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One-dimensional Complex $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ (medpt = *N,N*-bis-(3-aminopropyl)methylamine)

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Abstract

The novel compound, $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ (medpt = *N,N*-bis-(3-aminopropyl)methylamine), was isolated from a reaction mixture containing $Cu(ClO_4)_2 \cdot 6H_2O$, medpt and $K[Ag(CN)_2]$. The new complex was characterized by IR spectroscopy, magnetochemical studies and by X-ray single crystal diffraction. The structure contains $[Cu(medpt)]^{2+}$ units being bridged by $[Ag(CN)_2]^-$ units resulting in chains of the composition $[–\mu–CN–Cu(medpt)–\mu–NC–Ag–]_n$, and dicyanoargentate anions. Ag...Ag interactions link free $[Ag(CN)_2]^-$ anions to the chain. The copper(II) atom is five coordinated to two cyanide-nitrogen and three medpt-nitrogen atoms in a distorted square-pyramidal arrangement.

Keywords: Copper(II) complexes, dicyanoargentates(I), cyano-bridged complexes, X-ray structure analysis

1. Introduction

Our research interest is focused on the synthesis and characterization of cyano-bridged coordination compounds. In our previous work, we have reported the properties and structures of binuclear[1] and trinuclear oligomers,[2] one-dimensional (1D) chains[3] and two-dimensional (2D) sheets[4] in which the cyanide anion was incorporated as bridging entity. These complexes can be built by linking appropriate building blocks by the brick and mortar method.[5] Here we present the three-dimensional molecular structure a novel cyano-bridged copper(II) dicyanoargentate(I) complex. Previously, compounds of the general formula $[Cu(L)_2][Ag_2(CN)_4]$, where L have been the chelating bidentate ligands 1,2-diaminopropane,[6] 1,3-diaminopropane,[7] ethylenediamine[8] and 2,2´-bipyridine[9] have been studied. When a tridentate ligand diethylenetriamine (dien) was used, a more complicated structure containing the cation $[–Cu(dien)–NC–Ag–CN–]_n$ and the two different anions $[Ag(CN)_2]^-$ and $[Ag_2(CN)_3]^-$ was formed.[10] With the aim to prepare new cyano-bridged copper(II) dicyanoargentate(I) complexes we used a blocking tridentate amine ligand, namely *N,N*-bis-(3-aminopropyl)methylamine (medpt), which was reacted with $Cu(ClO_4)_2 \cdot 6H_2O$ and $K[Ag(CN)_2]$ to give the title complex.

2. Experimental

2. 1. Synthesis and Characterization

All chemicals were of reagent grade and were used without further purification. The C, H, N analysis was carried out on an EA 1108 instrument (Fisons). IR spectrum was recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellet. Magnetochemical data were obtained by the Faraday method at room temperature using a Sartorius M-25D electrobalance.

Complex $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ Synthesis

A solution of 0.19 g (0.5 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ and 0.08 mL (0.5 mmol) of *N,N*-bis-(3-aminopropyl) methylamine in 20 mL water was added to a solution of

0.20 g (1 mmol) of $K[Ag(CN)_2]$ in 15 mL water. After a month standing, dark blue crystals were obtained from blue solution. The crystalline product was filtered off, washed with a small amount of water and dried in air. The yield was 60%. Anal. Calcd. for $C_{11}H_{19}Ag_2CuN_7$: C, 25.0%; H, 3.6%; N, 18.6%. Found C 25.0%; H, 3.8%; N, 18.1%. IR (KBr, cm^{-1}): $\nu(NH_2)$: 3436 (s), 3286 (s), 3234 (s), 3158 (s); ν(CN): 2178 (sh), 2164 (s), 2133 (s); μ_{eff}(RT): 1.85 BM.

2. 2. X-ray Structure Analysis

Diffraction data for the studied compound was collected on a Stoe IPDS 2 diffractometer at 173(2) K using graphite monochromated Mo$K\alpha$ radiation. The structure was solved by direct methods using the program SHELXS97[11] and refined by full matrix least squares on F^2 with SHELXL97.[11] The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL97 default parameters. All non-hydrogen atoms were refined anisotropically. A semi-empirical absorption correction was applied using MULscanABS.[12] The resulting crystal data and details concerning data collection and refinement are quoted in Table 1. The crystallographic data for the studied compound have also been deposited with the Cambridge Crystallographic Data Centre as supplementary material with the deposition number: CCDC 682944. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/.

3. Results and Discussion

The structure of the new compound contains $[Cu(medpt)]^{2+}$ units being bridged by $[Ag(CN)_2]^-$ units resulting in chains of composition $[-\mu$–CN–Cu(medpt) $-\mu$–NC–Ag–$]_n$ and dicyanoargentate anions. Ag...Ag interactions link the $[Ag(CN)_2]^-$ units to the chain (Fig. 1). The Ag(I) atom from the chain is coordinated by two cyanide ligands, both of them bridge in an AgC_2 arrangement. The copper(II) atom is pentacoordinated by two cyanide-nitrogen and three medpt – nitrogen atoms in a distorted square-pyramidal arrangement. Three nitrogen atoms from the medpt ligand and one nitrogen atom from cyano bridge form the basal plane of the square pyramid while the nitrogen from the second cyano bridge occupies the axial position. The in-plane Cu–N bond lengths range from 2.005(5) to 2.095(6) Å, the axial Cu–N bond distance is significantly longer with 2.167(5) Å. The value of the τ parameter (0.14) confirms the square-pyramidal shape of the coordination polyhedron (ideal τ value for the square-pyramidal coordination sphere is 0 and for the trigonal bipyramidal coordination sphere 1).[13] The μ-cyano groups act as bridging ligands between the Cu(II) and Ag(I) centers in Ag–C≡N–Cu linkages. The bridging cyanides coordinate to the copper ions in a bent fashion with C–N–Cu bond angles of 172.9(5) and 167.5(5)°. Similar short Ag...Ag (argentophilic) interactions [3.1403(7) Å in this compound] are observed in other silver-containing compounds reported in the literature. As example can be mentioned $Cu(pn)_2Ag_2CN_4$ (pn = 1,2-diaminopropane) in which the corresponding Ag...Ag distance is 3.2614(2) Å.[6]

In the IR spectrum, characteristic vibrations ν(C≡N) were assigned. The presence of the cyano bridge is shown by the splitting ν(C≡N) stretching band which appears at about 2000–2200 cm^{-1} for cyano complexes.[14] According to the literature, the formation of the cyano bridge shifts the ν(C≡N) towards higher frequencies (Nakamoto, 1978).[15] In the present complex the strong bands at 2178 and 2164 cm^{-1} may be attributed to ν(C≡N) of the bridging cyanides; the other is due to the terminal one.

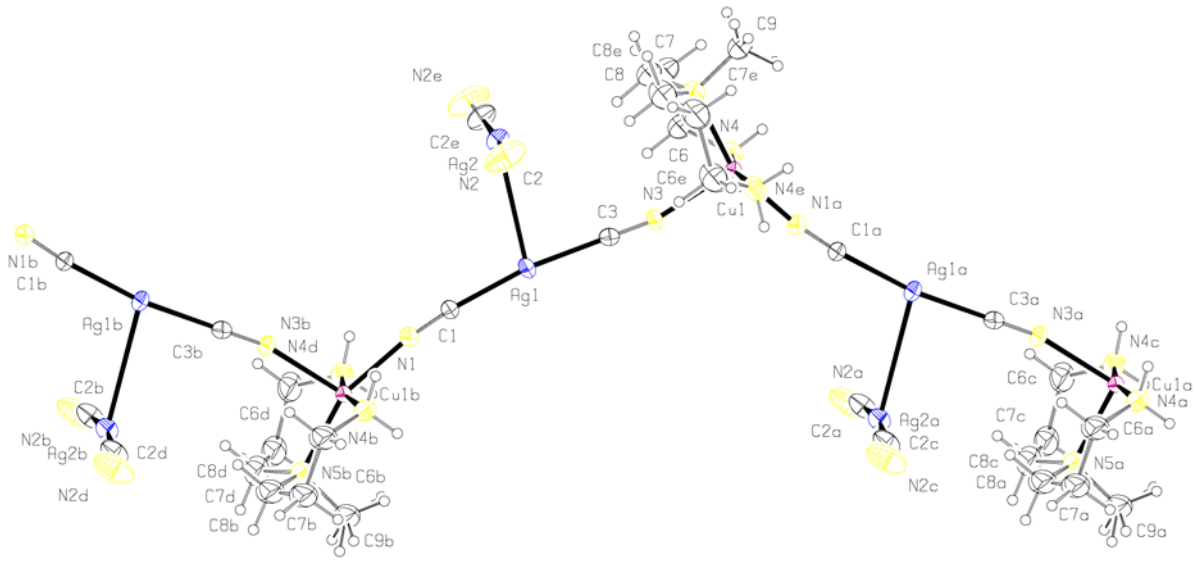

Figure 1. A view of polymeric chain structure of $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ with the atom – labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 1. Crystal data, data collection and structure refinement for $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$.

Formula	$C_{11}H_{19}Ag_2CuN_7$
M_r	528.61
Crystal system	orthorhombic
Space group	*Pnma*
a (Å)	18.1439(10)
b (Å)	13.0614(8)
c (Å)	7.4594(5)
Z	4
R_{int}	0.0640
Independ. refl.	1742
Observed refl.	1525
Refinement on	F^2
Final *R* and R_w	0.036, 0.094
Contribut. refl.	1742
Parameters	89
$\Delta\rho_{max,min}$ (e Å^{-3})	0.94, –1.05

Table 2. Selected bond distances (Å) and angles (°) for $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$

C1-N1	1.146(7)	Ag2-C2^{i}	2.039(7)
C1-Ag1	2.042(6)	Cu1-N4	2.005(5)
C2-N2	1.114(8)	Cu1-N4^{i}	2.005(5)
C2-Ag2	2.039(7)	Cu1-N1^{ii}	2.020(5)
C3-N3	1.134(8)	Cu1-N5	2.095(6)
C3-Ag1	2.049(6)	Cu1-N3	2.167(5)
C1-Ag1-C3	172.0(2)	N4^{i}-Cu1-N5	93.62(13)
C2^{i}-Ag2-C2	171.4(3)	N1^{ii}-Cu1-N5	158.4(2)
N4-Cu1-N4^{i}	166.6(2)	N4-Cu1-N3	95.23(12)
N4-Cu1-N1^{ii}	84.56(12)	N4^{i}-Cu1-N3	95.23(12)
N4^{i}-Cu1-N1^{ii}	84.56(12)	N1^{ii}-Cu1-N3	106.1(2)
N4-Cu1-N5	93.62(13)	N5-Cu1-N3	95.6(2)

i: x, –y+1/2, z, ii: x–1/2, y, –z+1/2

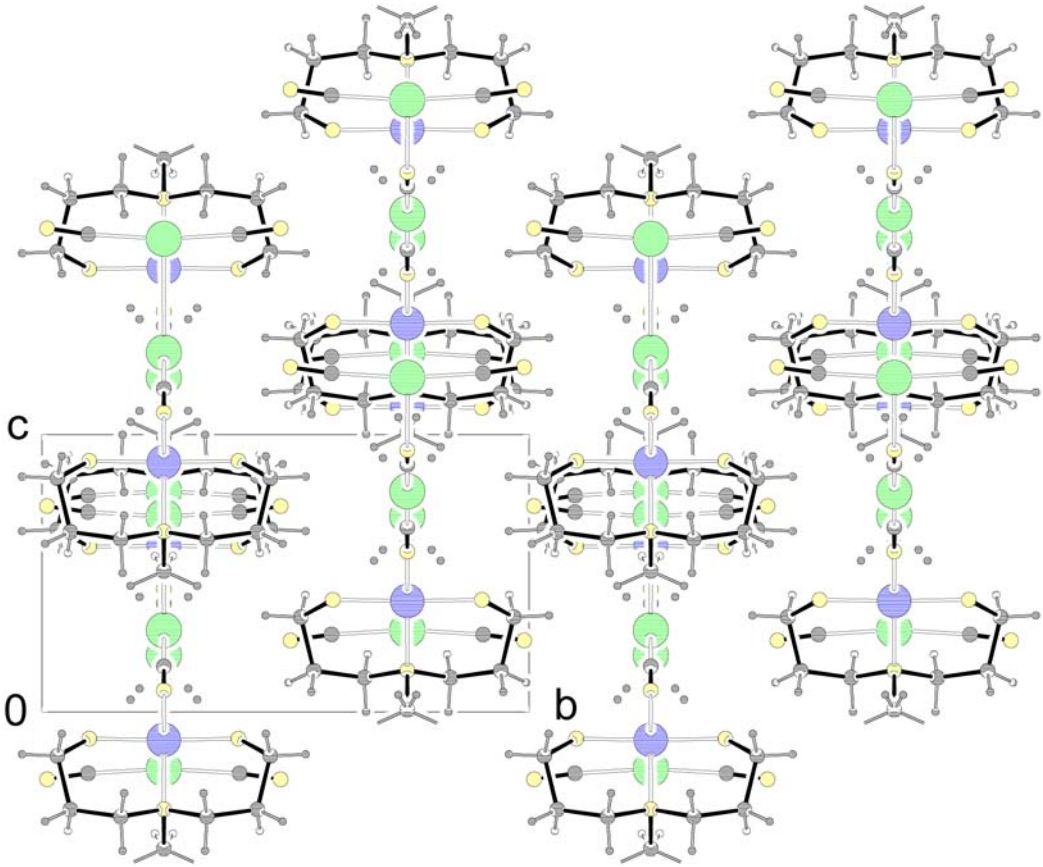

Figure 2. Packing diagram of $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ viewed down the *a* axis.

Because of the diamagnetism of dicyanoargentate anion, the paramagnetism of the studied coumpond is caused only by copper(II) (S = 1/2). The observed value of the magnetic moment at room temperature (μ_{eff} = 1.85 μ_B) corresponds to the literature data for magnetically diluted copper(II) compounds.[16]

4. References

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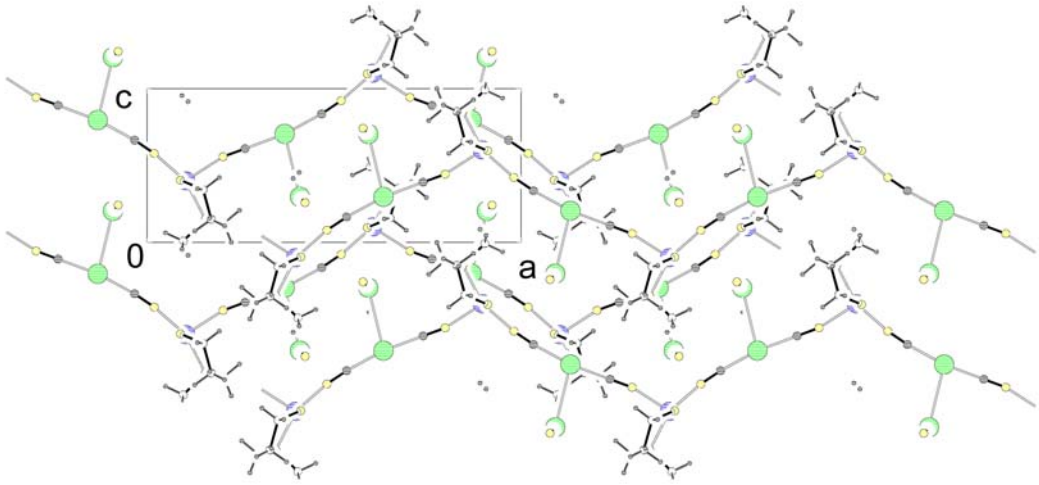

Figure 3. Packing diagram of $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ viewed down the *b* axis.

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Povzetek

Z reakcijo $Cu(ClO_4)_2 \cdot 6H_2O$, medpt (medpt = *N,N*-bis-(3-aminopropil)metilamin) in $K[Ag(CN)_2]$ smo pripravili novo spojino $\{[Cu(medpt)][Ag(CN)_2]_2\}_n$ in jo karakterizirali z IR spektroskopijo, magnetnimi meritvami in rentgensko strukturno analizo. V strukturi so $[Cu(medpt)]^{2+}$ kationi povezani z $[Ag(CN)_2]^-$ anioni v verige, in prosti dicianoargentni anioni. Ag…Ag interakcije povezujejo proste $[Ag(CN)_2]^-$ anione v drugo verigo. Bakrov(II) atom s koordinacijskim številom pet je koordiniran z dvema cianidnima dušikovima atomoma in tremi medpt-dušikovi atomi v popačeni kvadratni piramidi.