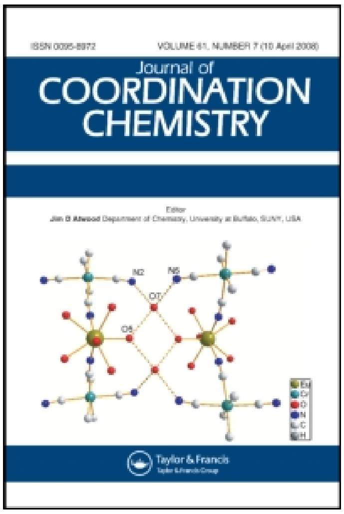

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Synthesis, structure and luminescent property of a novel Ag(I) complex: $[Cu(pn)_2][Ag_3(CN)_5]$

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Synthesis, structure and luminescent property of a novel Ag(I) complex: $[Cu(pn)_2][Ag_3(CN)_5]$

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Assembly of $[Ag(CN)_2]^-$ units with diaminecopper(II) cation $[Cu(pn)_2]^{2+}$ (pn = 1,3-diaminopropane), gives the ionic complex $[Cu(pn)_2][Ag_3(CN)_5]$. Single crystal X-ray analysis shows that this complex crystallizes in the triclinic, space group $P\bar{1}$, $a = 7.675(3)$, $b = 8.707(4)$, $c = 8.807(4)$ Å, $\alpha = 66.624(7)$, $\beta = 67.045(7)$, $\gamma = 79.179(7)°$, $Z = 1$. The whole complex has 3D architecture through metal–metal interactions and other weak interactions. The complex displays weak luminescence determined by argentophilicity at room temperature in the solid state.

Keywords: Diaminecopper(II); Argentophilicity; Luminescent property

1. Introduction

Research in the design and synthesis of supramolecular architectures is of interest because of their structural diversity and potential applications in the fields of catalysis, electrical conductivity and molecular magnetic materials [1–3]. Effort has been devoted to cyanometalate anions such as $[Ag(CN)_2]^-$, which has been extensively used as building blocks in supramolecular coordination polymers. Such cyanometalates use their cyano groups as bridging ligands and produce polymeric structures through silver–silver interactions [4, 5]. The silver–silver (argentophilic) interactions analogous to gold–gold interactions serve to increase supramolecular dimensionality [6].

Silver(I) dicyanide complexes also attract attention for their potential applications in the fields of luminescent materials [7, 8]. In this article, we report the synthesis, structure and luminesence of the silver(I) complex $[Cu(pn)_2][Ag_3(CN)_5]$.

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2. Results and discussion

2.1. *X-ray diffraction studies*

The molecular structure perspective drawing of the title complex is shown in figure 1 and selected bond lengths and angles are given in table 1.

Single crystal X-ray analysis reveals an ionic, asymmetric structure consisting of the $[Ag_3(CN)_5]^{2-}$ anion which is the linear silver trimer formed via argentophilic interactions (Ag(1)–Ag(2) = 3.0169(10) Å and Ag(1) – Ag(2) – Ag(1A) = 180°) and the $[Cu(pn)_2]^{2+}$ cation. In addition, C(3) and N(3) are disordered.

As shown in figure 2, 1D chains are formed from connection of the linear silver trimers through cyano-bridges. At the same time $[Ag_2(CN)_3]^-$ units are formed [6c, 9]. which are not linear (C(1A)–Ag(1A)–N(3A) = 163.7(2)°) possibly due to argentophilic interactions [6]. Each $[Cu(pn)_2]^{2+}$ is connected to two cyano groups of $[Ag_2(CN)_3]^-$

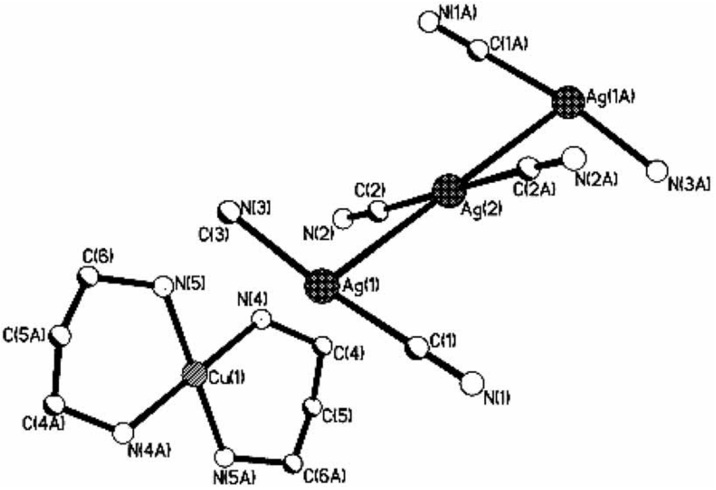


Figure 1. Molecular structure of the complex $[Cu(pn)_2][Ag_3(CN)_5]$ (hydrogen atoms omitted for clarity).

Table 1. Selected bond lengths (Å) and angles (°) for the complex $[Cu(pn)_2][Ag_3(CN)_5]$.

Ag(1)–C(1)	2.050(6)	Cu(1)–N(4)#2	2.013(5)
Ag(2)–C(2)	2.057(7)	Cu(1)–N(4)	2.013(5)
Ag(1)–Ag(2)	3.0169(10)	Cu(1)–N(5)#2	2.038(4)
Ag(2)–C(2)#1	2.057(7)	Cu(1)–N(5)	2.038(4)
Ag(2)–Ag(1)#1	3.0169(10)		
C(1)–Ag(1)–N(3)	163.7(2)	N(4)#2–Cu(1)–N(4)	180.000(1)
C(1)–Ag(1)–Ag(2)	78.04(17)	N(4)#2–Cu(1)–N(5)#2	87.89(19)
N(3)–Ag(1)–Ag(2)	103.02(18)	N(4)–Cu(1)–N(5)#2	92.11(19)
C(2)–Ag(2)–C(2)#1	180.000(1)	N(4)#2–Cu(1)–N(5)	92.11(19)
C(2)–Ag(2)–Ag(1)#1	107.12(17)	N(4)–Cu(1)–N(5)	87.89(19)
C(2)#1–Ag(2)–Ag(1)#1	72.88(17)	N(5)#2–Cu(1)–N(5)	180.000(1)
C(2)–Ag(2)–Ag(1)	72.88(17)	C(4)–N(4)–Cu(1)	121.0(4)
C(2)#1–Ag(2)–Ag(1)	107.12(17)	Cu(1)–N(5)–H(5A)	107.0
Ag(1)#1–Ag(2)–Ag(1)	180.0	Cu(1)–N(5)–H(5B)	107.0

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

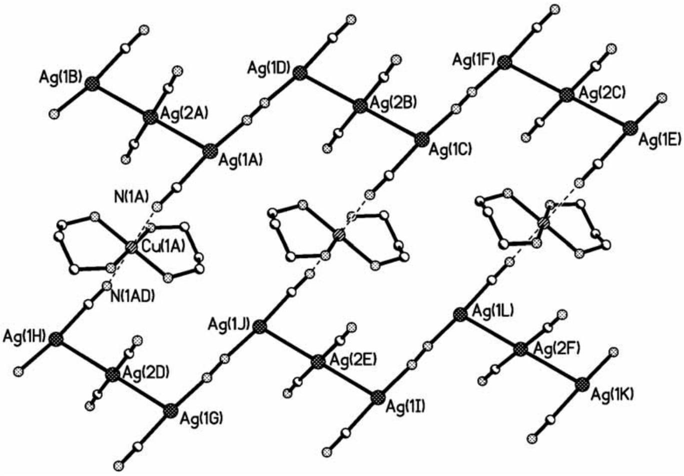
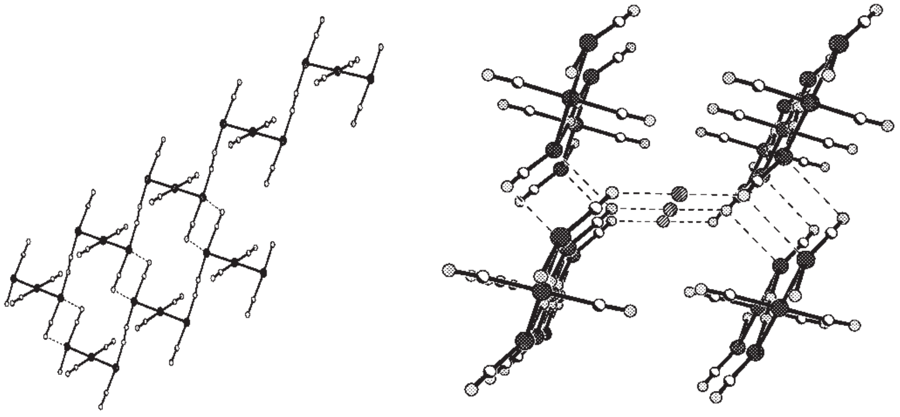


Figure 2. 2D arrays containing $[Cu(pn)_2]^{2+}$ cations and $[Ag_3(CN)_5]^{2-}$ groups.



(a) (b)

Figure 3. (a) 2D silver(I) arrays formed through the weak cyano(N)···Ag interactions. (b) 3D networks of complex (all pn ligands are omitted for clarity).

anions through $N_{cyano}\cdots$Cu interactions, with the distance of 2.533 Å, which is in the range of the previously reported distorted copper complexes (Cu–N bond length = 2.2–2.7 Å) [10]. Therefore each copper(II) centre adopts a distorted octahedral coordination, with the equatorial Cu–N bond lengths of 2.013(5) and 2.038(4) Å. The 1D zigzag silver(I) chains are formed into 2D arrays through weak $N_{cyano}\cdots$Ag interactions with the distance of Ag···N 3.042 Å (figure 3a), shorter than the sum of the van der Waals radii (3.27 Å) [11]. The 2D arrays are held via these weak interactions into 3D networks (figure 3b).

For the title complex, silver–silver interactions and other interactions such as the $N_{cyano}\cdots$Ag interactions may play important roles in increasing structural dimensionality [12].

There are several differences between the structure of the title complex and the previously reported structure of $[Cu(pn)_2Ag(CN)_2][Ag(CN)_2]$ containing no

$[Ag_2(CN)_3]^-$ units [13]. In $[Cu(pn)_2Ag(CN)_2][Ag(CN)_2]$, the Ag–Ag interaction between the bridging $[Ag_2(CN)_3]^-$ and the free $[Ag_2(CN)_3]^-$ is 3.2270(3) Å, which is much weaker than that observed in the title complex (3.0169(10) Å). On the other hand, 1D chains form between $[Cu(pn)_2]^{2+}$ and bridging $[Ag_2(CN)_3]^-$ units with the Cu–N bond of 2.203(2) Å, which is much stronger than observed in the title complex (2.533 Å). Finally, no Ag···N interactions exist in $[Cu(pn)_2Ag(CN)_2][Ag(CN)_2]$.

2.2. *Spectral properties*

The room temperature UV-Vis spectra of title complex have a strong absorption band at 258 nm, which may be assigned to low-energy MLCT absorption bands [7]. In the visible range, the peak at 610 nm can be attributed to the d–d transition of Cu(II) [14, 15].

ESR experimental and simulation spectra of the title complex at X-band microwave frequencies at 110 K are shown in figure 4. The values of the g tensor can be obtained with $g_x = 2.06$, $g_y = 2.07$ and $g_z = 2.20$, which can be used to derive the ground state [16, 17]. In axially elongated octahedral and square planar complexes, the unpaired electron occupies the $d_{x^2-y^2}$ orbital with a $^2B_{1g}$ ground state resulting in $g_0 > g_\perp$. The observed g values suggest that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital with axially elongated octahedral environment consistent with the X-ray diffraction analysis.

The excitation maximum for the title complex in the solid state is at 313 nm, while the emission maximum is at 495 nm (figure 5). The luminescence may be attributed to the metal–metal interactions of d^{10} systems observed for many complexes, particularly of gold and silver [18, 19]. The value of the emission band is consistent with the emission band (490–530 nm) of $*[Ag(CN)^{2-}]_n$ (delocalized exciplexes), reported by Patterson [20]. The results indicate an electron excited from the filled 4d orbitals (HOMO) to the empty 5p orbitals (LUMO) and the reverse process related to an excited electron from the 5p orbitals back to the 4d orbitals [21].

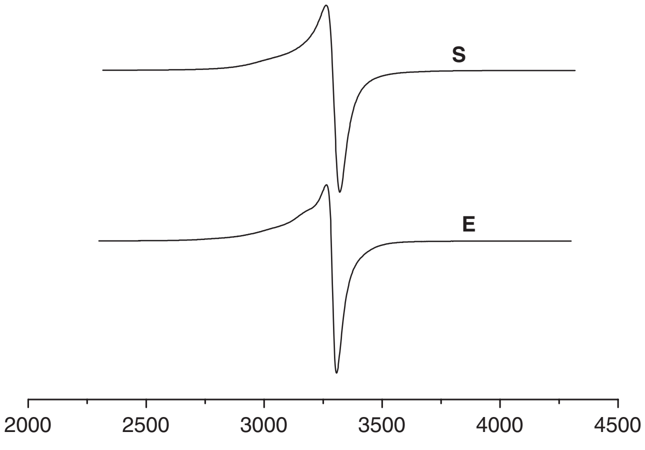


Figure 4. ESR experimental spectrum (E) and ESR simulation spectrum (S) of the complex at 110 K.

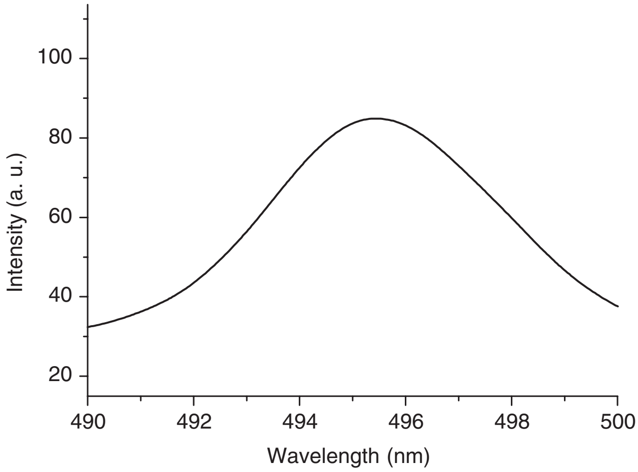


Figure 5. Emission spectra of the solid complex at room temperature.

3. Experimental

3.1. *Physical measurements*

Infrared spectrum as a KBr pellet was recorded on a Bruker Tensor 27 spectrophotometer in the range of 4000–400 cm^{-1}. The UV-vis spectrum in DMSO was recorded on a Jasco V-570 UV-Vis scanning spectrophotometer. The ESR spectrum was recorded on an ER 200D-SRC ESR spectrophotometer. The luminescence spectra were recorded in the solid state on a Cary Eclipse luminescence spectrophotometer.

3.2. *Starting materials*

$KAg(CN)_2$ was of analytical grade and was obtained from commercial sources and used without further purification. $[Cu(pn)_2]SO_4 \cdot 2H_2O$ was synthesized according to the literature [22].

3.3. *Synthesis of the complex $[Cu(pn)_2][Ag_3(CN)_5]$*

An aqueous solution (20 mL) containing $KAg(CN)_2$ (0.0796 g, 0.4 mmol) and $[Cu(pn)_2]SO_4 \cdot 2H_2O$ (0.0660 g, 0.2 mmol) was refluxed for 1 h with stirring, and filtered. The purple crystals (yield, 35%, based on Ag salts) were obtained within a couple of days from slow evaporation of the filtrate. $C_{11}H_{20}Ag_3CuN_9$: Calcd C, 22.01%, H, 3.59%, N, 20.68%; Found C, 21.95%, H, 3.35%, N, 20.94%. Main IR bands (KBr, cm^{-1}): 3338s ($\nu_{N\text{–}H}$), 2138s, 2119s ($\nu_{C\equiv N}$). UV-Vis bands: 258 nm ($\varepsilon = 7619\,mol^{-1}\,cm^{-1}$), 606 nm ($\varepsilon = 111\,mol^{-1}\,cm^{-1}$).

3.4. *X-ray structure analysis*

The crystallographic study was performed on a Siemens Smart diffractometer equipped with CCD area detector by ϕ and ω technique. A total of 2364 reflections were collected. The structure was solved by direct methods (SHELX-97) and refined

Table 2. Crystal data and structure refinement for the complex $[Cu(pn)_2][Ag_3(CN)_5]$.

Empirical formula	$C_{11}H_{20}Ag_3CuN_9$
Formula weight	665.51
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	7.675(3)
b	8.707(4)
c	8.807(4)
α	66.624(7)
β	67.045(7)
γ	79.179(7)
Volume (Å^3)	497.1(4)
Z	1
Calculated density (Mg m^{-3})	2.223
Absorption coefficient (mm^{-1})	3.978
F(000)	319
Crystal size (mm^3)	$0.26 \times 0.18 \times 0.14$
θ range for data collection (°)	2.55–26.48
Limiting indices	$-9 \le h \le 9$, $-10 \le k \le 10$, $-5 \le l \le 11$
Reflections collected	2919
Unique reflections	2034 [R(int) = 0.0271]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2034/0/112
Goodness-of-fit on F^2	0.998
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.0854$
R indices (all data)	$R_1 = 0.0682$, $wR_2 = 0.0953$
Largest peak and hole (e Å^{-3})	0.461 and −0.795
Primary method of solution	Direct
Computing data collection	Bruker SMART
Computing cell refinement	Bruker SMART
Computing structure solution	SHELXS-97
Computing structure refinement	SHELXL-97

by full-matrix least-squares with isotropic thermal parameters for a non-hydrogen atom on F^2 [23]. The hydrogen atoms were added geometrically and riding on the concerned atoms and refined with fixed thermal factors. Further details of the structure analyses are summarized in table 2.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with Cambridge Crystallographic Data Center as supplementary publication CCDC No. 225310 Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: -44-1223-336033; Email for inquiry: fileserv@ccdc.cam.ac.uk; email for deposition: deposit@ccdc.cam.ac.uk).

Acknowledgments

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