−Au(4)−Au(3)#2	94.6(6)	C(3)−N(3)−Cu(1)	164.2(15)
C(6)−Au(4)−Au(3)	85.4(6)	C(4)−N(4)−Cu(2)	164.8(15)
Au(3)#2−Au(4)−Au(3)	180.0	C(14)−N(9)−Cu(1)	114.1(10)
C(7)−Au(5)−C(7)#3	180.000(3)	C(9)−N(9)−Cu(1)	103.6(11)
C(7)−Au(5)−Au(3)	90.8(5)	C(10)−N(10)−Cu(1)	107.8(10)
C(7)#3−Au(5)−Au(3)	89.2(5)	C(11)−N(10)−Cu(1)	100.8(10)
Au(3)−Au(5)−Au(3)#3	180.0	C(13)−N(11)−C(12)	114.7(16)
C(8)−Au(6)−C(8)#4	180.000(1)	C(13)−N(11)−Cu(1)	104.4(11)
N(1)#5−Cu(1)−N(3)	93.5(6)	C(12)−N(11)−Cu(1)	109.2(11)
N(1)#5−Cu(1)−N(9)	91.8(6)	N(1)−C(1)−Au(1)	176.9(16)
N(3)−Cu(1)−N(9)	172.2(6)	N(2)−C(2)−Au(1)	174.4(15)
N(1)#5−Cu(1)−N(11)	166.2(6)	N(3)−C(3)−Au(2)	175.4(16)
N(3)−Cu(1)−N(11)	90.8(6)	N(4)−C(4)−Au(3)	172.4(16)
N(9)−Cu(1)−N(11)	82.7(6)	N(5)−C(5)−Au(3)	175.5(17)
N(1)#5−Cu(1)−N(10)	108.1(6)	N(6)−C(6)−Au(4)	178(2)
N(3)−Cu(1)−N(10)	100.9(6)	N(8)−C(8)−Au(6	173.2(19)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1$, -z; #2: $-x+1, -y+1, -z+1$; #3: $-x+1, -y+2, -z+1$; #4: $-x+1, -y+2$, -z; #5: $-x+2, -y+1, -z$.

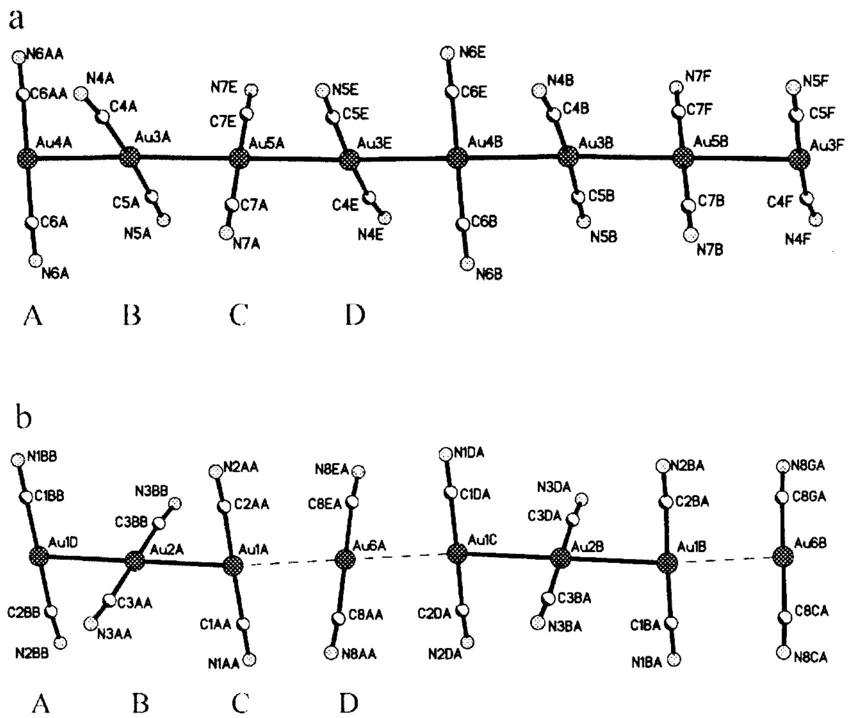

Figure 6. The two kinds of gold chains in complex **2**

coordinate with two sites occupied by nitrogen atoms of the cyano groups; thus the copper atoms function as bridges. In the *bc* plane, the copper ions linking two kinds of chains with single and double bridges form a 3D polymer of **2** (Figure 7). Leznoff has reported some Au−Cu complexes similar to **2**,[7] which also demonstrated the importance of Au···Au interactions in forming coordination polymers.

Complexes **1** and **2** exhibit different structures and topologies, which is probably mainly due to the different coordination numbers of Ag and Au (the Ag^I centre is three coordinate and trigonal, whereas the Au^I centre is linear). In addition, the different metallic radii of Ag and Au have led to the fact that silver−silver interactions have been reported and calculated to be weaker than gold−gold interactions,[3] which may also be the reason for the different structures of **1** and **2**. In the FT-IR spectra (KBr discs), there are three sharp ν_{CN} bands at 2174.4, 2136.2, and 2113.7 cm^{-1} for **1**, and at 2189.9, 2151.9, and 2138.5 cm^{-1} for **2**. The IR band at 2113.7 cm^{-1} is unusually low for an $[Ag(CN)_2]^-$-containing system (free $[Ag(CN)_2]^-$ is at 2139 cm^{-1}); this is somewhat hard to rationalise. It is noticeable that the vibration frequencies of the three bands in **1** are lower than those in **2**, which could be due to the slightly stronger coordination of the cyano group with Au than

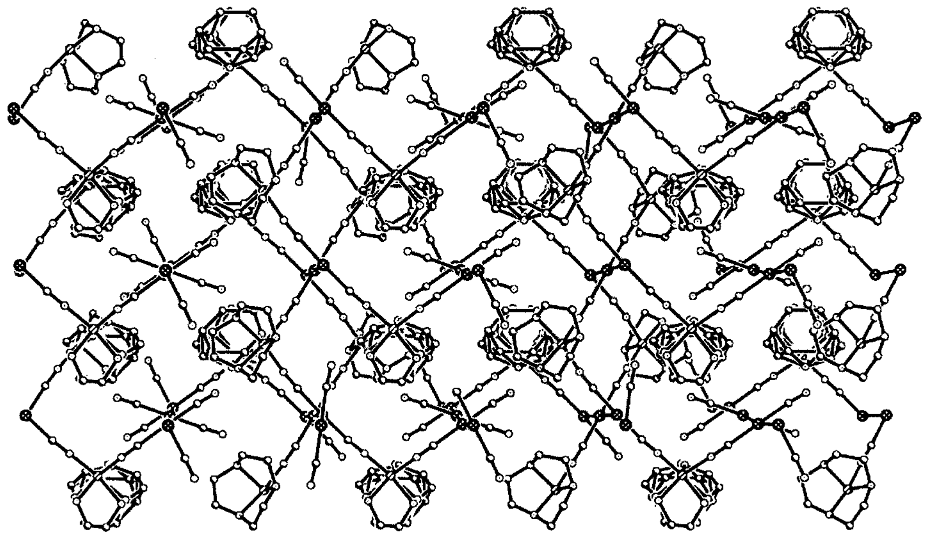

Figure 7. View of the three-dimensional polymeric structure of complex **2** along the *b* axis; hydrogen atoms are omitted for clarity

with Ag. The UV/Vis spectra of both **1** and **2** in DMF solution (concentration 0.10 mol/L) have similar strong absorption bands in the 200−270 nm range; **2** also displays two weak peaks at 279 and 289 nm, which may be assigned to the lower-energy MLCT absorption bands ($^1\Pi_u$-1 and $^3\Pi_u$-1).[9] Although Patterson has reported the UV/Vis spectra of $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$, we get different results in our work because of the different solvents and the nature of our complexes. In the visible range, the peaks at 566 nm (for **1**) and at 643 nm (for **2**) can be attributed to the *d-d* bands of Cu^{II}.[10]

Experimental Section

Materials and Methods: All of the starting materials were of reagent grade and were used without further purification. The macrocycle ligand tacn was prepared according to the procedures previously described.[11,12] C, H, N elemental analyses were carried out with a Perkin−Elmer analyzer, model 240. Electronic spectra were recorded with a Shimadzu UV-2101PC spectrophotometer in the 200−2000 nm range at room temperature. The FT-IR spectra were recorded with KBr pellets in the range 4000−400 cm^{-1} with a Bio-Rad FTS 135 spectrometer.

Synthesis of $C_{12}H_{15}Ag_4CuN_9$ (1): A solution of $CuCl_2·2H_2O$ (0.17 g, 1 mmol) in water (2.5 mL) was slowly added to a solution of tacn (0.13 g, 1 mmol) in methanol (2.5 mL) with stirring. The deep blue solution was stirred for 30 min and then filtered. The above-mentioned deep blue filtrate was introduced to one arm of an H-shaped tube and a solution of $K[Ag(CN)_2]$ (0.20 g, 1 mmol) in water (5 mL) was added to the other arm. After a few weeks, deep blue blocks of complex **1** (0.302 g, 68%, based on Ag salts) were obtained. $C_{12}H_{15}Ag_4CuN_9$: calcd. C 18.55, H 1.79, N 16.48; found C 18.46, H 1.92, N 16.14.

Synthesis of $C_{10}H_{15}Au_2CuN_7$ (2): This was synthesised according to the procedure described above (using similar reaction conditions), but using $K[Au(CN)_2]$ instead of $K[Ag(CN)_2]$, to provide deep blue needles of **2** (0.317 g, 46%, based on gold salts). $C_{10}H_{15}Au_2CuN_7$: calcd. C 17.15, H 2.31, N 14.26; found C 17.37, H 2.17, N 14.19.

X-ray Crystallographic Study: Single crystal X-ray diffraction measurements of the two complexes were carried out with a Bruker Smart 1000 CCD area detector using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Intensity data were measured at 293(2) K by the $\omega/2\theta$ technique. Semi-empirical absorption analysis was performed using the SADABS program. The structures were solved by direct-method successive Fourier difference analysis (SHELXS-97)[13] and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXS-97).[13] Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The crystallographic data and processing parameters for structural analyses of complexes **1** and **2** are summarised in Table 3.

CCDC-219629 (for **1**) and -219957 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinements for compounds **1** and **2**

Compound	1	2
Empirical formula	$C_{12}H_{15}Ag_4CuN_9$	$C_{10}H_{15}Au_2CuN_7$
M_w	445.91	690.76
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	Pbcm	$P\bar{1}$
a [Å]	6.640(2)	8.321(3)
b [Å]	16.270(5)	12.946(4)
c [Å]	18.073(5)	15.859(5)
α [Å]	90	82.284(6)
β [°]	90	88.419(5)
γ [°]	90	73.558(5)
V [Å^3]	1952.5(10)	1623.6(9)
Z	7	4
$D_{calcd.}$ [$g·cm^{-3}$]	2.655	2.826
Absorption coefficient [mm^{-1}]	5.028	19.325
Reflections collected	7493	7562
Unique data measured	1771	5358
Goodness-of-fit on F^2	1.028	1.031
R_1, wR_2 [$I > 2\sigma(I)$]	0.0402, 0.0758	0.0593, 0.1433
R_1, wR_2 (all data)	0.0703, 0.0854	0.0964, 0.1682

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[1] [1a] B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022. [1b] M. Munakata, L. P. Wu, T. Kuroda-Sowa, *Adv. Inorg. Chem.* **1999**, *46*, 173.

[2] For example: [2a] S. Leninger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853. [2b] H. Zhang, X. M. Wang, K. C. Zhang, B. K. Teo, *Coord. Chem. Rev.* **1999**, *183*, 157. [2c] H. Zhang, X. M. Wang, H. Zhu, W. Xiao, B. K. Teo, *J. Am. Chem. Soc.* **1997**, *119*, 5463.

[3] [3a] R. L. White-Morris, M. Stender, D. S. Tinti, A. L. Balch, *Inorg. Chem.* **2003**, *42*, 3237. [3b] C. J. Shorrock, B. Y. Xue, P. B. Kim, R. J. Batchelor, B. O. Patrick, D. B. Leznoff, *Inorg. Chem.* **2002**, *41*, 6743.

[4] [4a] M. Gorol, N. C. M. Zanetti, H. W. Roesdy, M. Noltemeyer, H. G. Schmidt, *Chem. Commun.* **2003**, 46. [4b] E. J. Fernandez, J. M. L. de Luzuriaga, M. Monge, M. E. Olmos, J. Perez, A. Laguna, A. A. Mohamed, J. P. Fackler, *J. Am. Chem. Soc.* **2003**, *125*, 2022. [4c] R. E. Cramer, D. W. Smith, W. VanDoorne, *Inorg. Chem.* **1998**, *37*, 5895.

[5] [5a] H. Schmidbaur, *Nature* **2001**, *413*, 31. [5b] A. Hamel, N. W. Mitzel, H. Schmidbaur, *J. Am. Chem. Soc.* **2001**, *123*, 516. [5c] A. A. Mohamed, J. Chen, A. E. Bruce, M. R. M. Bruce, *Inorg. Chem.* **2003**, *42*, 2203. [5d] D. Sun, R. Cao, J. Weng, M. Hong, Y. Liang, *J. Chem. Soc., Dalton Trans.* **2002**, 291. [5e] Q. M. Wang, T. C. W. Mak, *Chem. Eur. J.* **2003**, *9*, 44.

[6] [6a] P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597. [6b] P. M. Van Calcar, M. M. Olmstead, A. L. Balch, *J. Chem. Soc., Chem. Commun.* **1995**, 1773. [6c] M. J. Irwin, L. M. Muir, K. W. Muir, R. J.

Puddephatt, D. S. Yufit, *Chem. Commun.* **1997**, 219. [6d] R. J. Puddephatt, *Chem. Commun.* **1998**, 1055. [6e] M. J. Irwin, G. Jia, N. C. Payne, R. J. Puddephatt, *Organomettallics* **1996**, *15*, 51. [6f] M. Contel, J. Garrido, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, *Organometallics* **1996**, *15*, 4939. [6g] W. Schneider, A. Bauer, H. Schmidbaur, *Organometallics* **1996**, *15*, 5445. [6h] T. J. Mathieson, A. G. Langdon, N. B. Milestone, B. K. Nicholson, *J. Chem. Soc., Dalton Trans.* **1999**, 201. [6i] A. J. Amoroso, A. J. Blake, J. P. Danks, D. Fenske, M. Schröder, *New J. Chem.* **1999**, *23*, 345. [6j] C. W. Liu, I. J. Shang, C. M. Hung, J. C. Wang, T. C. Keng, *J. Chem. Soc., Dalton Trans.* **2002**, 1974. [6k] W. E. van Zyl, J. M. López-de-Luzuriaga, A. A. Mohamed, R. J. Staples, J. P. Fackler Jr., *Inorg. Chem.* **2002**, *41*, 4579. [6l] V. J. Catalano, M. A. Malwitz, *Inorg. Chem.* **2003**, *42*, 5483. [6m] K. M. Lee, H. M. J. Wang, I. J. B. Lin, *J. Chem. Soc., Dalton Trans.* **2002**, 2852. [6n] K. Nomiya, H. Yokoyama, *J. Chem. Soc., Dalton Trans.* **2002**, 2483. [6o] Q. M. Wang, T. C. W. Mak, *Inorg. Chem.* **2003**, *42*, 1637. [6p] H. Ehlich, A. Schier, H. Schmidbaur, *Inorg. Chem.* **2002**, *41*, 3721. [6q] Q. M. Wang, T. C. W. Mak, *Dalton Trans.* **2003**, 25. [6r] A. A. Mohamed, J. Chen, A. E. Bruce, M. R. M. Bruce, *Inorg. Chem.* **2003**, *42*, 2203.

[7] [7a] W. F. Yeung, W. T. Wong, J. L. Zuo, T. C. Lau, *J. Chem. Soc., Dalton Trans.* **2000**, 629. [7b] Z. D. B. Leznoff, B. Y. Xue, R. J. Batchelor, F. W. B. Einstein, B. O. Ratrick, *Inorg. Chem.* **2001**, *40*, 6026. [7c] C. J. Shorrock, B. Y. Xue, P. B. Kim, R. J. Batchelor, B. O. Patrick, D. B. Leznoff, *Inorg. Chem.* **2002**, *41*, 6743. [7d] M. I. Bruce, B. C. Hall, B. W. Skelton, M. E. Smith, A. H. White, *J. Chem. Soc., Dalton Trans.* **2002**, 995. [7e] T. Soma, T. Iwamoto, *Inorg. Chem.* **1996**, *35*, 1849. [7f] E. Colacio, F. Lloret, R. Kivekas, J. S. Varela, M. R. Sundberg, R. Uggla, *Inorg. Chem.* **2003**, *42*, 560. [7g] C. J. Shorrock, H. Jong, R. J. Batchelor, D. B. Leznoff, *Inorg. Chem.* **2003**, *42*, 3917.

[8] [8a] B. J. Hathaway, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon: Oxford, **1987**; vol. 5, p. 533. [8b]H. Z. Kou, H. M. Wang, D. Z. Liao, P. Cheng, Z. H. Jiang, S. P. Yan, X. Y. Huang, G. L. Wang, *Aust. J. Chem.* **1998**, *51*, 661. [8c] H. Yuge, T. Iwamoto, *J. Chem. Soc., Dalton Trans.* **1994**, 1237.

[9] [9a] M. A. Rawashdeh-Omary, M. A. Omary, H. H. Patterson, *J. Am. Chem. Soc.* **2000**, *122*, 10371. [9b] M. A. Rawashdeh-Omary, M. A. Omary, H. H. Patterson, J. P. Fackler Jr., *J. Am. Chem. Soc.* **2001**, *123*, 11237.

[10] S. Sabbani, K. D. Samar, *Inorg. Chem. Commun.* **2003**, *6*, 10.

[11] J. E. Richman, T. J. Atkins, *J. Am. Chem. Soc.* **1974**, *96*, 2268.

[12] A. McAuley, P. R. Norman, O. Olubuyide, *Inorg. Chem.* **1984**, *23*, 1938.

[13] [13a] G. M. Sheldrick, SHELXS 97, Program for the Solution of Crystal Structures, University of Göttingen, **1997**. [13b] G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, **1997**.

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