Novel Negatively Charged Cyanocuprate(I) Host [Cu$_4$(CN)$_7$]$^{3-}$ Built of Tetrahedral Cu(I) Coordination Centers: Crystal Structure of [{NH$_2$(CH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NH$_2$}$_2$H][Cu$_4$(CN)$_7$]

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Abstract. The title inclusion compound [{NH$_2$(CH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NH$_2$}$_2$H][Cu$_4$(CN)$_7$] was obtained as single crystals from an aqueous solution containing CuCN, KCN, and *N*-(2-aminoethyl)piperazine. It crystallizes in the monoclinic space group $P2/n$, $a = 12.3829(9)$, $b = 8.5970(9)$, $c = 12.6633(7)$ Å, $\beta = 109.984(5)°$, $z = 2$, $R = 0.035$ for 2921 independent reflections. The inclusion structure is composed of the hydrogen-bonded dimeric onium guest [{NH$_2$(CH$_2$CH$_2$)$_2$NCH$_2$CH$_2$NH$_2$}$_2$H]$^{3+}$ and the negatively-charged three-dimensional host [Cu$_4$(CN)$_7$]$^{3-}$ in which the CN-bridged framework Cu(I) atoms are all tetrahedral. A polyacene-like one-dimensional array of hexagons cornered by Cu(I) atoms and edged by —CN— linkages is arrayed in parallel to the b axis and stacked approximately along the c axis. The Cu(I) corner shared in the one-dimensional array extends an N-coordinate CN group along the c axis to a pair of unshared Cu(I) corners for which the C end behaves as a bifurcated ligand to build up the three-dimensional host structure. The cavity is composed of two networks of the hexagons at the top and bottom and pillared by six >CN– groups and accommodates a dimeric guest of *N*-(2-aminoethyl)piperazinium cations protonated at each 4-N with the cations being hydrogen-bonded to each other through the 2-NH$_2$ groups sharing another H$^+$.

Key words. Cyanocuprate(I) complex, crystal structure, three-dimensional framework, bifurcated cyano group, *N*-(2-aminoethyl)piperazine, hydrogen-bond, dimeric onium guest.

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1. Introduction

We have been developing multi-dimensional cyanometallate host structures constructed of tetracyanonickelate(II) [1,2], tetracyanocadmate(II) [1,3,4], tetracyanocuprate(I) [5], or dicyanoargentate(I) [6] etc. moieties as building blocks. Among them, polycyanopolycadmates(II) $[Cd_x(CN)_y]^{2x-y}$ involving not only tetrahedral but also octahedral and/or trigonal-bipyramidal Cd atoms give a variety of multidimensional host structures with different compositions: cristobalite- and tridymite-like $[Cd(CN)_2]$, zeolite-like $[Cd_3(CN)_7]^-$, etc. [1, 3]. Cyanocuprates(I) $[Cu_x(CN)_y]^{x-y}$ of different composition also give various multidimensional structures other than the discrete anions $[Cu(CN)_3]^{2-}$ [7] and $[Cu(CN)_4]^{3-}$ [8]: a one-dimensional chain of $[Cu(CN)_2]^-$ [9], a two-dimensional network of $[Cu_2(CN)_3]^-$ [10], a three-dimensional framework of $[Cu(CN)_2]^-$ [11], etc. The coordination structure of Cu(I) is tetrahedral in the discrete $[Cu(CN)_4]^{3-}$ and in the three-dimensional $[Cu(CN)_2]^-$ anions but trigonal in the others. Four inclusion structures have been reported for the cyanocuprate(I) complexes: $[NBu_4][Cu(CN)_2]$ [12], $[\kappa$-(BEDT-TTF)$_2][Cu_2(CN)_3]$ [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene] [13], $[Me_2SPh][Cu_2(CN)_3]$ [14], and $[(BzV)_3 \cdot H_2O][Cu_9(CN)_{15}]$ (BzV = 1,1'-dibenzyl-4,4'-bipyridinium) [15], the last having a complicated three-dimensional lattice involving tetrahedral and trigonal Cu(I) atoms in a 1 : 2 ratio.

We examined the preparation of zeolite-like three-dimensional host structures built of polycyanopolycuprate(I) similar to those of $[Cd_3(CN)_7]^-$ hosts along with N-(2-aminoethyl)piperazine (aepipz) as the source of the onium cations to neutralize the negative charge of the host moieties. The inclusion structure of $[(aepipzH)_2H][Cu_4(CN)_7]$, the product eventually obtained, reported in this paper is comprised of a negatively charged three-dimensional host of $[Cu_4(CN)_7]^{3-}$ and a hydrogen-bonded dimer of protonated aepipzH$^+$ cations combined with another H$^+$.

2. Experimental

2.1. PREPARATION

0.45 g of CuCN, 0.98 g of KCN, and 0.65 g of N-(2-aminoethyl)piperazine (aepipz) were dissolved in 100 mL of H$_2$O. The pH of the solution was adjusted to ca. 9 by adding an appropriate amount of citric acid. The solution was allowed to stand in a refrigerator at ca. 5°C for a few weeks, when colorless plate-like crystals were obtained. *Anal. Found*: C, 32.4; H, 4.76; N, 26.1%. *Calcd.* for $C_{19}H_{33}Cu_4N_{13}$: C, 32.7; H, 4.77; N, 26.1%.

No crystals of inclusion compounds accommodating neutral guests were obtained, although guests such as C_6H_6, PhMe, CCl$_4$, CH$_2$Cl$_2$, MeCN, MeOH, and EtOH were examined.

2.2. X-RAY CRYSTALLOGRAPHY

A single crystal with dimensions of $0.40 \times 0.22 \times 0.18$ mm^3 was subjected to intensity data collection on a Rigaku AFC-7R automated four-circle diffractometer by 2θ–ω scan technique. The cell dimensions were refined using 25 reflections in $34.68 \leq 2\theta \leq 39.36°$. The crystal data are: $C_{19}H_{33}Cu_4N_{13}$, $M = 697.74$, monoclinic, $P2/n$ (No. 13), $a = 12.3829(9)$, $b = 8.5970(9)$, $c = 12.6633(7)$ Å, $\beta = 109.984(5)°$, $U = 1266.9(2)$ Å^3, $Z = 2$, $D_m = 1.837$ (flotation method in bromoform/toluene), $D_x = 1.829$ g cm^{-3}, $\mu(MoK_\alpha) = 3.349$ mm^{-1}. The $(0k0)$ reflections are rather weak for k odd, but significantly observed. The resolved structure has the pseudo-2_1 screw parallel to the b axis, except for C(1), N(1) and CN(5) atoms. Three standard reflections were monitored after every 150; no remarkable decay was observed. Corrections were made for Lp, absorption, and extinction.

Cu atoms were located from Patterson synthesis using SHELXS86 [16]. The successive Fourier and Fourier-difference syntheses using SHELXL93 [17] revealed all atoms. At the preliminary stage of the structure refinement all the atoms of the CN groups were seen with a 50% probability of C and N. Judging from the difference in the displacement parameters, discrimination was then possible for the CN group with the bifurcated C(1) for Cu(1) similar to the case of CuCN·NH$_3$ [18], but impossible for that bridging between Cu(1) and Cu(2), although the C and N are crystallographically independent of each other. As for the CN group between Cu(2) and its equivalent, C and N were located on crystallographically equivalent positions. Non-H atoms were anisotropically and H atoms were isotropically refined through the full-matrix least-squares on F^2 using 2921 independent reflections among 3320 measured in the range of $4 < 2\theta < 55°$ for 232 parameters. The weighting scheme applied was: $w = 1/[\sigma^2(F_0^2) + (0.0311P)^2 + 1.0490P]$ where $P = (F_0^2 + 2F_c^2)/3$. Final values are: $(\Delta/\sigma)_{max} = 0.001$, $\Delta\rho_{max} = 0.433$, $\Delta\rho_{min} = -0.548$ eÅ^{-3}, $R = 0.0271$ and $wR(F^2) = 0.0673$ for 2502 observed reflections with $F_0^2 > 2\sigma(F_0^2)$, and $R = 0.0353$ and $wR(F_0^2) = 0.0713$ for all independent ones. Atomic scattering factors including those for real and imaginary anomalous dispersion corrections were taken from ref. 19.

3. Results and Discussion

The atomic coordinates with the equivalent isotropic displacement parameters are listed in Table I; selected interatomic distances and angles are in Table II; ORTEP [20] views of the structure are shown in Figure 1.

As shown in Figure 1(a), the $[Cu_4(CN)_7]^{3-}$ host involves two crystallographically independent Cu atoms and two kinds of CN groups which differ in their bridging behaviour. The CN linkages among the Cu atoms form a polyacene-like one-dimensional extension of condensed hexagons parallel to the ab plane; Cu(1) is at the unshared corner and Cu(2) at the shared corner of the hexagon in the condensed structure. The one-dimensional belts with the hexagonal network form

Table I. Atomic coordinates and equivalent isotropic displacement parameters.

Atom	x/a	y/b	z/c	$U_{eq}/Å^2$ [a]
Cu(1)	0.14800(2)	0.20491(3)	0.25965(3)	0.03189(10)
Cu(2)	0.40627(3)	0.29567(4)	0.66208(3)	0.03461(11)
C(1)	0.2824(2)	0.2323(3)	0.3996(2)	0.0289(5)
N(1)	0.3353(2)	0.2523(2)	0.4929(2)	0.0321(4)
CN(1) [b]	0.0719(2)	0.0020(3)	0.2355(2)	0.0320(4)
CN(2) [b]	0.0227(2)	−0.1143(2)	0.2166(2)	0.0276(4)
CN(3) [b]	0.4999(2)	0.4914(2)	0.6884(2)	0.0291(4)
CN(4) [b]	0.5529(2)	0.6036(2)	0.7141(2)	0.0287(4)
CN(5) [b]	0.2853(2)	0.2916(3)	0.7298(2)	0.0325(5)
N(11)	0.8127(2)	0.2333(2)	0.4756(2)	0.0260(4)
C(12)	0.7004(2)	0.1645(3)	0.4171(2)	0.0349(5)
C(13)	0.6348(2)	0.1403(3)	0.4961(2)	0.0384(6)
N(14)	0.6207(2)	0.2932(3)	0.5453(2)	0.0328(4)
C(15)	0.7347(2)	0.3635(3)	0.6057(2)	0.0336(5)
C(16)	0.7990(3)	0.3827(3)	0.5247(2)	0.0380(6)
C(17)	0.8803(2)	0.2521(3)	0.4017(2)	0.0359(5)
C(18)	1.0072(2)	0.2660(3)	0.4700(3)	0.0423(6)
N(19)	1.0419(2)	0.1354(3)	0.5492(2)	0.0489(6)

[a] $U_{eq} = (1/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

[b] Refined with a 50% probability each of C and N.

a layer along the ab plane, and the layer is stacked perpendicular to the c axis. The CN group parallel to the c axis links the one-dimensional belts on the same layer by the bifurcated coordination at C(1) to two Cu(1) and pillars the stacked layers by coordination at N(1) to Cu(2), i.e., the CN group has the linkage mode [Cu(1)]$_2$ >C(1)–N(1)–Cu(2) [Figure 1(c)].

The stacking of the layers pillared by the bifurcated-CN affords interlayer space for the guest aepipz which is protonated at 4-N. A pair of the aepipzH$^+$ cations are accommodated as a hydrogen-bonded dimer in the cavity enclosed by two hexagonal networks of the one-dimensional belt at the top and the bottom and pillared by six bifurcated-CN groups. The hydrogen bond is formed between N(19) and its equivalent, N(19′), the amino groups of the 2-aminoethyl branches, intervened with an H$^+$: N(19)···N(19′), 2.677(5) Å; N(19)–H(193), 0.87(5) Å; N(19)···H(193′), 1.82(5) Å; N(19)–H(193)···N(19′) = 166(7)°. H(193) is distributed across the inversion center (0, 0, 1/2); it refined as a 50% occupancy. The configuration of the piperazine ring is the chair form and that of the aminoethyl skeleton is gauche. Consequently the N(19)···N(11) distance of 2.797(3) Å and the N(19)–H(191)···N(11) angle is 105(4)°, the angle being unacceptable for hydrogen bond formation. N(14) and N(19) are rather close to some cyanide groups:

Table II. Interatomic distances (Å) and angles (°).

Distance	Å	Distance	Å	Distance	Å
Cu(1)–C(1)	1.988(2)	C(1)–N(1)	1.151(3)	C(13)–N(14)	1.490(3)
Cu(1)–CN(1)	1.957(2)	CN(1)–CN(2)	1.153(3)	N(14)–C(15)	1.486(3)
Cu(1)–CN(4)^{i}	1.992(2)	CN(3)–CN(4)	1.149(3)	C(15)–C(16)	1.508(3)
Cu(1)–C(1)^{ii}	2.460(2)	CN(5)–CN(5)^{iv}	1.155(4)	C(17)–C(18)	1.517(4)
Cu(2)–N(1)	2.053(2)	N(11)–C(12)	1.458(3)	C(18)–N(19)	1.469(4)
Cu(2)–CN(2)^{iii}	2.075(2)	N(11)–C(16)	1.462(3)	N(11)...N(19)	2.797(3)
Cu(2)–CN(3)	2.006(2)	N(11)–C(17)	1.462(3)	N(19)...N(19)^{v}	2.677(5)
Cu(2)–CN(5)	1.964(2)	C(12)–C(13)	1.504(4)	Cu(1)...Cu(1)^{ii}	2.6196(6)

Angle	°	Angle	°
C(1)–Cu(1)–CN(1)	117.18(9)	Cu(1)–C(1)–Cu(1)^{ii}	71.26(7)
C(1)–Cu(1)–CN(4)^{i}	113.11(9)	Cu(2)–N(1)–C(1)	171.3(2)
C(1)–Cu(1)–C(1)^{ii}	107.37(7)	Cu(2)^{vi}–CN(2)–CN(1)	168.2(2)
CN(1)–Cu(1)–CN(4)^{i}	119.10(8)	Cu(2)–CN(3)–CN(4)	173.2(2)
CN(1)–Cu(1)–C(1)^{ii}	104.00(8)	Cu(2)–CN(5)–CN(5)^{iv}	178.90(12)
CN(4)^{i}–Cu(1)–C(1)^{ii}	91.23(8)	C(12)–N(11)–C(16)	110.1(2)
N(1)–Cu(2)–CN(2)^{iii}	102.22(8)	C(12)–N(11)–C(17)	112.0(2)
N(1)–Cu(2)–CN(3)	110.06(9)	C(16)–N(11)–C(17)	110.5(2)
N(1)–Cu(2)–CN(5)	109.51(9)	N(11)–C(12)–C(13)	110.9(2)
CN(2)^{iii}–Cu(2)–CN(3)	106.18(8)	C(12)–C(13)–N(14)	108.9(2)
CN(2)^{iii}–Cu(2)–CN(5)	112.84(9)	C(13)–N(14)–C(15)	110.3(2)
CN(3)–Cu(2)–CN(5)	115.21(9)	N(14)–C(15)–C(16)	108.9(2)
Cu(1)–C(1)–N(1)	160.4(2)	N(11)–C(16)–C(15)	111.0(2)
Cu(1)–CN(1)–CN(2)	176.5(2)	N(11)–C(17)–C(18)	110.6(2)
Cu(1)^{vii}–CN(4)–CN(3)	178.7(2)	C(17)–C(18)–N(19)	109.4(2)
Cu(1)^{ii}–C(1)–N(1)	128.3(2)		

Symmetry codes: (i) $x - 1/2, -y + 1, z - 1/2$; (ii) $-x + 1/2, y, -z + 1/2$; (iii) $x + 1/2, -y, z + 1/2$; (iv) $-x + 1/2, y, -z + 3/2$; (v) $-x + 2, -y, -z + 1$; (vi) $x - 1/2, -y, z - 1/2$; (vii) $x + 1/2, -y + 1, z + 1/2$; (viii) $1 - x, -y, 1 - z$.
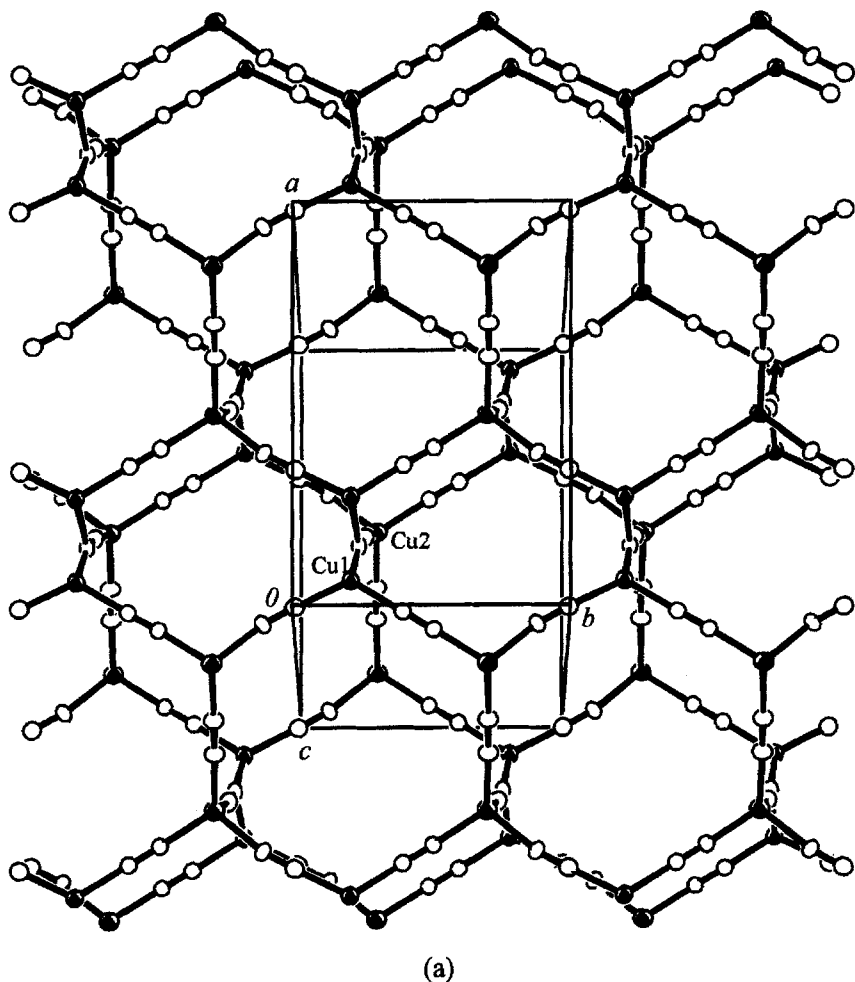
(a)

Fig 1a–c. The structure of $[(aepipzH)_2H][Cu_4(CN)_7]$. (a) Projection of the $[Cu_4(CN)_7]^{3-}$ host framework perpendicular to the ab plane. (b) The hydrogen-bonded dimeric cation $[(aepipzH)_2H]^{3+}$ in the cavity. (c) The coordination geometries about Cu centers involving the bifurcated-CN groups. Symmetry codes correspond with those of Table II.

$N(14)\cdots M(34)$, 3.325(3) Å, $H(141)\cdots M(34)$, 2.52(3) Å, $N(14)$–$H(141)\cdots M(34)$, 159(3)°, $N(19)\cdots M(55)$, 3.230(3) Å, $H(192)\cdots M(55)$, 2.66(4) Å, and $N(19)$–$H(192)\cdots M(55)$, 125(4)°, where $M(34)$ and $M(55)$ are the midpoints between $CN(3)$ and $CN(4)$, and between $CN(5)$ and its equivalent. The distances and angles may suggest electrostatic interactions between the positively-charged guest and the negatively-charged host.

As for the topology of the host, $[Cu_2(CN)_3]^-$ gives a graphite-like, two-dimensional network [10]. The increase of the number of CN groups per Cu atom from 1.5 for $[Cu_2(CN)_3]^-$ to 1.75 for $[Cu_4(CN)_7]^{3-}$ leads not only to the
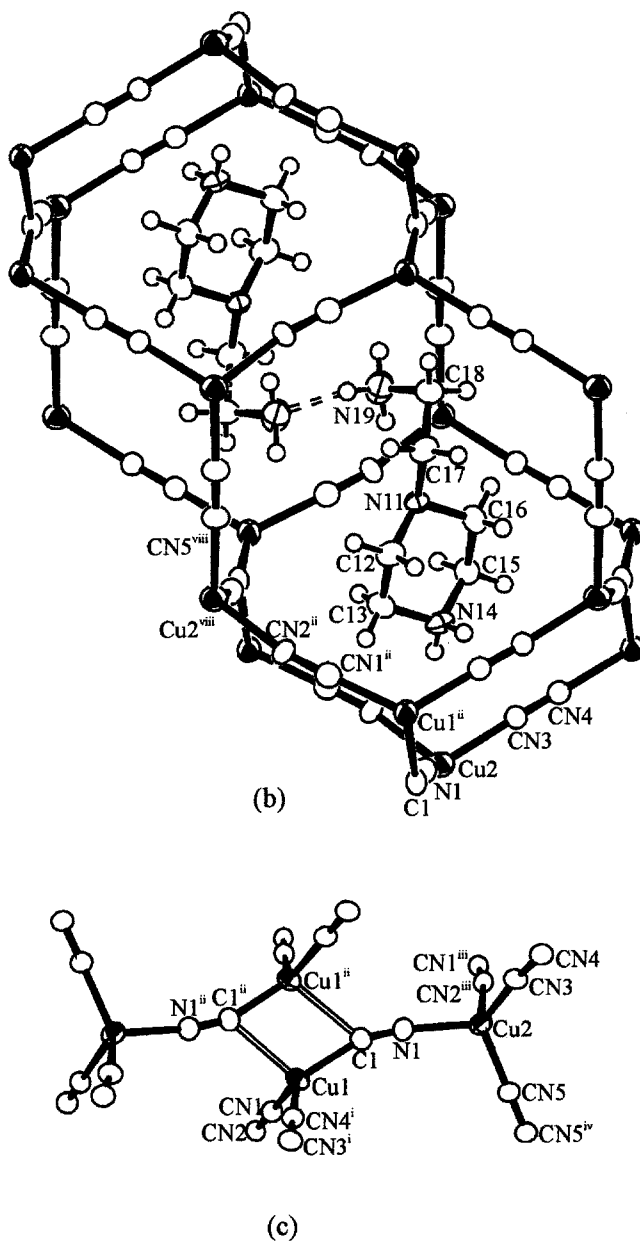
(b)

(c)

Fig 1b–c.

break up of the network into the array of the polyacene-like belts but also to the pillaring by the additional bifurcated-CN group. Accompanied by the change in the linkage structure the coordination environment about Cu(1) is much distorted from a regular tetrahedron similar to that of $[Me_2SPh][Cu_2(CN)_3]$ [14]. The Cu(1)–C(1) bond distance of 1.988(2) Å at one side of the bifurcated coordination is increased

to 2.460(2) Å at the other side with the remarkably narrow Cu(1)–C(1)–Cu(1′) angle of 71.26(7)°. These values are comparable with the values of 1.959(9) Å, 2.419(8) Å, and 73.8(3)° in [Me$_2$SPh][Cu$_2$(CN)$_3$] [14].

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