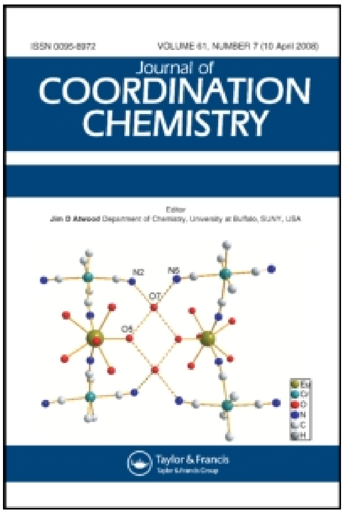

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A novel, wave-like, two-dimensional anionic host with Cationic and neutral guests: crystal structure of $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$

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A NOVEL, WAVE-LIKE, TWO-DIMENSIONAL ANIONIC HOST WITH CATIONIC AND NEUTRAL GUESTS: CRYSTAL STRUCTURE OF $[C_6H_{11}NH_3][Cu_2(CN)_3]\cdot 2C_6H_5NH_2$

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A novel inclusion compound, $[C_6H_{11}NH_3][Cu_2(CN)_3]\cdot 2C_6H_5NH_2$, has been synthesized and structurally characterized by X-ray crystallographic methods. It crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.839(1)$, $b = 18.894(2)$, $c = 14.080(3)$ Å, $\beta = 93.76(1)°$, $V = 2346.5(7)$ Å^3, $Z = 4$. The structure is composed of the anionic layered two-dimensional host $[Cu_2(CN)_3]^-$ and the cationic onium guest $[C_6H_{11}NH_3]^+$ and neutral guests, $C_6H_5NH_2$. Each Cu(I) atom is bonded to three cyanide ligands and exhibits trigonal coordination. Cu(I)–CN–Cu(I) bridges from puckered hexagons with all edges shared. The cyclohexylammonium and aniline guests are situated between host layer sheets. The cyclohexylammonium ion has a chair conformation and lies perpendicular to the host layer. The aniline molecules are arranged perpendicular and inclined at approximately 45° to the host layer, respectively. Both guest molecules are held together by a network of hydrogen bonds.

Keywords: Cyanocuprate(I) complex; Crystal structure; Cyclohexylamine; Aniline; Hydrogen bonding

INTRODUCTION

Organic–inorganic hybrid supramolecular architectures in crystal engineering has great interest for scientists in different areas such as chemistry, solid-state physics and biology, because of their applications in material science, catalysis and metallobiochemistry [1–4]. For designing organic–inorganic hybrid supramolecular frameworks, we [5–10] and others [11,12] have used various pseudohalide ions, such as CN^-, SCN^-, N_3^-, OCN^-, $SeCN^-$ and CNO^-, and complementary ligands such as NH_3, H_2O, unidentate aliphatic and aromatic amines, ambidentate α,ω-diaminoalkanes, etc. Among them, polycyanopolycuprate(I) $[Cu_x(CN)_y]^{x-y}$ ions give various

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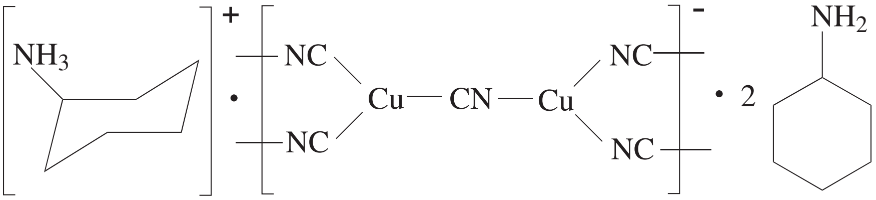

FIGURE 1 Structural diagram of $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$.

multidimensional structures, containing discrete anions $[Cu(CN)_3]^{2-}$ [13] and $[Cu(CN)_4]^{3-}$ [14], one-dimensional chains $[Cu(CN)_2]^-$ [15], two-dimensional networks $[Cu_2(CN)_3]^-$ [16], and three-dimensional frameworks $[Cd(CN)_2]^-$ [17] and $[Cu_4(CN)_7]^{3-}$ [18], etc. On the other hand, introduction of complementary ligands into the cadmium host structure gives rise to the change of $[Cu(CN)_2]_n$ framework [11]. The cyclohexylamine ligand appears to play two roles in building up the host framework $[Cd_3(CN)_6(C_6H_{11}NH_2)_2]_n \cdot nC_6H_5CH_3$ [5]: one is to occupy the channel space and the other is to block a coordination site of a Cd atom. Therefore, suitable combinations of central metal ions, complementary ligands, and guest molecules lead to a variety of pseudohalidemetallate frameworks. However, supramolecular structures with a cyclic amine as a complementary ligand have not yet been explored in detail in comparison with aliphatic or aromatic amines.

As an extension of the study, we have introduced a copper ion as a central metal and cyclohexylamine as a complementary ligand in order to develop a novel organic–inorganic hybrid supramolecular structure. We report here the preparation and crystal structure of the two-dimensional copper(I) complex, $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$, with a cyclohexylamine group as shown in Fig. 1.

EXPERIMENTAL

Synthesis and Analysis of $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$

$CuCl_2 \cdot 2.5H_2O$ (1.7 g, 10 mmol) and KCN (2.94 g, 10 mmol) were dissolved in 30 cm^3 of water. Cyclohexylamine (2.5 cm^3, 20 mmol) was added to the solution, dropwise with stirring. The pH of the solution was adjusted to 9 by adding 2-aminoethanol and citric acid. A small amount of white precipitate was filtered off and *ca* 5 cm^3 of aniline added. The resulting solution was allowed to stand in a refrigerator at 5°C. After a few weeks, dark-blue, plate-like crystals were obtained.

IR spectra were recorded on a BioRad Digilab FTS-165 infrared spectrophotometer using KBr wafers. The strong peak at 2150 cm^{-1} was assigned to CN stretching. Cyclohexylamine and aniline were assigned by relevant IR absorption bands [19]. Carbon, hydrogen and nitrogen were determined by a CE EA-1110 instrument. Cu was determined using a Jobin-Yvon Ultima-C inductively coupled plasma emission spectrometer. The composition of the crystal was deduced from elemental analyses; the formula $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$ is consistent with the results of single-crystal X-ray diffraction analysis. Yield: *ca* 65%. Anal. Calcd. for $C_{21}H_{28}N_6Cu_2$(%): C, 51.07; H, 5.69; N, 17.12; Cu, 25.9. Found: C, 51.31; H, 5.74; N, 17.10; Cu, 25.85.

TABLE I Crystal data and structure refinement details for $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$

Empirical formula	$C_{21}H_{28}N_6Cu_2$
Formula weight	491.57
Temperature (K)	291(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.839(1)
b (Å)	18.894(3)
c (Å)	14.080(3)
β (°)	93.76(1)
V (Å^3)	2346.5(7)
Z	4
Density (calculated) (g cm^{-3})	1.391
μ(Mo Kα) (mm^{-1})	1.830
F(000)	1016
θ range for data collection (°)	1.8–26.5
Index range	$-1 \leq h \leq 11$, $-1 \leq k \leq 23$, $-17 \leq l \leq 17$
Reflections measured	6195
Independent reflections	4862 ($R_{int} = 0.0374$)
Data/restraints/parameters	4862/0/263
Goodness of fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0760$, $wR_2 = 0.1813$
Largest diff. peak and hole (eÅ^{-3})	0.363 and −0.393

X-ray Crystallography

A dark-blue plate was coated with epoxy glue in order to prevent liberation of guest molecules from the specimen under ambient conditions. The epoxy-coated crystal was mounted on an Bruker P4 four-circle X-ray diffractometer and intensity data were collected in the θ–2θ scan mode using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters and an orientation matrix for the compound were determined from a least-squares fit to 50 accurately centred reflections with θ between 2.15 and 13.04°. Three standard reflections were monitored every 97 reflections; no decay was observed through the data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the ψ-scans was applied [20].

All calculations were performed using the Bruker SHELXTL crystallographic software package [21]. Space group was assigned on the basis of systematic absences and intensity statistics and confirmed by the successful refinement. The structure was solved by direct methods [22] and successively refined by full-matrix least-squares methods followed by difference Fourier maps. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were placed in calculated positions with isotropic thermal parameters. Final difference electron density maps contained no significant features. Further details of crystallographic and experimental data are given in Table I.

RESULTS AND DISCUSSION

Atomic coordinates of non-hydrogen atoms and with equivalent thermal parameters are given in Table II. Selected bond lengths and angles for $[C_6H_{11}NH_3][Cu_2(CN)_3] \cdot 2C_6H_5NH_2$ are listed in Tables III. ORTEP drawings of the complex and the crystal packing are shown in Figs. 2 and 3, respectively.

TABLE II Atomic coordinates and equivalent thermal parameters for $[C_6H_{11}NH_3][Cu_2(CN)_3]\cdot 2C_6H_5NH_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}(Å^2)
Cu(1)	0.8553(1)	0.2177(1)	0.5243(1)	0.074(1)
Cu(2)	0.3738(1)	0.2157(1)	0.6827(1)	0.076(1)
C(1)	0.5516(7)	0.2047(4)	0.6169(5)	0.060(2)
N(1)	0.6648(8)	0.2073(4)	0.5810(5)	0.085(2)
C(2)	0.1737(7)	0.2056(4)	0.6309(5)	0.064(2)
N(2)	1.0510(8)	0.2076(4)	0.5980(4)	0.079(2)
C(3)	0.3855(8)	0.2405(5)	0.8125(5)	0.074(2)
N(3)	0.8764(7)	0.2426(5)	0.3904(6)	0.099(2)
N(10)	0.2698(11)	0.3098(4)	0.3201(7)	0.146(4)
C(11)	0.3547(11)	0.3456(4)	0.3878(7)	0.087(3)
C(12)	0.5030(11)	0.3639(5)	0.3780(6)	0.095(3)
C(13)	0.5891(11)	0.3941(6)	0.4491(8)	0.114(3)
C(14)	0.5275(13)	0.4081(6)	0.5339(8)	0.119(4)
C(15)	0.3839(14)	0.3900(7)	0.5474(8)	0.126(4)
C(16)	0.2958(11)	0.3593(6)	0.4771(9)	0.116(4)
N(20)	1.0745(13)	0.3383(7)	0.7793(9)	0.193(6)
C(21)	1.0689(11)	0.4028(7)	0.7387(8)	0.102(3)
C(22)	0.9733(13)	0.4151(8)	0.6565(9)	0.126(4)
C(23)	0.9577(13)	0.4784(10)	0.6202(9)	0.128(5)
C(24)	1.0338(18)	0.5332(8)	0.6630(12)	0.141(5)
C(25)	1.1326(17)	0.5232(10)	0.7419(12)	0.149(6)
C(26)	1.1424(12)	0.4599(10)	0.7794(10)	0.135(5)
N(30)	0.8390(11)	0.3224(4)	0.9133(5)	0.129(3)
C(31)	0.7321(11)	0.3877(5)	0.9124(6)	0.093(3)
C(32)	0.6652(10)	0.3994(5)	0.8157(6)	0.096(3)
C(33)	0.5685(11)	0.4661(7)	0.8123(7)	0.126(4)
C(34)	0.6485(14)	0.5278(6)	0.8551(8)	0.125(4)
C(35)	0.7264(11)	0.5155(6)	0.9495(7)	0.106(3)
C(36)	0.8131(12)	0.4481(5)	0.9531(6)	0.102(3)

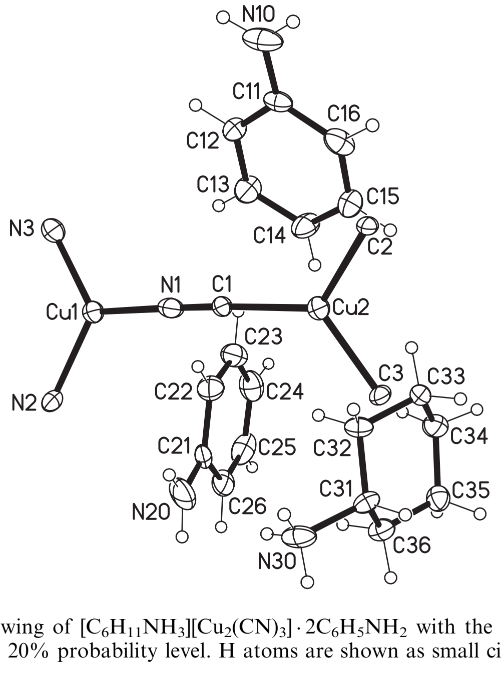

FIGURE 2 ORTEP drawing of $[C_6H_{11}NH_3][Cu_2(CN)_3]\cdot 2C_6H_5NH_2$ with the atom numbering. Thermal ellipsoids are drawn at the 20% probability level. H atoms are shown as small circles of arbitrary radius.

TABLE III Selected bond lengths (Å) and angles (°) for $[C_6H_{11}NH_3][Cu_2(CN)_3]\cdot 2C_6H_5NH_2$

Cu(1)–N(1)	1.919(7)	Cu(1)–N(2)	1.968(7)
Cu(1)–N(3)	1.964(8)	Cu(2)–C(1)	1.887(7)
Cu(2)–C(2)	1.878(7)	Cu(2)–C(3)	1.884(7)
C(1)–N(1)	1.152(8)	C(2)–N(2)^{i}	1.151(9)
C(3)–N(3)^{ii}	1.150(9)	N(10)–C(11)	1.36(1)
C(11)–C(12)	1.37(1)	C(12)–C(13)	1.34(1)
C(13)–C(14)	1.37(1)	C(14)–C(15)	1.34(1)
C(15)–C(16)	1.35(1)	C(16)–C(11)	1.42(1)
N(20)–C(21)	1.35(2)	C(21)–C(22)	1.41(1)
C(22)–C(23)	1.31(2)	C(23)–C(24)	1.35(2)
C(24)–C(25)	1.38(2)	C(25)–C(26)	1.31(2)
C(26)–C(21)	1.37(2)	N(30)–C(31)	1.55(1)
C(31)–C(32)	1.47(1)	C(32)–C(33)	1.52(1)
C(33)–C(34)	1.47(1)	C(34)–C(35)	1.48(1)
C(35)–C(36)	1.49(1)	C(36)–C(31)	1.45(1)
N(1)–Cu(1)–N(2)	122.4(2)	N(1)–Cu(1)–N(3)	124.4(3)
N(2)–Cu(1)–N(3)	113.2(3)	C(1)–Cu(2)–C(2)	126.3(3)
C(1)–Cu(2)–C(3)	120.6(3)	C(2)–Cu(2)–C(3)	113.1(3)
Cu(1)–N(1)–C(1)	176.3(7)	Cu(1)–N(2)–C(2)^{iii}	171.0(6)
Cu(1)–N(3)–C(3)^{iv}	177.3(8)	Cu(2)–C(1)–N(1)	170.6(7)
Cu(2)–C(2)–N(2)^{i}	172.3(8)	Cu(2)–C(3)–N(3)^{ii}	172.7(7)
N(10)–C(11)–C(12)	123.0(1)	N(10)–C(11)–C(16)	120.0(1)
C(11)–C(12)–C(13)	122.0(9)	C(12)–C(13)–C(14)	119.6(9)
C(13)–C(14)–C(15)	121.0(1)	C(14)–C(15)–C(16)	121.0(1)
C(15)–C(16)–C(11)	120.1(9)	C(16)–C(11)–C(12)	116.9(9)
N(20)–C(21)–C(22)	120.0(1)	N(20)–C(21)–C(26)	122.0(1)
C(21)–C(22)–C(23)	121.0(1)	C(22)–C(23)–C(24)	119.0(3)
C(23)–C(24)–C(25)	122.0(2)	C(24)–C(25)–C(26)	118.0(2)
C(25)–C(26)–C(21)	123.0(2)	C(26)–C(21)–C(22)	117.0(1)
N(30)–C(31)–C(32)	109.6(8)	N(30)–C(31)–C(36)	109.8(8)
C(31)–C(32)–C(33)	110.3(8)	C(32)–C(33)–C(34)	112.9(8)
C(33)–C(34)–C(35)	115.0(1)	C(34)–C(35)–C(36)	112.0(9)
C(35)–C(36)–C(31)	115.0(9)	C(36)–C(31)–C(32)	114.0(8)

Symmetry transformations used to generate equivalent atoms: ${}^{i}x-1, y, z$; ${}^{ii}x-1/2, -y+1/2, z+1/2$; ${}^{iii}x+1, y, z$; ${}^{iv}x+1/2, -y+1/2, z-1/2$.

As shown in Fig. 2, the asymmetric unit consists of negatively charged $[Cu_2(CN)_3]^-$ ions, positively charged $[C_6H_{11}NH_3]^+$ ions and neutral $C_6H_5NH_2$ molecules in a 1 : 1 : 2 ratio. The Cu(I) atoms of the host anion are joined to three cyanide ligands and exhibit trigonal planar coordination. It is well known that copper(II) is easily reduced to copper(I) by cyanide in aqueous solution [23]. The Cu(1)–$\mathrm{N_{NC}}$ bond lengths range from 1.968(7) to 1.919(7) Å are slightly longer than the Cu(2)–$\mathrm{C_{CN}}$ bond lengths (1.887(7) to 1.878(7) Å). It is worth noting that the Cu–N bond length in cyano copper(I) complexes is usually greater by about 0.1 Å than that of the Cu–C bond [16]. Some variations in the Cu(1)–N–C and Cu(2)–C–N bond angles are not unusual. The cyclohexylamine guest molecule is protonated to neutralize the host anion. The cyclohexyl ring has a chair conformation. As listed in Table III, the bond lengths and angles relating to the cyclohexylammonium cation and neutral aniline guests are not unusual.

As shown in Fig. 3, the anionic host framework of the title compound has a two-dimensional polymeric structure containing Cu(I)–CN–Cu(I) bridges. Copper cyanide bridges are made up of puckered hexagons of composition $(CuCN)_6$, and all edges are shared. As for the topology of the host layer formed from $(CuCN)_6$ hexagons, $[Cu_2(CN)_3]^-$ gives a graphite structure with a wave-like conformation. The guest

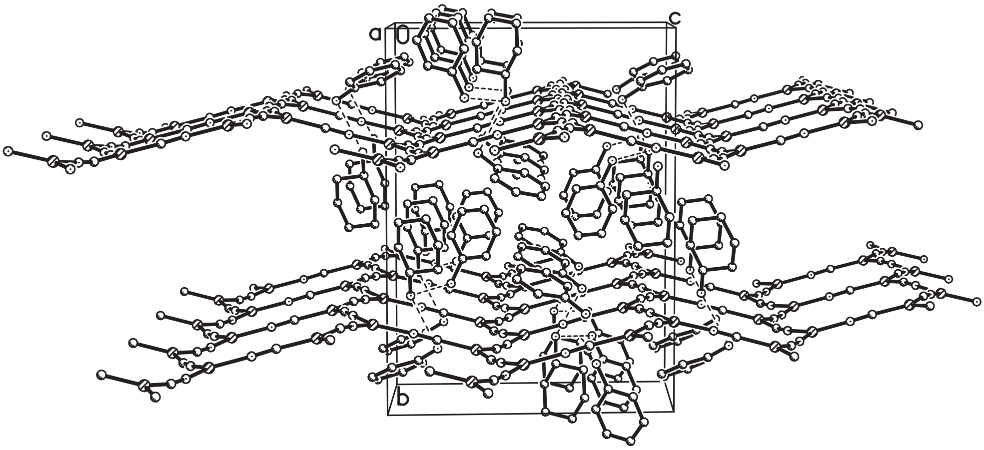

FIGURE 3 Perspective view of $[C_6H_{11}NH_3][Cu_2(CN)_3]\cdot 2C_6H_5NH_2$ along the *a* axis.

molecules are situated between the host layer sheets. Interactions between negatively charged host and positively charged guest may be electrostatic. The cyclohexylammonium ion is arranged perpendicular to the host layer. The aniline molecules are arranged both perpendicular and inclined approximately at 45° to the host layer. Both guest groups are linked together by a network of hydrogen bonds through $N^{-}_{\text{cyclohexylammonium}}-H\cdots N_{\text{aniline}}$; cyclohexylammonium hydrogen bonds with a neighboring aniline molecule in the same layer [N(30)–H(30a)···N(20) 2.92(2) Å, 155.0°] and with an aniline molecule in another layer [N(30)–H(30b)···N(10) 2.87(1) Å, 157.4°]. The crystal structure is stabilized by these hydrogen-bonding interactions involving guest molecules.

Acknowledgments

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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