DALTON
COMMUNICATION

Syntheses and structures of novel heterobimetallic Cu(II)–Au(I) complexes Cu(cyclen)$[Au(CN)_2]_2$ and Cu(pyz)$[Au(CN)_2]_2$

Wai-Fun Yeung,[a] Wing-Tak Wong,[b] Jing-Lin Zuo[c] and Tai-Chu Lau *[a]

[a] *Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Hong Kong, P.R. China. E-mail: bhtclau@cityu.edu.hk*
[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China*
[c] *Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China*

Received 24th December 1999, Accepted 2nd February 2000

Two novel cyano Cu^{II}–Au^{I} bimetallic complexes, Cu(cyclen)$[Au(CN)_2]_2$ 1 (cyclen = 1,4,7,10-tetraazacyclododecane) and Cu(pyz)$[Au(CN)_2]_2$ 2 (pyz = pyrazine) were prepared; 1 has a dimeric structure arising from $Au^{I}\cdots Au^{I}$ interactions, while 2 consists of linear pyrazine-bridged copper chains intercalated to produce a 2-D pleated sheet structure.

In recent years, considerable research effort has been put into the crystal engineering of supramolecular structures which have intriguing properties and potential applications in catalysis, electrical conductivity, molecular-based magnets and host–guest chemistry.[1–4] Covalent bonding, hydrogen bonding or other intermolecular interactions are widely used tools for the design of various structural topologies. A popular approach to the synthesis of these materials is to use $[M(CN)_x]^{n-}$ building blocks in conjunction with a transition metal ion complex. Architectures of 1-D, 2-D or 3-D networks using $[M(CN)_6]^{n-}$ ($n = 2$ or 3, M = Fe, Co, Cr, V, Mn) and $[M(CN)_4]^{2-}$ (M = Ni, Pt, Cd, Zn, Cu) have been studied extensively in the past decade.[5] However, the use of linear cyanometalates has received much less attention, and we are interested in employing the linear $[Au(CN)_2]^-$ as a building block for the construction of heterobimetallic polymeric materials. Apart from being able to act as a bridging ligand using its cyanide groups, $[Au(CN)_2]^-$ can also produce polymeric structures *via* $Au^{I}\cdots Au^{I}$ interactions. Although the crystal engineering of supramolecular structures by $Au^{I}\cdots Au^{I}$ interactions is well documented,[6] most of the reported structures contained only gold with no other metals, and there are very few reports on heterobimetallic M–Au supramolecular compounds. One example is the trinuclear species $[\{Au(\mu\text{-mes})AsPh_3\}_2Ag]ClO_4$ (mes = mesityl), which are connected by short $Au^{I}\cdots Au^{I}$ contacts to form a chain polymer.[6f] In this paper we report the syntheses and characterizations of two novel cyano-bridged Cu–Au heterobimetallic complexes by employing $[Au(CN)_2]^-$ as a starting material; Cu(cyclen)$[Au(CN)_2]_2$ 1 (cyclen = 1,4,7,10-tetraazacyclododecane) which has a dimeric structure arising from $Au^{I}\cdots Au^{I}$ interactions and Cu(pyz)$[Au(CN)_2]_2$ 2 (pyz = pyrazine) which forms a linear chain by making use of bridging pyrazine, the chains are further intercalated together to form a 2-D structure.

Treatment of $K[Au(CN)_2]$ with $Cu(CH_3COO)_2\cdot H_2O$ and cyclen at room temperature gave a highly insoluble compound 1.† The IR spectrum shows ν_{CN} at 2177 and 2138 cm^{-1} which are assigned to the free and coordinated $Au(CN)_2^-$ respectively. The X-ray structure of the cation of 1 shows that the Cu(II) centre is bonded to the four nitrogen atoms of cyclen and a nitrogen atom of a $Au(CN)_2^-$ with a distorted square pyramidal geometry (Fig. 1).‡ The Cu–N≡C unit is bent with a Cu–N(1)–C(1) bond angle of 157°. The cations pair up to form dimeric units linked by $Au\cdots Au$ interactions (Fig. 2). The $Au(1)\cdots Au(1)$ distance is 3.162(2) Å, which is shorter than twice the van der Waals radius for gold (3.32 Å)[7] and comparable to those of known $Au\cdots Au$ interactions.[6a] The dicyanoaurate anions also form dimeric units as a result of significant

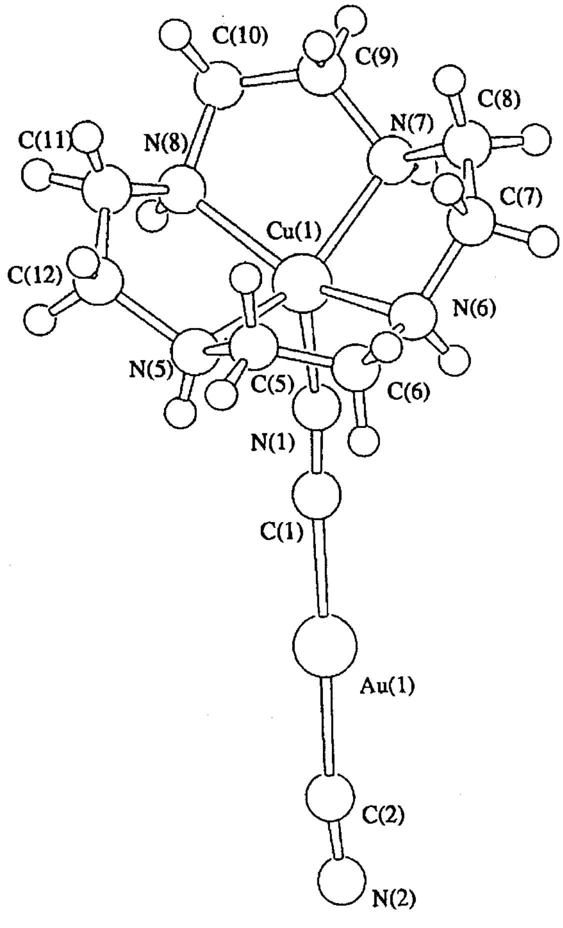

Fig. 1 ORTEP[9] drawing of Cu(cyclen)$[Au(CN)_2]$ **1**. Selected bond lengths (Å) and angles (°): Cu(1)–N(5) 2.03(3), Cu(1)–N(6) 2.02(2), Cu(1)–N(7) 1.98(2), Cu(1)–N(8) 1.98(2), Cu(1)–N(1) 2.10(3), N(1)–C(1) 1.16(4), N(2)–C(2) 1.09(3), N(3)–C(3) 1.22(5), N(4)–C(4) 1.13(5), Au(1)–C(1) 1.97(3), Au(1)–C(2) 2.01(3), Au(2)–C(3) 1.84(4), Au(2)–C(4) 1.98(4); $Au(1)\cdots Au(1)$–C(1) 81.8(7), C(1)–Au(1)–C(2) 178(1), N(1)–Cu(1)–N(5) 96(1), N(1)–Cu(1)–N(6) 103(1), N(1)–Cu(1)–N(7) 112.9(10), N(1)–Cu(1)–N(8) 109(1), N(5)–Cu(1)–N(6) 86(1), N(6)–Cu(1)–N(7) 86(1), N(7)–Cu(1)–N(8) 84(1), N(5)–Cu(1)–N(8) 85(1), N(5)–Cu(1)–N(7) 150(1), N(6)–Cu(1)–N(8) 146(1), Au(1)–C(1)–N(1) 176(3), Au(1)–C(2)–N(2) 174(3), Au(2)–C(3)–N(3) 175(3), Au(2)–C(4)–N(4) 166(3), $Au(1)\cdots Au(1)$–C(2) 98.4(7), C(3)–Au(2)–C(4) 177(1), Cu(1)–N(1)–C(1) 157(2).

DOI: 10.1039/a910350n

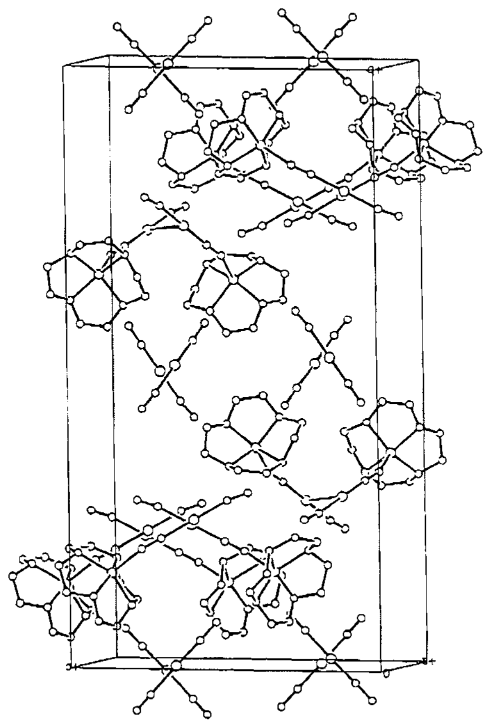

Fig. 2 Crystal packing of **1**.

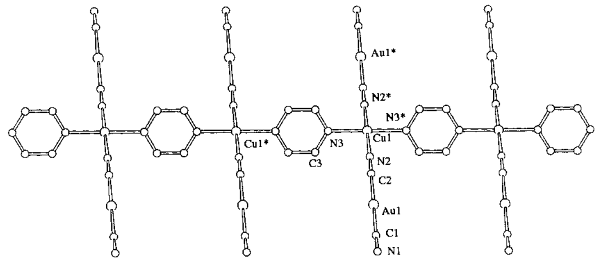

Fig. 3 View of an infinite polymeric chain of Cu(pyz)[Au(CN)$_2$]$_2$ **2**. Selected bond lengths (Å) and angles (°): Cu(1)–N(2) 1.96(1), Cu(1)–N(3) 2.06(1), Au(1)–C(1) 1.98(2), Au(1)–C(2) 2.00(2), N(1)–C(1) 1.15(2), N(2)–C(2) 1.13(2), N(3)–C(3) 1.32(1), C(3)–C(3) 1.42(2); C(1)–Au(1)–C(2) 179.4(8), N(2)–Cu(1)–N(3) 90.0, N(3)–Cu(1)–N(3) 180.0, Cu(1)–N(3)–C(3) 120.9(6), N(2)–Cu(1)–N(2) 180.0, Cu(1)–N(2)–C(2) 171(1), Au(1)–C(1)–N(1) 173(1), Au(1)–C(2)–N(2) 178(1).

Au · · · Au interactions. The Au(2) · · · Au(2) distance is 3.264 Å, which is similar to those of other dicyanoaurate salts; for example, the Au · · · Au distance is 3.272(4) Å in [24-pyrimidinium crown-6][Au(CN)$_2$]$_4$(NO$_3$)$_2$·2H$_2$O.[8]

Treatment of K[Au(CN)$_2$] with CuSO$_4$·5H$_2$O and pyrazine in water at room temperature gave a highly insoluble compound **2**.† The IR spectrum shows two strong ν_{CN} frequencies at 2206 cm^{-1} and 2157 cm^{-1}, which are at higher frequencies than that of K[Au(CN)$_2$] (2138 cm^{-1}). The X-ray structure of **2** is shown in Fig. 3.‡ Each Cu(II) centre adopts a square planar geometry and is bonded to two pyrazine ligands and two Au(CN)$_2^-$ in the *trans* configuration. The pyrazine ligands bridge the copper centres together to produce a 1-D structure. The infinite chains are further intercalated together to produce a 2-D pleated sheet structure (Fig. 4). The gold atoms in the structure align together to form a unique infinite chain with Au · · · Au distances of 3.4732(5) Å. Although such long distances usually imply negligible aurophilicity, the alignment of the gold atoms suggests that in this case the observed 2-D structure may not simply be due to crystal packing, and that Au · · · Au interactions may play a significant role.

The magnetic susceptibility of complex **2** was studied in the temperature range of 75–300 K. The temperature dependence of the molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) per Cu(II) ion of **2** is depicted in Fig. 5. At 300 K, the μ_{eff} is 1.92 μ_B which is slightly larger than the spin-only value of 1.73 μ_B, suggesting the presence of some magnetic interaction. When the temperature is lowered, the μ_{eff} decreases gradually and reaches an approximate plateau value of 1.76 μ_B at 100 K, indicating the presence of an effective spin $S = 1/2$. The μ_{eff} decreases abruptly on further lowering the temperature and reaches a value of 1.64 μ_B at 73.6 K, suggesting the presence of an antiferromagnetic interaction for **2**. The magnetic properties of this complex will be studied further.

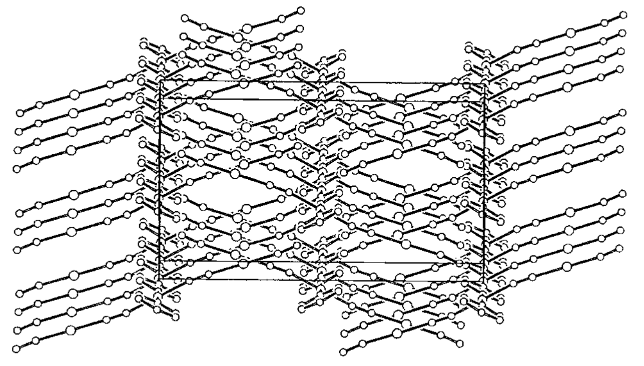

Fig. 4 A view of the crystal packing of Cu(pyz)[Au(CN)$_2$]$_2$ **2** projected down the *a* axis.

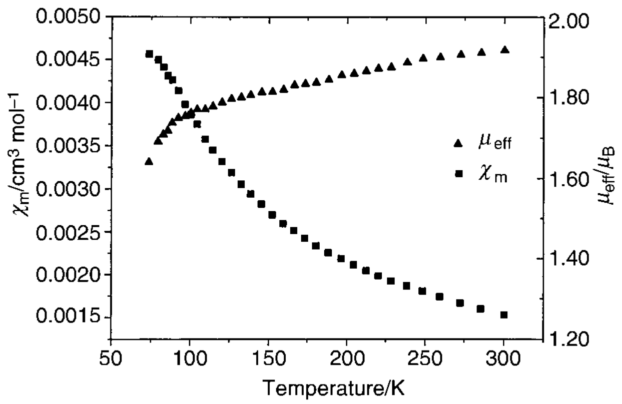

Fig. 5 Magnetic data for **2** at 75–300 K.

In conclusion, our results suggest that [Au(CN)$_2$]$^-$ is a useful starting material for the preparation of various M–Au complexes. A wide variety of structures based on these heterobimetallic complexes can be anticipated as a result of combinations of covalent bonding, π-interactions, hydrogen bonding and significant contributions from Au^I · · · Au^I interactions.

Acknowledgements

T. C. L. acknowledges financial support from the Hong Kong Research Grants Council and the City University of Hong Kong (DAG 7100014). W. F. Y. acknowledges the receipt of a postgraduate studentship and a postgraduate tuition scholarship from the City University of Hong Kong. W. T. W. acknowledges financial support from the Hong Kong Research Grants Council and the University of Hong Kong. J. L. Z. acknowledges financial support from the State National Nature Science Foundation of China (NSF29823001).

Notes and references

† Preparation of Cu(cyclen)[(Au(CN)$_2$)]$_2$ **1**. Cu(CH$_3$COO)$_2$·H$_2$O (100 mg, 0.5 mmol) and cyclen (86 mg, 0.5 mmol) were dissolved in methanol (10 ml). The resulting deep blue solution was added to an aqueous solution (5 ml) of K[Au(CN)$_2$] (288 mg, 1.0 mmol). Slow evaporation of the deep blue solution gave dark blue needle-shaped crystals. Yield: 60% based on Cu. Anal. Calc. for Au$_2$CuN$_8$C$_{12}$H$_{20}$: C, 19.64; H, 2.75 N, 15.27%. Found: C, 19.70; H, 2.75; N, 15.10%. IR νCN (KBr/cm^{-1}): 2177 (s), 2138 (s).

Preparation of Cu(pyz)[Au(CN)$_2$]$_2$ **2**. The reactants CuSO$_4$·5H$_2$O (125 mg, 0.5 mmol) pyrazine (40 mg, 0.5 mmol) and K[Au(CN)$_2$] (288 mg, 1.0 mmol) contained in three separate sample tubes were placed together in a 100 cm^3 beaker. The sample tubes and beaker were then carefully filled with water. Blue needle-shaped crystals were obtained after leaving the beaker undisturbed at room temperature for a few days. Yield: 30%. (Anal. Calc. for $Au_2CuN_6C_8H_4$: C, 14.96; H, 0.62; N, 13.09%. Found: C, 15.01; H, 0.63; N, 12.98%). IR ν_{CN} (KBr/cm^{-1}): 2206 (s), 2157 (s).

‡ Crystal data for **1**: $Au_2CuN_8C_{12}H_{20}$, $M = 733.82$, orthorhombic, primitive, space group *Pbcn* (no. 60), $T = 298$K, $a = 7.267(1)$, $b = 31.143(2)$, $c = 16.758(2)$ Å, $V = 3792.6(6)$ Å^3, $Z = 8$, $\mu = 166.10$ cm^{-1}, $D_c = 2.570$ g cm^{-3}, $F(000) = 2680.00$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å), 1725 reflections out of 13138 with $I > 1.50\sigma(I)$ were measured with $2\theta_{max}$ 51.3°. The structure was solved by direct methods (SHELXS86)[10] and expanded using difference Fourier techniques. $R = 0.077$, $R_w = 0.075$ with goodness-of-fit of 1.68.

Crystal data for **2**: $CuAu_2N_6C_8H_4$, $M = 637.61$, orthorhombic, C-centered, space group *Cmca* (no. 64), $T = 298$ K, $a = 6.883(1)$, $b = 10.094(1)$, $c = 17.831(1)$ Å, $V = 1238.8(2)$ Å^3, $Z = 4$, $\mu = 253.94$ cm^{-1}, $D_c = 3.418$ g cm^{-3}, $F(000) = 1108$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å), 547 reflections out of 687 with $I > 1.50\sigma(I)$ were measured. The structure was solved by direct methods (SIR92)[11] and expanded using difference Fourier techniques. $R = 0.042$, $R_w = 0.050$ with a goodness-of-fit of 1.62. CCDC reference number 186/1834. See http://www.rsc.org/suppdata/dt/a9/a910350n/ for crystallographic files in .cif format.

1 D. E. De Vos, P. L. Buskens, D. L. Vanoppen, P.-P. Knops-Gerrits and P. A. Jacobs, in *Comprehensive Supramolecular Chemistry*, eds. G. Alberti and T. Bein, Pergamon Press, Oxford, 1996, vol. 7, p. 647.

2 (*a*) T. Sheng, X. Wu, W. Zhang, Q. Wang, X. Gao and P. Lin, *Chem. Commun.*, 1998, 263; (*b*) A. Garoufis, S. Kasselouri, C. P. Raptopoulou and A. Terzis, *Polyhedron*, 1998, **18**, 581; (*c*) S. Takano, T. Naito and T. Inabe, *Chem. Lett.*, 1998, 1249.

3 (*a*) Y. Pei, O. Kahn, K. Nakatani, E. Codjovi, C. Mathonière and J. Sletten, *J. Am. Chem. Soc.*, 1991, **113**, 6558; (*b*) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Inorg. Chem.*, 1999, **38**, 229.

4 (*a*) G. W. Gokel and K. Koga (Editors), *United States–Japan Seminar on Host–Guest Chemistry*, Kluwer Academic Press, Netherlands, 1989; (*b*) J. A. Swift, A. M. Reynolds and M. D. Ward, *Chem. Mater.*, 1998, **10**, 4159.

5 (*a*) K. R. Dunbar and R. A. Heintz, in *Progress in Inorganic Chemistry*, ed., K. D. Karlin, Wiley-Interscience, New York, 1997, vol. 45, p. 283; (*b*) T. Iwamoto, in *Comprehensive Supramolecular Chemistry*, eds. D. D. MacNicol, F. Toda and R. Bishop, Pergamon Press, Oxford, 1996, vol. 6, ch. 19.

6 (*a*) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (*b*) P. M. Van Calcar, M. M. Olmstead and A. L. Balch, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 1773; (*c*) M. J. Irwin, L. M.-Muir, K. W. Muir and R. J. Puddephatt and D. S. Yufit, *Chem. Commun.*, 1997, 219; (*d*) R. J. Puddephatt, *Chem. Commun.*, 1998, 1055; (*e*) M. J. Irwin, G. Jia, N. C. Payne and R. J. Puddephatt, *Organometallics*, 1996, **15**, 51; (*f*) M. Contel, J. Garrido, M. C. Gimeno, P. G. Jones, A. Laguna and M. Laguna, *Organometallics*, 1996, **15**, 4939; (*g*) W. Schneider, A, Bauer and H. Schmidbaur, *Organometallics*, 1996, **15**, 5445; (*h*) T. J. Mathieson, A. G. Langdon, N. B. Milestone and B. K. Nicholson, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 201; (*i*) A. J. Amoroso, A. J. Blake, J. P. Danks, D. Fenske and M. Schröder, *New J. Chem.*, 1999, **23**, 345.

7 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

8 R. E. Cramer, D. W. Smith and W. VanDoorne, *Inorg. Chem.*,1998, **37**, 5895.

9 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

10 G. M. Sheldrick, SHELXS86, Program for crystal structure determination, University of Göttingen, 1986.

11 G. Cascarano, L. Favia and C. Giacovazzo, SIR92, *J. Appl. Crystallogr.*, 1992, **25**, 310.

Communication a910350n