

Syntheses and structures of novel heterobimetallic Cu(II)–Au(I) complexes Cu(cyclen)[Au(CN)₂]₂ and Cu(pyz)[Au(CN)₂]₂

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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...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)₄]^{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...Au^I interactions. Although the crystal engineering of supramolecular structures by Au^I...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(μ-mes)AsPh₃]₂Ag}ClO₄ (mes = mesityl), which are connected by short Au^I...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...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(CH₃COO)₂·H₂O 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...Au interactions (Fig. 2). The

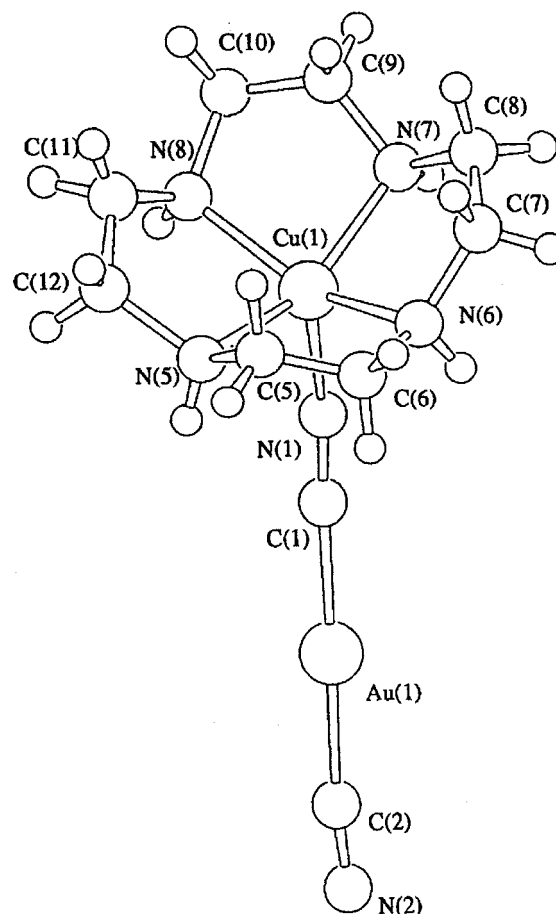


Fig. 1 ORTEP⁹ drawing of Cu(cyclen)[Au(CN)₂]₂ **1**. Selected bond lengths (Å) and angles (°): Cu(1)–N(5) 2.03(3), Cu(1)–N(6) 2.02(2), Cu(1)–N(7) 1.98(2), Cu(1)–N(8) 1.98(2), Cu(1)–N(1) 2.10(3), N(1)–C(1) 1.16(4), N(2)–C(2) 1.09(3), N(3)–C(3) 1.22(5), N(4)–C(4) 1.13(5), Au(1)–C(1) 1.97(3), Au(1)–C(2) 2.01(3), Au(2)–C(3) 1.84(4), Au(2)–C(4) 1.98(4); Au(1)...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)...Au(1)–C(2) 98.4(7), C(3)–Au(2)–C(4) 177(1), Cu(1)–N(1)–C(1) 157(2).

Au(1)...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...Au interactions.^{6a} The dicyanoaurate anions also form dimeric units as a result of significant

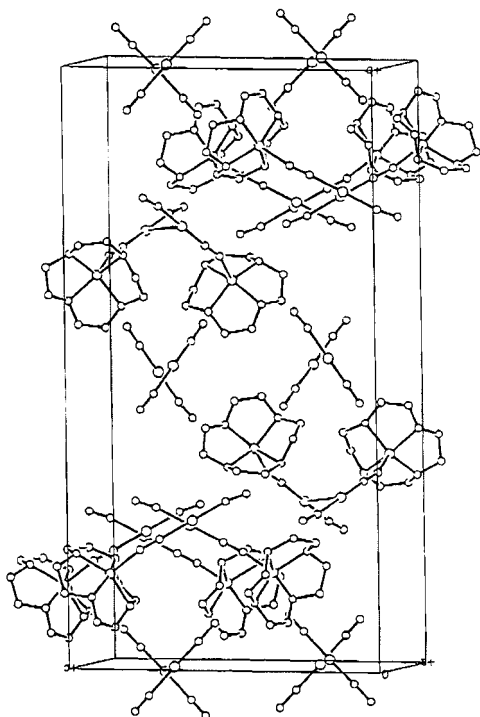


Fig. 2 Crystal packing of 1.

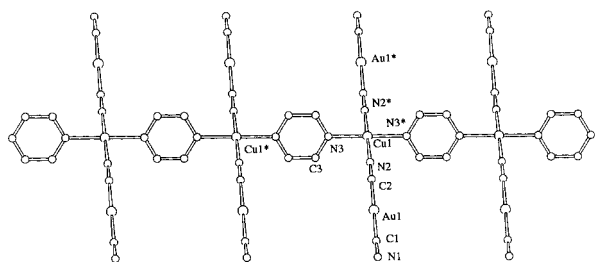


Fig. 3 View of an infinite polymeric chain of $\text{Cu}(\text{pyz})[\text{Au}(\text{CN})_2]_2$ **2**. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–N(2) 1.96(1), Cu(1)–N(3) 2.06(1), Au(1)–C(1) 1.98(2), Au(1)–C(2) 2.00(2), N(1)–C(1) 1.15(2), N(2)–C(2) 1.13(2), N(3)–C(3) 1.32(1), C(3)–C(3) 1.42(2); 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).

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

Treatment of $\text{K}[\text{Au}(\text{CN})_2]$ with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 $\text{K}[\text{Au}(\text{CN})_2]$ (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 $\text{Au}(\text{CN})_2^-$ 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 $\text{Au} \cdots \text{Au}$ 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 $\text{Au} \cdots \text{Au}$ 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,

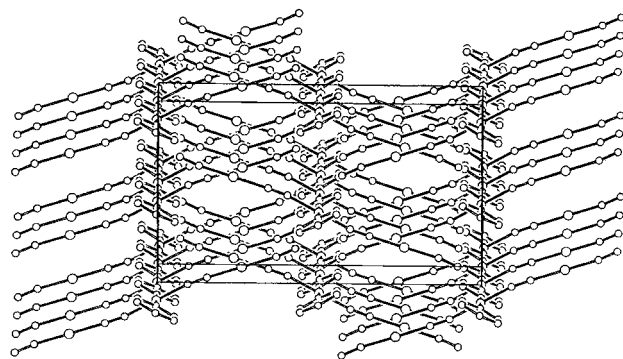


Fig. 4 A view of the crystal packing of $\text{Cu}(\text{pyz})[\text{Au}(\text{CN})_2]_2$ **2** projected down the *a* axis.

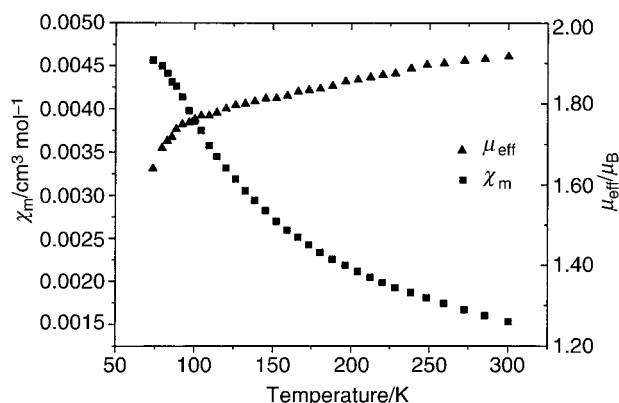


Fig. 5 Magnetic data for **2** at 75–300 K.

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.

In conclusion, our results suggest that $[\text{Au}(\text{CN})_2]^-$ 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 $\text{Au}^I \cdots \text{Au}^I$ interactions.

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Notes and references

[†] Preparation of $\text{Cu}(\text{cyclen})[\text{Au}(\text{CN})_2]_2$ **1**. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (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 $\text{K}[\text{Au}(\text{CN})_2]$ (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 $\text{Au}_2\text{CuN}_8\text{C}_{12}\text{H}_{20}$: C, 19.64; H, 2.75; N, 15.27%. Found: C, 19.70; H, 2.75; N, 15.10%. IR ν_{CN} ($\text{KBr}/\text{cm}^{-1}$): 2177 (s), 2138 (s).

Preparation of $\text{Cu}(\text{pyz})[\text{Au}(\text{CN})_2]_2$ **2**. The reactants $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (125 mg, 0.5 mmol) pyrazine (40 mg, 0.5 mmol) and $\text{K}[\text{Au}(\text{CN})_2]$ (288

mg, 1.0 mmol) contained in three separate sample tubes were placed together in a 100 cm³ 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 Au₂CuN₆C₈H₄: 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**: Au₂CuN₆C₁₂H₂₀, $M = 733.82$, orthorhombic, primitive, space group *Pbcn* (no. 60), $T = 298\text{K}$, $a = 7.267(1)$, $b = 31.143(2)$, $c = 16.758(2)$ Å, $V = 3792.6(6)$ Å³, $Z = 8$, $\mu = 166.10$ cm⁻¹, $D_c = 2.570$ g cm⁻³, $F(000) = 2680.00$, graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å), 1725 reflections out of 13138 with $I > 1.50\sigma(I)$ were measured with $2\theta_{\text{max}} = 51.3^\circ$. 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**: CuAu₂N₆C₈H₄, $M = 637.61$, orthorhombic, C-centered, space group *Cmca* (no. 64), $T = 298\text{K}$, $a = 6.883(1)$, $b = 10.094(1)$, $c = 17.831(1)$ Å, $V = 1238.8(2)$ Å³, $Z = 4$, $\mu = 253.94$ cm⁻¹, $D_c = 3.418$ g cm⁻³, $F(000) = 1108$, graphite-monochromated Mo-K α 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.

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