[CuCN·Me_3SnCN·$C_4H_4N_2$]: A Threefold-Interpenetrating, Distorted-Diamondoid Framework ($C_4H_4N_2$ = Pyrazine)

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Introduction

Both the uncharged 4,4′-bipyridine (bpy) molecule and the likewise rodlike, anionic $\{CN\text{-}Sn(R_3)\text{-}NC\}^-$ unit (R = alkyl) may act as a nanometer-sized spacer ligand in, inter alia, *diamondoid* Cu(I)-containing coordination polymers. Thus, in $[Cu(bpy)_2(PF_6)]$, **1**, four diamond-like ${}^{3}_{\infty}[Cu(\mu\text{-bpy})_2{}^{+}]$ frameworks interpenetrate each other,[1] while in $[(nBu_4N)(Et_3Sn)_2Cu(CN)_4]$ = $[CuCN\cdot 2Et_3SnCN\cdot(nBu_4N)CN]$, **2**, one single, but notably more distorted, diamondoid ${}^{3}_{\infty}[Cu\{\mu\text{-CNSn}(Et_3)\text{-NC}\}_2{}^{-}]$ framework is realized.[2] Although both **1** and **2** display comparable intraframe Cu···Cu separations slightly longer than 1 nm, we have not yet arrived at a likewise quasi-diamondoid, *mixed*-spacer system of the type ${}^{3}_{\infty}[Cu(\mu\text{-bpy})\{\mu\text{-CNSn}(R_3)\text{-NC}\}]$. Instead, reaction of bpy and Me_3SnCl with $K_3[Cu(CN)_4]$ has led to the significantly bpy-poorer assembly: $[CuCN\cdot Me_3SnCN\cdot 0.5bpy]$ = $[Cu(\mu_2\text{-bpy})_{0.5}\{\mu_3{:}\mu_2\text{-CNSn}(Me_3)NC\}]$, **3**, wherein one carbon atom of each $\{CNSn(Me_3)NC\}$ spacer interacts with a *pair* of copper ions.[3] On the other hand, reaction of bpy with Et_3SnCl and $K_3[Cu(CN)_4]$ has afforded the appropriately composed product $[CuCN\cdot Et_3SnCN\cdot bpy]$ = ${}^{2}_{\infty}[Cu(\mu\text{-bpy})\{\mu\text{-CNSn}(Et_3)NC\}]$, **4**, which, however, does not adopt a diamondoid structure.[4]

The notably shorter (than e.g. bpy) 2,5-dimethylpyrazine (2,5-Me_2pyz) spacer is capable of generating the simply 1-fold diamondoid compound $[Cu(2,5\text{-}Me_2pyz)_2(PF_6)]$,[5] although unmethylated pyrazine (pyz), 2,3-Me_2pyz, and even 2,5-Me_2pyz (pyz*) seem to favor two-dimensional, cationic ${}^{2}_{\infty}[Cu_2(\mu\text{-pyz*})_3{}^{2+}]$ frameworks with three-coordinate Cu(I).[1,5,6]

Mixed-ligand polymers of the type [[Cu(bpy)(pyz)X] (X = encapsulated counteranion) have, to the best of our knowledge, not been described. We report here the synthesis and the crystal structure of the related mixed-ligand system: $[CuCN\cdot Me_3SnCN\cdot pyz]$ = ${}^{3}_{\infty}[Cu(\mu\text{-pyz})\{\mu\text{-CNSn}(Me_3)NC\}]$, **5**, which, despite the very different lengths of its two spacer ligands pyz and $\{CNSn(Me_3)NC\}^-$, does adopt a distorted-diamondoid structural pattern.

Table 1. Crystallographic Data for [CuCN·Me_3SnCN·Pyz] (**5**)

empirical formula $C_9H_{13}N_4CuSn$	fw = 359.46
$a = 20.177(7)$ Å	$\lambda = 0.710\,73$ Å
$b = 6.381(2)$ Å	$D_{calc} = 1.804$ g cm^{-3}
$c = 11.071(3)$ Å	$\mu = 34.70$ cm^{-1}
$\beta = 111.80(2)°$	$R(F_o)^{a,b} = 0.0368$
$V = 1323.4(7)$ Å^3	$R_w(F_o{}^2)^{a,b} = 0.1045$
$Z = 4$	$R(F_o)^{a,c} = 0.0396$
space group $C2/c$ (No. 15)	$R_w(F_o{}^2)^{a,c} = 0.1077$
$T = 293(2)$ K	

[a] Structure was refined on $F_o{}^2$ using all data: $R(F_o{}^2) = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2]^{1/2}$ and $w^{-1} = [\sigma^2(F_o{}^2) + (0.1238P)^2 + 1.3191P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. $R(F_o)$ is given for comparison with older refinements based on F_o with a typical threshold of $F_o \geq 4\sigma(F_o)$ and $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $I > 2\sigma(I)$. [c] All data.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **5**

Cu1−C1	1.928(4)	Sn1−N1	2.341(4)
Cu1−N3(pyz)	2.167(3)	Sn1−C11	2.066(8)
C1−N1	1.139(5)	Sn1−C12	2.157(13)
		Sn1−C13	2.120(10)
C1−Cu1−C1′	125.7(2)	Sn1−N1−C1	174.8(4)
C1−Cu1−N3	103.11(13)	N1−Sn1−N1′	180.0(7)
C1−Cu1−N3′	111.4(2)	Cu1−C1−N1	176.4(4)
N3−Cu1−N3′	99.3(2)		

Experimental Section

Synthesis. Solutions of 380 mg (1.9 mmol) of Me_3SnCl in 10 mL of dioxane and of 50 mg (0.62 mmol) of pyrazine in 10 mL of dioxane were added together. The resulting solution was added slowly to a solution of 180 mg (0.63 mmol) of $K_3[Cu(CN)_4]$ in 10 mL of H_2O. After 3−4 h, orange-yellow crystals started growing from the initially clear solution. Final yield after washing with cold H_2O and drying in vacuo: 117 mg (66.6% referred to $K_3[Cu(CN)_4]$), decomp above 160 °C (pyrazine sublimes off; liquid residue at 210 °C). Anal. Calcd (found) for $C_9H_{13}N_4CuSn$: C, 30.07 (30.09); H, 3.64 (3.79); N, 15.59 (15.60).

Characterization. Powders were characterized by X-ray diffraction using a Philips PW 1050 diffractometer (Cu Kα, Ni-filter). IR spectra were obtained on a Perkin-Elmer IR-1720 spectrometer (KBr, cm^{-1}), for pyz (in parentheses for pristine pyrazine), 3011 (3050), 1481 (1500), 1413 (1414), 1199 (1250), 1151 (1149), 1120 (1064), 1043 (1026), 794 (795); for cyanide, 2119 and 2104. CPMAS ^{13}C NMR spectra were recorded on a Bruker MSL 300 spectrometer.

X-ray Crystallography. Crystal parameters and details of the data collection and refinement are given in Table 1 (for full details see the Supporting Information). A suitable crystal of **5** was fixed in a thin-walled Lindemann capillary and transferred to a Siemens/Syntex $P2_1$ four-circle diffractometer. Data were collected using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The unit cell parameters were determined by least-squares refinement.

The structure was solved for the heavy atoms by three-dimensional Patterson synthesis for the space group $C2/c$ (No. 15), and the positions of the C and N atoms could be determined by standard difference Fourier and least-squares techniques. Positions of the hydrogen atoms were calculated and refined by a riding model. An absorption correction making use of the DIFABS strategy[7] was carried out.

Results and Discussion

The structure of **5** is based on infinite, but nonlinear -[-Cu-pyz-]- and -[-Cu-CN-Sn-NC-]- chains that cross each

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10.1021/ic9808549 CCC: $18.00

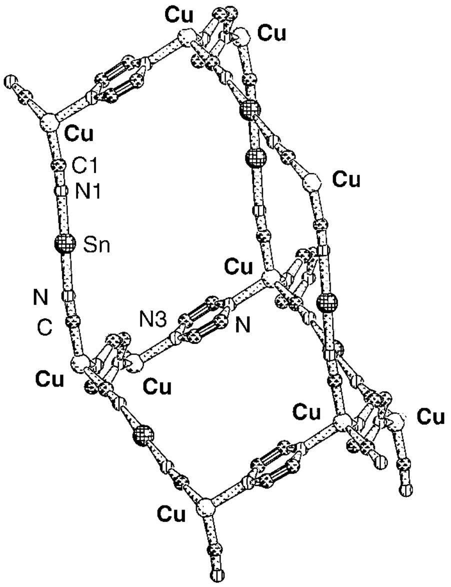

Figure 1. View of one singular distorted-adamandoid Cu$_{10}$ unit of **5**.

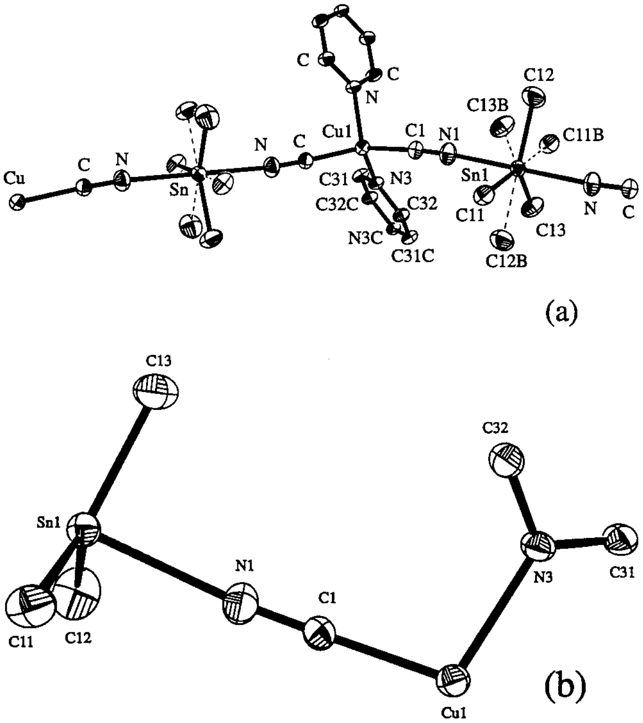

Figure 2. (a) Segment of a -[-CuCNSn(Me$_3$)NC-]- chain showing the disordered methyl carbon atoms; (b) asymmetric unit of **5** including the atomic numbering scheme. ORTEP plot with thermal ellipsoids at 30% probability.

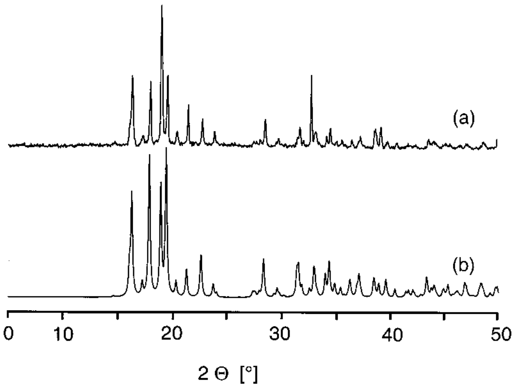

Figure 3. X-ray powder diffractograms of **5**: (a) experimental, (b) simulated XRP.

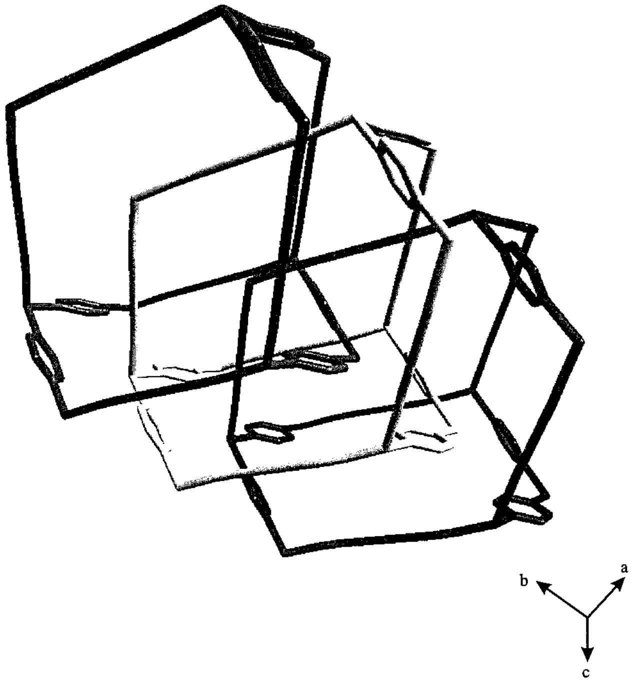

Figure 4. Schematic view of the three equivalent interpenetrating frames in **5**. The longer, straight lines symbolize the {CNSn(Me$_3$)NC} spacer.

other at the quasi-tetrahedral Cu(I) sites. Selected interatomic distances and angles are given in Table 2. Basic subunits of the resulting 3-D framework are distorted-adamandoid Cu$_{10}$ cages whose surfaces are surrounded either by Cu$_6$(pyz)$_4${Sn(NC)$_2$}$_2$ or by Cu$_6$(pyz)$_2${Sn(NC)$_2$}$_4$ rings (Figure 1). Both Cu$_6$ hexagons adopt chair conformations and display edges of significantly different lengths (Cu−pyz−Cu, 7.142(5) Å; Cu−CN−Sn−NC−Cu, 10.795(6) Å). Owing to nonlinearity of, and various dihedral angles within, the two chains, the CN groups do not strictly coincide with the linear Cu···Sn···Cu vectors (Figure 2a).

Despite the disordered methyl groups, the asymmetric unit of **5** is surprisingly simple (Figure 2b). The X-ray powder diffractogram of the bulk product of **5** corresponds reasonably well with that calculated from the single-crystal data set (Figure 3), and the CPMAS ^{13}C solid-state NMR spectrum of powdered **5** (δ 3.26, Me; δ 135, pyz; δ 145.9, CN) matches well with the asymmetric unit if rapid (on the NMR time scale) rotation of the Me$_3$Sn and pyz units around their N···N axes is accounted for. Because of the large internal voids within each of the Cu$_{10}$ cages, three equivalent frameworks are found to interpenetrate each other (Figure 4). We are aware of just one report on a corresponding 3-fold interpenetrating, *distorted*-diamondoid framework.[8] Thus, in [CuCN·cnpy] = $^{3}_{\infty}$[Cu(μ-CN)(μ-cnpy)], **6** (cnpy = 4-cyanopyridine), distorted-adamandoid Cu$_{10}$ cages with Cu···Cu edges of 5.04 and 9.60 Å, respectively, exist. Interestingly, the compound [Ag(cnpy)$_2$(BF$_4$)] was shown to afford a *fourfold*-interpenetrating diamondoid framework,[9] while 2,7-diazapyrene-coordinated Cu(I) prefers 3-fold interpenetration.[10] Obviously, the space demand of its tin-bonded methyl groups prevents **5** from adopting 4- or even 5-fold interpenetration.[11]

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Probably as a consequence of the particular way of “self-inclusion” realized by the framework of **5**, the Cu−N distances of **5** exceed those found in other pyrazine complexes of Cu(I),[12] in that the Cu−pyz−Cu distance of **5** equals almost the Ag−pyz−Ag distance (7.225 Å) reported for [Ag(pyz)(NO_3)].[13] The Sn−N distances (in the longer edges) compare well with those of **3**.[3] We are presently investigating if **5** may be selectively oxidized, or doped, by reaction with variable quantities of I_2, Cl_2, or NO_2.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available free of charge via the Internet at http://pubs.acs.org.

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