An aurophilicity-determined 3-D bimetallic coordination polymer: using $[Au(CN)_2]^-$ to increase structural dimensionality through gold···gold bonds in $(tmeda)Cu[Au(CN)_2]_2$

Daniel B. Leznoff,*[a] Bao-Yu Xue,[a] Brian O. Patrick,[b] Victor Sanchez[b] and Robert C. Thompson[b]

[a] *Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, B.C., V5A 1S6, Canada. E-mail: dleznoff@sfu.ca*

[b] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., V6T 1Y6, Canada*

Received (in Columbia, MO, USA) 25th August 2000, Accepted 5th December 2000
First published as an Advance Article on the web 23rd January 2001

A coordination polymer with the $[Au(CN)_2]^-$ building block has been prepared and it exhibits weak Au(I)-mediated ferromagnetic interactions; the structure illustrates that aurophilicity is a powerful tool to increase dimensionality, generating a three-dimensional system from a 1-D polymer.

The design of multidimensional coordination polymers is an area of intense current interest.[1] In particular, as many useful properties (magnetism, conductivity, host–guest chemistry, *etc.*) manifest themselves in 2- or 3-D networks, it is important to be able to generate high-dimensionality systems. The incorporation of moieties capable of forming hydrogen bonding interactions into coordination polymers is perhaps the most well-developed method for increasing structural dimensionality.[2] On the other hand, gold(I) centres are known to form weakly bonding interactions with themselves; these 'aurophilic' interactions have the same order-of-magnitude strength as hydrogen bonds.[3] The supramolecular chemistry of gold(I) is replete with systems that are polymeric by virtue of these Au–Au interactions,[4] but aurophilic interactions have not generally been used as a tool to increase structural dimensionality in coordination polymers containing metals other than gold.

Dicyanoaurate, $[Au(CN)_2]^-$, is an ideal building block to explore this concept. The molecule is linear, should readily form coordination polymers as do other anionic metal–cyanide units,[5] is sterically unencumbered and forms aurophilic interactions in the solid state.[6] We present here the first coordination polymer using this building block in which aurophilic interactions increase the dimensionality from one to three dimensions. $M[Au(CN)_2]_2$ (M = Co, Zn) complexes have been reported to form unusual quartz-like nets in which Au···Au bonding plays a secondary role.[7]

The reaction of an aqueous solution of $Cu(ClO_4)_2{\cdot}6H_2O$ containing one equivalent of tmeda (*N,N,N′N′*-tetramethylethylenediamine) with an aqueous solution of $K[Au(CN)_2]$ (2 equiv.) produced an immediate blue precipitate.[8] Elemental analysis indicated a compound of stoichiometry $(tmeda)Cu[Au(CN)_2]_2$ (**1**). The IR spectrum of **1** is diagnostic due to the presence of multiple absorptions in the CN region. $K[Au(CN)_2]$ has a single absorbance at 2141 cm^{-1}; **1** has three CN absorbances at 2152, 2174 and 2191 cm^{-1}. The high-energy bands likely correspond to bridging CN groups.[5] Single crystals of **1** could be obtained by slow diffusion of the two reagent solutions in an H-shaped tube. Infrared data were identical for both the powder and the crystals.

The X-ray crystal structure of **1** confirms the molecular formula of $(tmeda)Cu[Au(CN)_2]_2$ and reveals a polymeric network.[9] Note that, unlike many other linear building blocks that have been examined (*e.g.* pyrazine, 4,4′-bipyridyl),[10] $[Au(CN)_2]^-$ is anionic, and hence chemically uncharged polymers are generated.[11] The Cu(II) centre in **1** has a five-coordinate, distorted square pyramidal geometry, with one tmeda and three CN nitrogen atoms completing the coordination sphere. The asymmetric unit contains three unique gold centres—Au(2) and Au(3) have CN groups with both ends bound to a Cu(II), while Au(1) has one Cu(II)-bonded CN group and the other CN group is free. As shown in Fig. 1, the Cu(1)–NC–Au(2)–CN–Cu(1*)–NC–Au(3)–CN– fragment infinitely repeats in the *b* direction, giving rise to a coordinately bonded 1-D zig-zag chain. The Cu–N(4) bond length of 2.270(8) Å is significantly longer than the other four Cu–N bond lengths, hence the dangling $[Au(CN)_2]$ unit (Au(1)) is less strongly bound to the Cu centre than those in the polymer backbone. The intrachain Cu(1)–Cu(1*) distance is 10.18(1) Å.

Each gold centre is a site for potential aurophilic interactions to occur. Indeed, the picture of the solid-state structure is incomplete without including them. The Au(2) and Au(3) atoms in the backbone of the 1-D zig-zag chain form *interchain* Au···Au bonds of 3.5378(8) Å in the *a* direction (*i.e.* out of the plane of the paper). This distance is less than the sum of the van der Waals radii of two Au atoms (3.60 Å)[3] and is hence a viable, weak Au···Au interaction. This effectively joins two 1-D chains together to form a 2-D array of alternating 1-D zig-zag chains in the *ab* plane, as shown in Fig. 1. Each Au(2) and Au(3) centre is loosely four-coordinate.[6]

On the dangling $Au(CN)_2$ unit, Au(1) forms moderate Au···Au interactions of 3.345(1) Å with Au(1*) on the adjacent

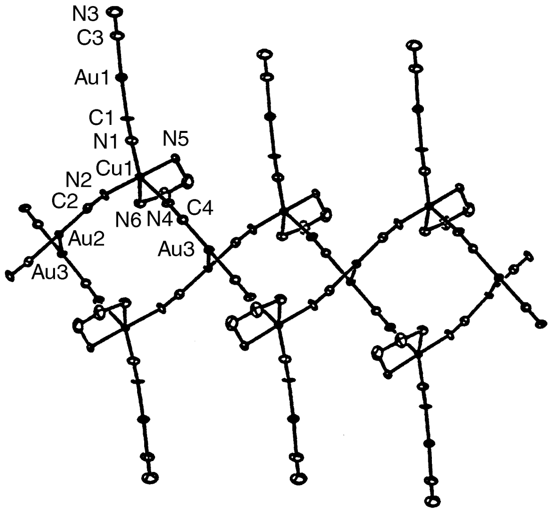

Fig. 1 Extended 2-D structure viewed down the *a* axis of $(tmeda)Cu[Au(CN)_2]_2$ (**1**), with its numbering scheme, showing a 1-D coordinately bonded zig-zag chain in the *b* direction, connected in the *a* direction by Au···Au bonds to an adjacent, inverse-sense chain (ORTEP, 50% ellipsoids). Tmeda-methyl groups have been removed for clarity. Selected bond lengths (Å) and angles (°): Cu–N(1) 2.006(9), Cu–N(2) 1.992(8), Cu–N(4) 2.270(8), Cu–N(5) 2.048(8), Cu–N(6) 2.080(8), Au(2)–Au(3) 3.5378(8), Cu–Cu* 10.18(1); N(1)–Cu–N(2) 91.6(4), N(1)–Cu–N(4) 103.6(3), N(1)–Cu–N(5) 90.5(3), N(1)–Cu–N(6) 157.2(3), N(2)–Cu–N(4) 89.3(4), N(2)–Cu–N(5) 176.2(4), N(2)–Cu–N(6) 91.2(4), N(4)–Cu–N(5) 93.3(3), N(4)–Cu–N(6) 99.0(3), N(5)–Cu–N(6) 85.7(4), Cu–N(1)–C(1) 165.2(9), Cu–N(2)–C(2) 171.2(9), Cu–N(4)–C(4) 166.9(9).

DOI: 10.1039/b007342n

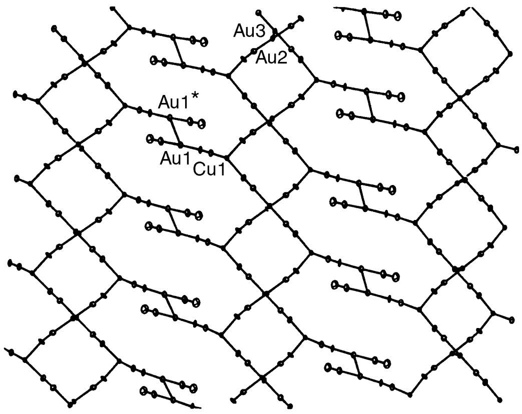

Fig. 2 Complete three–dimensional structure of **1**. Tmeda ligands have been removed for clarity. Au(1)–Au(1*): 3.345(1) Å.

1-D chain in the *b* direction (*i.e.* in the plane of the page), yielding a ladder-rung type motif running parallel to the 1-D chains. This Au···Au bonding in the *bc* plane, connecting the 2-D array of chains illustrated in Fig. 1, transforms the structure into a true three-dimensional system, as shown in Fig. 2. The presence of gold···gold interactions has effectively increased the dimensionality from a 1-D coordination polymer to a 3-D system.

The variable temperature magnetic susceptibility of **1** was measured from 2 to 300 K at a field strength of 1 T.[12] At 300 K, μ_{eff} is equal to 1.94 μ_B, a value typical for a system of isolated Cu(II), d^9, centres. This value steadily increases on decreasing the temperature, behaviour indicative of ferromagnetic interactions, to a maximum value of 2.05 μ_B at 25 K, below which temperature it decreases on further cooling. This latter decrease could arise either from the onset of saturation effects or very weak antiferromagnetic exchange. From a magnetic point of view, **1** could be considered as a 1-D chain, assuming that negligible magnetic interactions are propagated through the Au···Au bonds. We were unable to model the magnetic data over the entire range of temperatures studied. However, the χ_M *vs.* *T* data above 30 K were successfully fitted to theory employing the polynomial expression of Baker *et al.* for a 1-D ferromagnetic chain of $S = 1/2$ spins.[13] The magnetic moment *versus* temperature data are shown in Fig. 3, where the solid line is calculated from theory employing the best fit values of $g = 2.22$ and *J*, the exchange coupling constant, 2.34 cm^{-1}. From this analysis it appears that the diamagnetic $\mathrm{Au(CN)_2}^-$ unit may propagate weak ferromagnetic coupling in this compound. Note that in the related $[\mathrm{Ni(en)_2}]_3[\mathrm{Fe(CN)_6}](\mathrm{PF_6})_2$ system, the diamagnetic Fe(II) cyanide unit also mediates ferromagnetic interactions between the Ni(II) centres.[14]

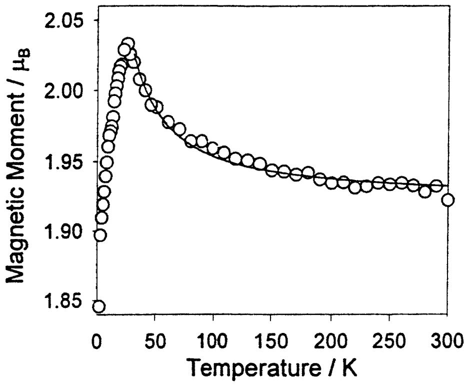

Fig. 3 Magnetic moment *versus* temperature plot for **1**. The solid line is theory (see text).

In summary, a new coordination polymer with the neglected $[\mathrm{Au(CN)_2}]^-$ building block has been prepared and crystallized. The structure confirms the concept that aurophilicity is a powerful tool to increase dimensionality in supramolecular coordination polymers.

Financial support from Simon Fraser University (D. B. L.) and NSERC of Canada (R. C. T.) is gratefully acknowledged.

Notes and references

1 O. M. Yaghi, H. L. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.

2 M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, **23**, 283; S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, 1994, **137**, 357; P. V. Bernhardt, *Inorg. Chem.*, 1999, **38**, 3481.

3 H. Schmidbaur, *Chem. Soc. Rev.*, 1995, **24**, 391.

4 B.-C. Tzeng, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1999, **38**, 3978; M. J. Irwin, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt and D. S. Yufit, *Chem. Commun.*, 1997, 219; A. Sladek and H. Schmidbaur, *Inorg. Chem.*, 1996, **35**, 3268; P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *J. Chem. Soc., Chem. Commun.*, 1995, 1773.

5 K. R. Dunbar and R. A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 283.

6 R. E. Cramer, D. W. Smith and W. Van Doorne, *Inorg. Chem.*, 1998, **37**, 5895; N. Blom, A. Ludi, H.-B. Bürgi and K. Tichy, *Acta Crystallogr., Sect. C*, 1984, **40**, 1767.

7 B. F. Hoskins, R. Robson and N. V. Y. Scarlett, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1203; S. C. Abrahams, L. E. Zyontz and J. L. Bernstein, *J. Chem. Phys.*, 1982, **76**, 5458; S. C. Abrahams, J. L. Bernstein, R. Liminga and E. T. Eisenmann, *J. Chem. Phys.*, 1980, **73**, 4585.

8 *Synthesis of* **1**: a 3 mL aqueous solution of $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$ (0.055 g, 0.15 mmol) and tmeda (1.5 mL, 0.1 mmol mL^{-1} stock solution, 0.15 mmol) was prepared. To this was added a 5 mL aqueous solution of $\mathrm{KAu(CN)_2}$ (0.086 g, 0.3 mmol) dropwise, resulting in an immediate blue-coloured precipitate. This solid was filtered and air-dried to give $\mathrm{(tmeda)Cu[Au(CN)_2]_2}$ (**1**) as a blue powder. Yield: 0.068 g (67%). Anal. Calcd. for $\mathrm{C_{10}H_{16}N_6Au_2Cu}$: C, 17.72; H, 2.38; N, 12.40. Found: C, 17.65; H, 2.61; N, 12.39%. IR (KBr): ν_{CN} 2152, 2174, 2191 cm^{-1}.

9 *Crystal data*: $\mathrm{C_{10}H_{16}N_6Au_2Cu}$; $M = 677.76$, triclinic, space group $P\bar{1}$, $a = 7.076(2)$, $b = 7.669(2)$, $c = 15.909(4)$ Å, $\alpha = 95.924(4)$, $\beta = 94.948(4)$, $\gamma = 113.897(6)°$, $V = 777.2(3)$ Å^3, $Z = 2$, $D_c = 2.896$ g cm^{-3}, μ(Mo-Kα) = 202.46 cm^{-1}, $T = 193$ K , 6558 data collected, 2919 unique ($R_{\mathrm{int}} = 0.053$), $R_1 = 0.075$ (all data). Data collection, structure solution and refinement of **1** were performed as detailed elsewhere.[15] CCDC 182/1879. See http://www.rsc.org/suppdata/cc/b0/b007342n/ for crystallographic files in .cif format.

10 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.

11 A. J. Blake, N. R. Champness, M. Crew, L. R. Hanton, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 1533.

12 Magnetic susceptibilities were measured on powdered samples using a Quantum Design (MPMS) SQUID magnetometer. The sample holder and details regarding the use of the equipment have been described elsewhere.[16] Magnetic susceptibilities were corrected for background and for the diamagnetism of all atoms.

13 G. A. Baker Jr., G. S. Rushbrook and H. E. Gilbert, *Phys. Rev. A*, 1964, **135**, 1272; W. E. Estes, W. E. Hatfield, J. A. C. van Ooijen and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1980, 2121.

14 N. Fukita, M. Ohba, H. Okawa, K. Matsuda and H. Iwamura, *Inorg. Chem.*, 1998, **37**, 842.

15 D. B. Leznoff, C. Rancurel, J.-P. Sutter, S. J. Rettig, M. Pink and O. Kahn, *Organometallics*, 1999, **18**, 5097.

16 M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson and J. Trotter, *Can. J. Chem.*, 1989, **67**, 1970.