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Bifurcated Bridging Cyano Group and Network of Hydrogen-bonded Water Molecules in a Novel Framework Host Inclusion Compound Triaquacadmium(II) Tricyanocuprate(I)-Acetonitrile (1/1)

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The dimeric structure unit of $[Cu_2(CN)_6]^{4-}$ in the title inclusion compound involves two bifurcated CN groups respectively linked to two Cu(I) at the C and a Cd(II) at the N to form the framework host accommodating the CH_3CN whose orientation is regulated with the hydrogen bonds among the guest and the waters of coordination in the host.

Remarkable progresses have recently been made in constructing the multi-dimensional framework structures of polycyanopolycadmate systems based on the linear bridging behavior of CN groups between two coordination centers.[1,2] One of our recent strategies is to make Cu(I) join in the coordination center for materializing variegated heteropolycyanocadmate framework structures; an example, $[H_{31}O_{14}][CdCu_2(CN)_7]$,[3] has a pyrite-like framework of the six-coordinate Cd^{2+} and the pyrosilicate-like $[Cu_2(CN)_7]^{5-}$,interpenetrating into a three-dimensional assembly of hydrogen-bonded water molecules which assembly is built of doughnut-shaped twelve-O rings and of trifurcated O atoms among the rings. Another unprecedented structure has been demonstrated in the present acetonitrile inclusion compound $[Cd(H_2O)_3Cu(CN)_3]\cdot CH_3CN$ obtained by absorption of acetonitrile vapor into an aqueous solution containing CuCN and $K_2[Cd(CN)_4]$.[4] Its single crystal X-ray structure, and ^{113}Cd and ^{2}H NMR in solid state, revealed the structural features as follows: the host contains the terdentate CN behaving as a bifurcated head at the C for a couple of Cu atoms and a unidentate tail at the N for Cd; a layered framework is formed by the CN-linked metal complex host; the aqua ligands at the Cd form a network of hydrogen-bonded water molecules covering the surface of the layered framework; the guest CH_3CN molecule is undergoing a rapid exchange between two sites inside the cavity formed in the host framework.

As shown in Fig. 1a, the host has a layer structure.[5] The metal complex layer of the 9.48 Å thickness ($= c\sin\beta$) is built of two kinds of the CN-linkages among the tetrahedral Cu and the octahedral Cd. The layers are combined successively along the c axis by the hydrogen bonds among the waters of coordination at the Cd atoms.

A rhombus on the body-center of the $C2/m$ unit cell (Fig. 1b) is built of each pair of Cu and C2, where C2 behaves as a bifurcated head to the two tetrahedral Cu atoms related with each other by the site symmetry $2/m$. The bifurcated CN group is linked at the N tail(N2) to the Cd atom on the mirror plane at $b = 0.5$; the Cd is in a six coordination with the three O atoms of the aqua ligands at the

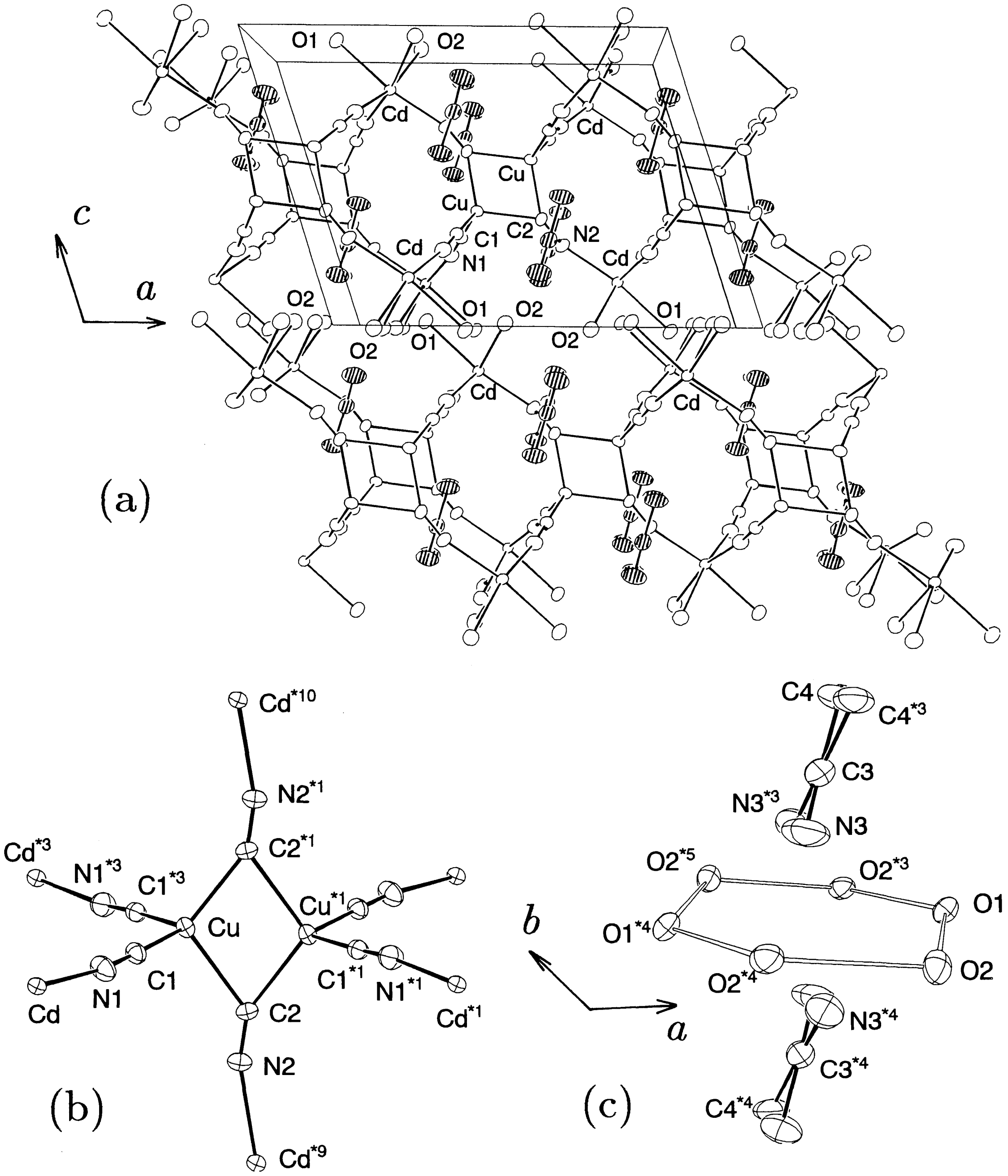

Fig. 1. The structure of $[Cd(H_2O)_3Cu(CN)_3]\cdot CH_3CN$. (a) View of the unit cell; the guest acetonitrile has been hatched. (b) The rhombus involved with each pair of bifurcated CN ligands and tetrahedral Cu coordinated with ambidentate CN ligands. Each of the CN ligands coordinates to an octahedral Cd at the N atom. The interatomic distances, d/Å, and angles, δ/°, are Cu–C1 1.944(6), Cu–C2 2.20(1), Cu–C2^{*1} 2.075(9), C1–N1 1.147(8), C2–N2 1.13(1), Cd–N1 2.236(6), Cd–N2 2.241(9), C1–Cu–C2 105.4(3), C1–Cu–C1^{*3} 114.5(3), C1^{*3}–Cu–C2^{*1} 111.8(3), C2–Cu–C2^{*1} 107.3(4), Cu–C2–Cu^{*1} 72.7(3). (c) The hexagonal network of the O atoms coordinating to octahedral Cd atoms and the guest CH_3CN molecule distributed between two sites. The interatomic distances, d/Å, and angles, δ/°, are O1···O2 3.035(6), O2···O2^{*4} 2.849(7), C3–N3 1.15(2), C3–C4 1.47(2), N3···O1 3.32(2), N3···O2 3.41(2), N3···O2^{*4} 3.06(2), N3···O1^{*4} 2.99(1), N3···O2^{*5} 3.71(3), N3···O2^{*3} 4.00(2), O2···O1···O2^{*3} 131.9(3), O1···O2···O2^{*4} 113.2(2).

facial positions, where the layer assembly by coordination bonding is terminated due to the unidentate character of the aqua ligand. The layer is extended along the *b* axis by the ambidentate CN linkages from the Cu to the Cd atoms on the mirror planes at $b = 0$ and 1, respectively. Eventually, the CdN_3O_3 six coordination is attained with the three O atoms of the aqua ligands, the two N atoms of the ambidentate CN bridges and the N of the bifurcated CN. As for orientational disorder of the bridging CN group sometimes occurring in multi-dimensional CN-linked structures,6) the ^{113}Cd CP/MAS NMR supported the CdN_3O_3 coordination from the single peak observed at 182 ppm;7) it means the tetrahedral Cu is in the C_4 coordination without any orientational disorder of the CN ligands. The bifurcated ketonic bridging is often seen for CO group of polynuclear metal carbonyls. However, the present bifurcated CN involves a third coordination center at the N like that found in $CuCN \cdot NH_3$.8)

All the O atoms of the aqua ligands of the Cd atoms are located within ± 0.16 Å from the *ab* plane. The trigons of the facial O atoms are interlocked to one another alternately from both sides of the *ab* plane in such an array that each one of O atoms of six trigons forms a hydrogen-bonded hexagon of the O atoms approximately on the *ab* plane. Eventually the network of the hydrogen-bonded O atoms is extended over the *ab* plane. For example, the hexagon O1-O2-O2^{*4}-O1^{*4}-O2^{*5}-O2^{*3}- is formed (Fig. 1c) by three each O atoms, O2, O2^{*3}, and O1^{*4}, from the framework above the *ab* plane and O1, O2^{*4}, and O2^{*5}, from that below the *ab* plane. The guest CH_3CN molecule is trapped between the bifurcated CN ligands, taking the molecular orientation that the N tail directs towards the center of the water hexagon; the atomic positions of the methyl-C(C4 and C4^{*3}) and nitrile-N (N3 and N3^{*4}) are in the disorder related to the mirror plane passing through C3, C3^{*4}, O1, and O1^{*4}. The powder pattern of the ^{2}H NMR observed for the CD_3CN-guest specimen supports that the molecular skeleton is undergoing a fast reorientation between the two sites separated by a 33–36° azimuthal angle and that the CD_3 group takes a fast rotation about the threefold axis at room temperature.9) The 2.99(1) Å distance between the nitrile-N(N3) and the O1^{*4} in the network suggests additional hydrogen-bond formation between the host and the guest. Since the similar inclusion compounds of acetone and methanol have been obtained, the hydrophilic interactions between the host and the guest appears to be a key for the formation of this type inclusion compounds.

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4) $K_2[Cd(CN)_4]$ (0.007 mol) and CuCN (0.014 mol) were dissolved in H_2O (100 cm^3) with vigorous stirring and gentle warming. The solution was filtered and allowed standing in a desiccator saturated with acetonitrile vapor at room temperature for a week. Colorless thin plates obtained gave the composition $C_5H_9N_4O_3CdCu$. Found:C, 16.1; H, 2.8; N, 15.1; Cd, 32.2; Cu, 18.6%. Calcd for

$C_5H_9N_4O_3CdCu$:C, 17.2; H, 2.6; N, 16.0; Cd, 32.2; Cu, 18.2%. The crystals are unstable under ambient conditions to liberate the guest rapidly. The composition is based on the results of crystal structure analysis. No significant decay was observed during the intensity data collection in the range $2\theta \leq 50°$ for the single crystal coated with epoxy resin; the occupancy factor of the guest atoms was practically 1 in the structure refinement.

5) Crystal data: $Cd(H_2O)_3Cu(CN)_3{\cdot}CH_3CN$, M = 349.11, monoclinic, space group $C2/m$ (No. 12), a = 13.601(3), b = 8.629(2), c = 9.958(3) Å, β = 107.90(2)°, U = 1112.0(4) $Å^3$, Z = 4, D_m = 2.06(4), D_x = 2.085 gcm^{-3}, μ(Mo Kα) = 38.7 cm^{-1}, $F(000)$ = 672, 1103 ($4° \leq 2\theta \leq 50°$) reflections measured for a crystal (0.30×0.20×0.07 mm) coated with epoxy resin on a Rigaku AFC-5 diffractometer at 298 K; $R = 0.031$, $Rw = 0.034$, and $GOF = 2.559$ in anisotropic refinement for all non-H atoms by the full-matrix least-squares procedures for absorption-corrected independent 927 reflections. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK CB2 1EZ.

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7) NMR data: a Chemagnetics CMX-300 spectrometer at 66.61 MHz, 5 μs ^{1}H 90° pulse, 5 ms contact time, 5 s recycle delay time, and 4 kHz spinning rate; $Cd(NO_3)_2{\cdot}4H_2O$ external standard for the chemical shift.

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9) NMR data: a Chemagnetics CMX-300 at 46.09 MHz, quadrupole echo pulse sequence$^{10)}$ with 2 μs 90° pulse width, 35 μs pulse spacing time, 10 s recycle delay time at 298 K. Observed line shape was a fast limit powder pattern whose QCC_{eff} and η_{eff} were 45.6 kHz and 0.1199, respectively. Line-shape simulation was carried out based on the fast limit theory$^{11)}$ using values of QCC_{eff} = 53.2 ± 0.4 kHz and $\eta = 0$ for the state where the CD_3 group is undergoing fast rotation about the CD_3CN molecular principal axis that has no motion.$^{12)}$

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