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[CuCN·Me_3SnCN·0.5bpy] (bpy = 4,4′-Bipyridine): A Novel Supramolecular Assembly Involving the No Longer Unusual $\{Cu_2(\mu\text{-}CN)_2(CN)_2\}$ Motif[†]

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Reaction of $K_3[Cu(CN)_4]$ with Me_3SnCl and 4,4′-bipyridine (bpy) affords the novel ternary adduct [CuCN·Me_3SnCN·0.5bpy], **2**, as yellow, cubelike crystals. The supramolecular architecture of **2** consists, according to a single-crystal X-ray study, of remarkably porous, approximately planar sheets held together by almost perpendicular bpy pillars. Basic building blocks of the sheets are $\{Cu_2(\mu\text{-}CN)_2(CN)_2\}$ fragments whose N atoms are connected, via Me_3Sn bridges, with the N atoms of adjacent fragments. **2** crystallizes in space group $P2_1/c$ with (at 20 °C) $a = 10.035(4)$ Å, $b = 11.980(3)$ Å, $c = 12.425(5)$ Å, $\beta = 110.94(3)°$, and $Z = 4$. The dinuclear building blocks resemble strongly those of the long known, but chemically more labile, *layered* coordination polymer [CuCN·NH_3], **1**. Although the lattice of **2** consists of two equivalent, ideally interpenetrating 3D frameworks, spacious, straight channels of a cross section of ca. 10 Å × 5 Å persist in this unprecedented structure. The likewise polymeric new adduct [CuCN·Me_3SnCN·H_2O] (**3**) obtained from $K_3[Cu(CN)_4]$ and Me_3SnCl in the absence of bpy may be considered as a formal precursor of **2**.

Introduction

Numerous binary copper(I)-containing adducts of the virtually simple composition [CuX·L] are known wherein X is an anionic and L an uncharged ligand.[1] Crystallographic studies have revealed that the structural chemistry of this class of complexes is unexpectedly diverse.[1,2] Compounds of this composition have turned out to be dinuclear, tetranuclear, or even polymeric, and several bridging ligands X^- including also CN^- and $ArCC^-$ (Ar = arene group) may lead to Cu···Cu contacts even shorter than in elemental copper.[2,3] One long-known example is the polymeric adduct [CuCN·NH_3], **1**, wherein the Cu^+ ions are held pairwise together by quite unusual μ_3-CN bridges (Figure 1).[3] In continuing our systematic exploration of binary and ternary metal cyanide adducts of the general composition $[M(CN)_k\cdot mR_3E(CN)]$ and $[M(CN)_n\cdot pR_3E(CN)\cdot qL]$, respectively, wherein M has been Fe, Co, or Ru, R an alkyl group, E a Sn or Pb atom, and L an uncharged Lewis base,[4,5] we describe here the ternary adduct [CuCN·Me_3SnCN·H_2O], **3**, and its virtual derivative [CuCN·Me_3SnCN·0.5bpy], **2** (bpy = 4,4′-bipyridine). Product **2** may also be considered as reminiscent of the earlier reported[6] ternary system [CuCN·$2Et_3SnCN$·$n\text{Bu}_4NCN$] = $[(n\text{Bu}_4N)(Et_3Sn)_2Cu(CN)_4]$, **4**. While **4** was obtained during the systematic search of organotin-based, zeolite-like systems,[6] **2** and **3** resulted unexpectedly when the synthesis of the Me_3SnCN-rich adduct [CuCN·$3Me_3SnCN$·bpy] (**5**) had been envisaged (vide infra). Most surprisingly, **2** has turned out to share unusual structural features with, inter alia, the so far quite exceptional ammonia adduct **1**.

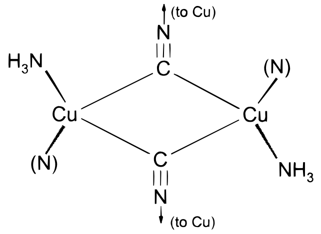

Figure 1. Schematic description of the structure of **1**.

Preparation and General Properties of [CuCN·Me_3SnCN·*n*bpy] (*n* = 0 and 0.5)

According to recent findings in our laboratory, the spectroscopically well-described binary adduct [$Fe(CN)_2$·$4Me_3SnCN$] = $[(Me_3Sn)_4Fe(CN)_6]$ (**6**)[4b] can readily be converted into ternary adducts of the type [$Fe(CN)_2$·$4Me_3SnCN$·*n*L], where L may be either bpy, pyridine (py), pyrazine (pyz), or dioxane.[5b] Obviously, while only two of the four Sn atoms of **6** may reach pentacoordination, all Sn atoms of [$Fe(CN)_2$·$4Me_3SnCN$·bpy] (**7**) should have environments of trigonal bipyramidal (tbp)

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configuration. Correspondingly, also compounds of the more recently studied type [CuCN·3R$_3$SnCN] = [(R$_3$Sn)$_3$Cu(CN)$_4$][7] might be able to add either two monodentate bases or, alternatively, one bidentate bpy unit. Unexpectedly, with R = Me the synthesis of the appropriate starting system [CuCN·3Me$_3$SnCN], **8**, had turned out to be more difficult than with slightly larger alkyl groups R,[7] as the elemental analysis of the product strongly suggested the composition [CuCN·Me$_3$SnCN]. Since **7** had been obtained alternatively by spontaneous self-assembly in reacting K$_4$[Fe(CN)$_6$] with Me$_3$SnCl and bpy (1:4:1),[5b] the synthesis of [CuCN·3Me$_3$SnCN·bpy] (**5**) was also attempted by reacting the salt K$_3$[Cu(CN)$_4$] directly with Me$_3$SnCl and bpy in the molar ratio 1:3:1.

Actually, an air-stable, lemon yellow precipitate was obtained when an aqueous solution of (initially crystalline) K$_3$[Cu(CN)$_4$] was added to a solution of Me$_3$SnCl and bpy in MeCN (1:3:1). Somewhat surprisingly, this precipitate did not occur most reproducibly when a clear solution of CuCN and KCN in the molar ratio 1:3 (expected to involve in situ prepared K$_3$[Cu(CN)$_4$]) was adopted. Moreover, the elemental analysis of the crystalline precipitate did not match with the Cu:Sn:N ratio of 1:4:6 as calculated for the initially expected species **5**. The experimentally determined ratio of about 1:1:3, along with the C/H/N analysis, clearly advocates for the composition CuCN·Me$_3$SnCN·0.5bpy (**2**). Although Me$_3$SnCl was always adopted in considerable excess, the yield of **2** never exceeded 30%. There was no evidence of any solvent inclusion when the synthesis was carried out in the presence of either MeCN or C$_4$H$_8$O$_2$ (dioxane). Attempts to arrive at **2** by reacting CuCN with Me$_3$SnCl, KCN, and bpy in the "appropriate" molar ratio 1:1:1:0.5 have so far remained unsuccessful.

The presence of bpy units in **2** is indicated by a number of IR absorptions (e.g., at 1600 (s), 1532 (m), 1484 (m), 1408 (s), 1217 (m), and 1086 (w) cm^{-1}). Cyanide stretching bands were found at 2091 (s), 2099 (s), and 2115 (m-s) cm^{-1} (IR), and at 2106 and 2124 cm^{-1} (Raman). One IR-active ν(SnC) band appears at 548 cm^{-1} (Raman: 519 (s), 556 (m) cm^{-1}). The CPMAS solid-state ^{13}C NMR spectrum of **2** displays one intense methyl carbon resonance at 0.3 ppm (accompanied by a pair of satellites due to the presence of ^{119}Sn) and a total of five resonances with $\delta > 100$ ppm (at 117.6, 124.0, 144.8, 147.6, and 150 (br) ppm). At least three different resonances are expected for one bpy unit,[8] and one or two signals for the cyanide carbon atoms. The yellow color of **2** results from an absorption band at 440 nm (two other absorptions were found at 370 and 255 nm). Chemically, **2** is remarkably stable against elemental oxygen, while spontaneous reaction takes place both with Cl$_2$ and with NO$_2$. For instance, crystalline **2** reacts rapidly with NO$_2$ molecules from an atmosphere enriched in this oxide. The green product displays strong ν(NO) bands at 1384 and 1412 cm^{-1} and gives rise to an ESR spectrum typical of Cu^{2+} ions in an anisotropic environment. When **2** was kept in vacuo at ca. 100 °C, most of the bpy component sublimed off, leaving a compact orange yellow solid. While the IR spectrum of the latter did not differ significantly from that of **2**, the X-ray powder diffractograms of this product and **2** turned out to be completely different. Under ambient pressure, **2** decomposes at ca. 300 °C (turning black).

The strictly bpy-free adduct **3** resulted as a white, polycrystalline precipitate when an aqueous solution of K$_3$[Cu(CN)$_4$] was added to an aqueous solution of Me$_3$SnCN in the molar ratio 1:3. The appearance of one IR-active ν(CN) band at 2111 cm^{-1} and of three Raman-active bands at 2095, 2118, and 2127 cm^{-1} rules out the eventual presence of pristine CuCN and Me$_3$SnCN, whose ν(CN) bands all occur above 2150 cm^{-1}.[6] The presence of H$_2$O is indicated by two strong IR absorptions at 3520 cm^{-1} (ν_{OH}) and 1640 cm^{-1} (δ_{OH}). Moreover, a significant weight loss of 6.1% is indicated between 70 and 120 °C by a first transition in the TGA curve of **3**. A loss of 5.12% would correspond to one H$_2$O molecule per formula unit. The appearance of two subsequent transitions between 130 and 220 °C (weight loss: 27.5%) and 250 and 420 °C (weight loss: 37.4%) suggests partial removal of Me$_3$SnCN in at least two steps. Unfortunately, single crystals of **3** suitable for a crystallographic X-ray study could so far not be obtained, nor did we arrive at **3** when reacting CuCN and Me$_3$SnCN directly in various solvents in the molar ratio 1:1.

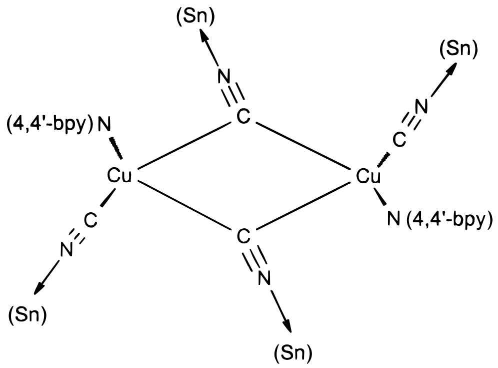

Figure 2. Schematic description of the structure of **2**.

Crystal Structure of 2

Anticipating here Cu-to-Sn-bridging CN and Cu-to-Cu-bridging bpy ligands, respectively, and hence pentacoordinate Sn, the most reasonable coordination number of the Cu(I) ion in **2** would be 3. However, according to a detailed crystallographic single-crystal X-ray study, quasi-tetrahedral CuC$_3$N fragments are present, sharing pairwise one C$_2$ edge in a way in which two CN ligands bridge two copper ions most probably (vide infra) by their *carbon* atoms (Figures 2 and 3). As in all earlier described coordination polymers,[4,5a,6] each cyanide N atom occupies an axial site of a bridging Me$_3$Sn unit, making the coordination sphere of each Sn(IV) ion trigonal bipyramidal (tbp). Thus, the cyanide ligands of **2** represent the no longer elusive (vide infra) type of "bifurcated" μ_3-CN bridges. For instance, {Cu$_2$(μ_3-CN)$_2$} building blocks similar to those in **2** have for long been known to constitute the layered structure of the adduct **1** = [CuCN·NH$_3$].[3] "Straightforward" reasoning would likewise predict a coordination number of 3 for the Cu(I) ions of **1**. Selected structural parameters of the two intertwined pseudotetrahedra of **1** and **2** are compared in Table 1.

The Cu−C distances in **2** match with earlier reported[9,10] data, the two shorter distances (Table 1) being longer than in copper(I) carbonyl complexes,[11] but slightly shorter than in some alkyne adducts.[12] The Cu···Cu′ contact exceeds that reported for **1** by

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[7] (a) Ibrahim, A. M. A. *J. Organomet. Chem.* **1998**, *556*, 1−9. (b) Ibrahim, A. M. A.; Siebel, E.; Fischer, R. D. Unpublished results.

[8] E.g., the novel adduct [Fe(CN)$_2$·4Me$_3$SnCN·bpy] gives rise to three CPMAS ^{13}C resonances of the bpy skeleton at 127, 145, and 148 ppm.[5b]

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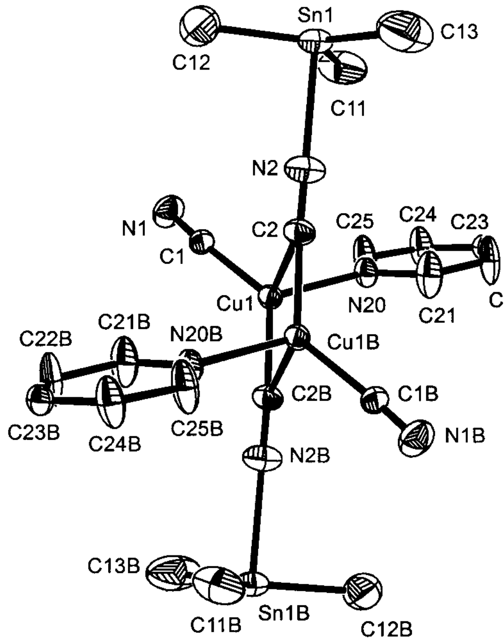

Figure 3. ORTEP plot of the structure of **2** with the appropriate atomic numbering scheme.

Table 1. Comparison of Representative Bond Distances (Å) and Angles (deg), Respectively, of **1** and **2**

	2	1
Cu1−Cu1c	2.624(2)	2.417
Cu1−C1	1.940(7)	(1.984)[a]
Cu1−C2	2.374(8)	2.129
Cu1−C2c	1.936(7)	2.090
Cu1−N20	2.102(6)	2.070
C1−N1	1.120(10)	
C2−N2	1.127(10)	
N1−Sn1	2.348(7)	
N2−Sn1	2.342(7)	
Cu1−C2−Cu1c	74.3(3)	69.9
C2−Cu1−C2c	105.7(3)	110.1
Cu1−C2−N2	117.9(7)	143.4
Cu1c−C2−N2	167.8(8)	146.7
C1−Cu1−N20	105.2(3)	107.6
Sn1−N1−C1	161.8(7)	177.2[b]
Sn1−N2−C2	176.6(6)	

[a] (Cyanide)*N*−Cu bond. [b] Cu−N−C angle.

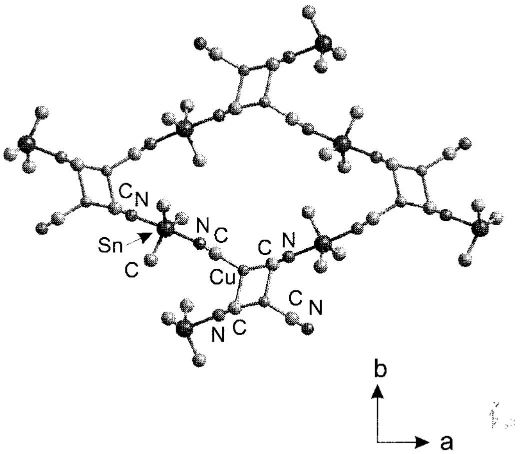

Figure 4. Macrocyclic segment of the infinite layer constituting **2**.

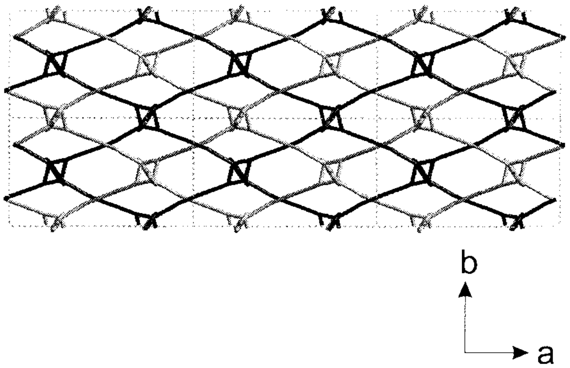

Figure 5. View perpendicular to one pair of adjacent layers (along *c*) constituting the lattice of **2**. All $\{Cu_2(\mu\text{-}CN)_2\}$ units of one sheet lie above the centers of the 22-atomic rings of the other sheet. Lines virtually connecting Cu pairs in this figure are the projections of bpy pillars. Methyl groups are omitted.

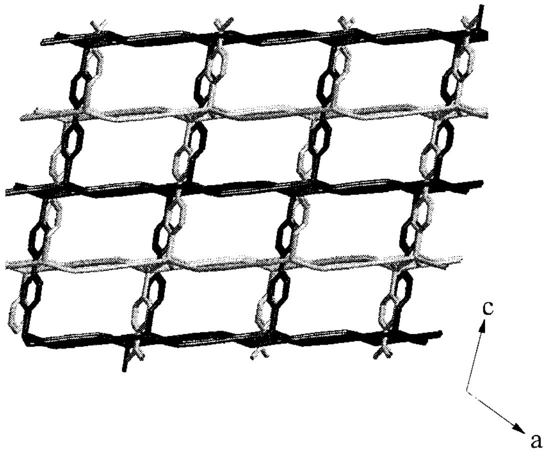

Figure 6. Architecture of **2** in total, viewed parallel to the layers presented in Figure 5 (i.e., along *b*).

about 0.2 Å. Interestingly, the Cu···Cu contacts in **1** and **2** are only slightly longer and shorter, respectively, than in metallic copper (2.55 Å).[13] Similarly short Cu···Cu contacts of 2.45 and 2.69 Å are also known to occur, e.g., in the tetrameric copper alkynyl adduct $[CuC_2Ph{\cdot}PMe_3]$.[14] The $\{Cu_2(\mu\text{-}CN)_2(CN)_2\}$ fragments of **2** are interconnected via $SnMe_3$ bridges to infinite, quasi-planar sheets (Figure 4). Owing to the existence of almost planar, 24-atomic $C_8N_8Cu_4Sn_4$ rings (Figure 5), these sheets contain nanometer-wide, roughly ellipsoidal pores (main diameters: 1.804 and 1.026 nm; for an even larger, 30-atomic ring, see ref 15). For comparison, the corresponding sheets of **1** involve only 12-atomic $C_4N_4Cu_4$ rings. The sheets of **2** are, moreover, regularly stacked, and linked together, by bpy pillars (with coplanar pyridyl units). Because of the unusually large vacant space within this three-dimensional framework, the actual lattice of **2** involves *two* equivalent, ideally interpenetrating frameworks in that each bpy pillar of one framework passes the center of a 24-atomic ring of the complementary framework (Figure 6). This thermodynamically probably more favorable arrangement seems to possess a notably large internal surface area, as the BET value of **2** amounts to 1087.8 $m^2\ g^{-1}$.

Interestingly, the framework structure of **2** is most reminiscent of that of the "ternary adduct" $[Cd(CN)_2{\cdot}2AgCN{\cdot}2bpy] = [Cd(bpy)_2\{Ag(CN)_2\}_2]$[16] wherein approximately planar ${}^2_\infty[Cd\{Ag(CN)_2\}_2]$ sheets are bpy-pillared (Cd-to-Ag). Here again, two

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equivalent 3D frameworks interpenetrate each other. A number of other copper(I) complexes containing bridging bpy ligands have been reported: While the cationic part of polymeric [{Cu(bpy)$_2$}PF$_6$] consists of four equivalent, interpenetrating diamond-like frameworks with tetracoordinate Cu(I),[17] that of [Cu(bpy)$_{1.5}$NO$_3$·1.5H$_2$O] involves even six interpenetrating 3D frameworks with three-coordinate Cu(I).[18] As the distance between two copper ions of **2** held apart by a −CNSnNC− spacer (1.056 nm) is not too different from that involving a bpy bridge (1.131 nm), **2** might in principle also be formulated as $^3_\infty$[Cu{μ-CNSnMe$_3$NC}(μ-bpy)$_{0.5}$], anticipating here a crystal structure similar to that of the cationic $^3_\infty$[Cu(μ-bpy)$_{1.5}{}^+$] framework.[18] The actual architecture of **2**, which clearly rules out this latter possibility, may thus be assumed to benefit more from the higher coordination number accessible for the Cu$^+$ ions in the {Cu$_2$(μ-CN)$_2$(CN)$_2$} building blocks. Although no more than two equivalent frameworks interpenetrate in the lattice of **2** (instead of six as in [{Cu(bpy)$_{1.5}$}NO$_3$·1.5H$_2$O][18]), leaving still comparatively wide, and predominantly vacant, channels of an approximately rectangular (ca. 0.5 nm × 1.0 nm) cross section (see Figure 6), **2** turns out to be thermally surprisingly stable. Interestingly, replacement of the bridging ligands CN$^-$ and Me$_3$SnCN by μ-Cl$^-$ and P(C$_6$H$_5$)$_3$, respectively, affords a one-dimensional coordination polymer containing {Cu$_2$(μ-Cl)$_2$} building blocks (Cu···Cu: 2.997 Å) interconnected by bpy units.[19]

Conclusion and Outlook

Although the {Cu$_2$(μ-CN)$_2$} fragment of **2** is less symmetrical than that of **1**[3] (see Figures 1 and 2), **2** may be considered as a novel example of the rapidly expanding class of copper(I) cyanides containing {Cu$_2$(μ-CN)$_2$} units with two bifurcated cyanide ligands as essential building blocks.[9,15,20−22] White et al. have even shown[20] that *almost* anhydrous CuCN crystallizes in layers owing to the presence of {Cu$_2$(μ-CN)$_2$(CN)$_2$} units. Bifurcated cyanide ligands may even help interconnecting layered coordination polymers to generate 3D frameworks,[9,15] and the closer inspection of already published structures is likely to detect even further examples.[23]

It may be recalled that usually the experimental confirmation of the anticipated *carbon*-to-copper coordination of the μ_3-CN ligand is not free of ambiguity.[3] Yet, in the case of **2** we could argue (a) that the actual Sn−*N* bond distances compare well with earlier reported data,[4−6] (b) that we are only aware of two compounds involving Me$_n$Sn (n = 3, 2) units and (also) Sn−*C*(cyanide) bonds with Sn−C distances as long as 2.49 and even 2.68 Å, respectively,[24] and (c) that the cyanide ^{13}C resonances are devoid of satellites due to internuclear coupling with relevant tin isotopes. Our present findings demonstrate that still now crystal engineering of *ternary* systems involving formally CuCN, R$_3$SnCN, and a nitrogen base appears not to be straightforward in view of either a successful synthesis or a correct prediction of the structure of a new product. Thus, product **2** results under preparative conditions chosen primarily for the synthesis of **5**. On the other hand, it has been demonstrated recently[25] that *binary* systems of the type [CuX·nL] (L = nitrogen base) have meanwhile become reasonably tractable subjects of crystal engineering. In contrast, we have found that the analytical composition and, hence, the structure, too, of some congeners of the title compound **2** may differ considerably in spite of virtually insignificant modifications of the starting systems. For instance, reaction of [(Et$_3$Sn)$_3$Cu(CN)$_4$] = [CuCN·3Et$_3$SnCN] with bpy affords polymeric [CuCN·Et$_3$SnCN·bpy] devoid of {Cu$_2$(μ-CN)$_2$} building blocks and with twice as many bpy molecules per Cu$^+$ ion as in **2**.[7,26] According to most recent theoretical studies, weak Cu···Cu bonding[27] may be considered as an ancillary structure-directing factor. Still comprehensive semiempirical arguments date back to the work presented by van Koten et al. 10 years ago.[28]

Experimental Section

Materials. K$_3$[Cu(CN)$_4$] was prepared by slightly modifying the reported methods.[29] At a bath temperature of 60 °C, 6.0 g (60.60 mmol) of CuCl was dissolved in a solution of 13.0 g (199.63 mmol) of KCN in 250 mL of H$_2$O. The heating of the bath was stopped when the volume of the resulting solution was reduced to half. Thereafter, solvent evaporation was continued in vacuo to near dryness. Complete dryness was achieved by pressing the resulting white solid on filtering paper in a current of N$_2$. Yield: 17.5 g (92.1%). All other chemicals and solvents were of analytical grade and used as received.

Infrared spectra were recorded on a Perkin-Elmer IR-1720 spectrometer, and Raman spectra on a Jobin Yvon U-1000 instrument. Solid-state CPMAS NMR spectra were obtained on a Bruker MSL 300 spectrometer, and optical (near-IR/vis) absorption spectra on a Cary/Varian 5E instrument. The X-ray powder diffractograms of **2** and its degradation product were recorded on a Philips PW 1050 diffractometer (Cu Kα, Ni filter), and the TGA study of **3** on a Netzsch STA 409 instrument equipped with a BALZER QMS 421 mass spectrometer. BET measurements of a sample dried in vacuo at 50 °C were carried out on a Carlo Erba Sorptomatic 1800 instrument.

Preparation of [CuCN·Me$_3$SnCN·0.5bpy], 2. With gentle stirring (without using a magnetic stirrer), a solution of 300 mg (1.053 mmol) of K$_3$[Cu(CN)$_4$] in ca. 10 mL of H$_2$O was added to a clear solution of 165 mg (1.056 mmol) of 4,4′-bipyridine and 630 mg (3.162 mmol) of Me$_3$SnCl in ca. 10 mL of acetonitrile. From the faintly yellow solution immediately obtained, well-shaped yellow crystals separated 3−4 days later. After filtration, subsequent washing with little water, acetronitrile, and acetone, and drying overnight, about 100 mg (0.28 mmol; yield: 26%) of yellow crystals that were well-shaped throughout were obtained. Anal. Calcd for C$_{10}$H$_{13}$N$_3$CuSn: C, 33.60; H, 3.67; N, 11.75; Cu, 17.78; Sn, 33.21. Found: C, 33.71; H, 3.70; N, 11.79; Cu, 17.95; Sn, 32.35. Corresponding analytical data were obtained when 1−2 mL of dioxane had been added to the starting solution of Me$_3$SnCl, indicating that neither MeCN nor C$_4$H$_8$O$_2$ molecules were incorporated

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(26) For the following new compounds of relevance for the title complex **2**, structural data have already been deposited on the Cambridge File: Et$_3$SnCN·CuCN·bpy (No. 407 643), Me$_3$SnCN·CuCN·pyz (pyz = pyrazine; No. 407 644), and Me$_3$SnCN·CuCN·pym (pym = pyrimidine, No. 407 656).

(27) Pyykkö, P.; Runeberg, N.; Mendizabal, F. *Chem. Eur. J.* **1997**, *3* 1451−1457.

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in the resulting crystals. On the other hand, only Cu-free, white crystals were obtained when Me_3SnCl was applied in quantities equimolar to those of $K_3[Cu(CN)_4]$.

Preparation of [CuCN·Me_3SnCN·H_2O}], 3. A solution of 300 mg (1.05 mmol) of $K_3[Cu(CN)_4]$ in 15 mL of H_2O was added to a solution of 630 mg (1.05 mmol) of Me_3SnCl in 10 mL of H_2O, whereafter immediately a white polycrystalline precipitate was obtained. After filtration, washing with little H_2O, and drying in vacuo, 250 mg (0.84 mmol; 79.8%) of **3** was isolated. Anal. Calcd for $C_5H_{11}N_2$-OCuSn: C, 20.19; H, 3.73; N, 9.42; Cu, 21.36; Sn, 39.91. Found: C, 19.86; H, 3.67; N, 8.76; Cu, 20.71; Sn, 39.62.

X-ray Structure Determination. Suitable crystals of **2** were fixed in thin-walled Lindemann capillaries. The single-crystal X-ray diffraction data were collected at 293(2) K on a Siemens $P2_1$ four-circle diffractometer with graphite-monochromated Mo Kα radiation adopting the Θ/2Θ scan technique. Data were corrected for Lorentz-polarization effects, and an empirical absorption correction was carried out by means of DIFABS. The numbers of reflections collected in total, of the unique reflections, and of the reflections used for structure solution satisfying $I > 2\sigma(I)$ were 5054, 3226 (for $R(\text{int}) = 0.0499$), and 3150, respectively. The structure was solved by the Patterson method and refined by the full-matrix least-squares method of all F^2 data using the SHELXL-93 program[30] on a DEC-MicroVAX computer. Non-hydrogen atoms were refined with anisotropic thermal parameters. The aromatic hydrogen atoms were refined using a riding model with a fixed C−H distance of 93 pm. Owing to the favorable data set, the methyl hydrogen atoms were refined by a difference electron density synthesis with a fixed C−H distance of 96 pm, assuming an ideal tetrahedral arrangement of the hydrogens around the methyl carbon atoms. In both cases, the isotropic thermal parameters were refined using “free variables” in order to constrain the thermal parameter of chemically equivalent hydrogens to be equal. The maximum residual electron density is located in a distance less than 1 Å around the heavy metals and can therefore not be attributed to disordered solvent molecules. Significant crystal data are listed in Table 2. Visualization was achieved by means of the CERIUS^2 software of BIOSYM/Molecular Simulations (MSI), Cambridge, U.K., using a Silicon Graphics INDIGO high impact R10000 computer. The structural analysis of a second single crystal grown from a solution containing also a fraction of dioxane (vide infra) gave rise to results strictly indentical with those reported above.

Table 2. Selected Crystallographic Data of **2**

empirical formula	$C_{20}H_{26}Cu_2N_6Sn_2$	λ (Mo Kα)	0.710 73
a (Å)	10.035(4)	fw	714.93 g mol^{-1}
b (Å)	11.980(3)	σ_{calc}	1.702 g cm^{-3}
c (Å)	12.425(5)	μ	32.89 cm^{-1}
β (deg)	110.94(3)	$R(F_o)^{a,b}$	0.0732
V (Å^3)	1395.1(9)	$R_w(F_o^2)^{a,b}$	0.1780
Z	2	$R(F_o)^{a,c}$	0.0924
space group	$P2_1/c$ (No. 14)	$R_w(F_o^2)^{a,c}$	0.2006
T (°C)	−120(2)		

[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.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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