



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 684 (2003) 329–337

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorganchem

New supramolecular organotin(IV)/-copper(I) cyanides containing the unique $\{\text{Cu}_2(\mu\text{-CN})_2\}$ building block

Hilka Hanika-Heidl^a, Safaa El-din H. Etaiw^b, Moustafa Sh. Ibrahim^b,
Ahmed S. Bader El-din^b, R. Dieter Fischer^{a,*}

^a Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

^b Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

Received 17 April 2003

Abstract

Reaction of $\text{Me}_3\text{SnCl}/\text{K}_3[\text{Cu}(\text{CN})_4]$ with the bipodal nitrogen bases ($\mu\text{-L}$): bis(4-pyridyl)-*trans*-ethene (bpe), bis(4-pyridyl)-1,2-ethane (bpeH_2), 4-cyanopyridine (cpy) and bis(4-pyridyl)-*trans*-1,4-divinylbenzene (pdvb) affords the new coordination polymers $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{bpe}]$ (**2**), $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{bpeH}_2]$ (**3**), $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot\text{cpy}]$ (**4**) and $[\text{CuCN}\cdot\text{pdvb}]$ (**5**). While **2** and **3** display layered structures with rhomboic $\{\text{Cu}_2(\mu\text{-CN})_2\}$ units as basic building blocks (Cu···Cu distances: 2.634 and 2.758 Å, respectively), **4** crystallizes in a distorted-diamondoid structure ${}^3_{\infty}[\text{Cu}^{\text{I}}\{\mu\text{-CNSn}(\text{Me}_3)\text{NC}\}\{\mu\text{-cpy}\}]$ with four equivalent and independent, interlocking frameworks. In contrast, **5** consists of strongly corrugated, stapled sheets composed of parallel running $[\text{Cu}\text{-pdvb}]_{\infty}$ -zigzag chains tied together by CN bridges. Compounds **2** and **3** belong to the rapidly growing family of supramolecular assemblies containing the quite unusual $[\text{Cu}_2(\mu\text{-CN})_2]$ unit the repeated appearance of which raises the question if cuprophilic interactions therein are the basic cause of the existence of that family.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Copper cyanide; Nitrogen bases; Crystal structures; Cuprophilicity

1. Introduction

The cyanide ligand CN^- is well known to bridge two metal atoms in a quasi-linear $\text{M}-\text{C}\equiv\text{N}\rightarrow\text{M}'$ fashion, whereas the connection of two metal centres exclusively by its carbon atom (which is most common for the isoelectronic CO ligand) is extremely rare. A quite exceptional case of almost 'carbon monoxide like' bridging of CN^- is, however, realized in fragments of the type $\{\text{Cu}_2(\mu\text{-CN})_2\}$ that may be considered as basic building blocks of an increasing number of two- or three-dimensional (2D/3D) supramolecular assemblies [1–13]. When we described the assembly $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{bpy}] = {}^3_{\infty}[\text{Cu}\{\mu_3\text{-CNSn}(\text{Me}_3)\text{NC}\}\{\mu_2\text{-bpy}\}_{0,5}]$ (**1**, bpy = 4,4'-bipyridine) in 1998 as a novel (i.e. organotin-containing) representative involving the 'no

longer unusual' $\{\text{Cu}_2(\mu\text{-CN})_2(\text{CN})_2\}$ motif [7], the structures of seven different coordination polymers reflecting the presence of $\{\text{Cu}_2(\mu\text{-CN})_2\}$ units had been spotted in the literature [1–7]. Since then, the total number has increased to about 20 [8–13]. Interestingly, structure analyses of two new examples [10,11] were even reported twice, although only the later presentation [12] is focused more clearly on the $\{\text{Cu}_2(\mu\text{-CN})_2\}$ pattern.

In the following, we wish to describe primarily the unexpected supramolecular architecture of two formal congeners of **1** of the general composition $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5(\mu_2\text{-L})]$, wherein L is either bis-*trans*-(4-pyridyl)ethene (bpe, **2**) or bis(4-pyridyl)-1,2-ethane (bpeH_2 , **3**). These new assemblies display $\{\text{Cu}_2(\mu\text{-CN})_2\}$ units with the so far longest Cu···Cu and Cu··· $\mu\text{-C}$ distances and might therefore provide, inter alia, helpful information for forthcoming theoretical studies. For comparison, the structures of two likewise new compounds of the related composition $[\text{CuCN}\cdot$

* Corresponding author.

E-mail addresses: safaa_etaiw@hotmail.com (S.E.-d.H. Etaiw), dieter.fischer@chemie.uni-hamburg.de (R.D. Fischer).

$n\text{Me}_3\text{SnCN}\cdot\mu\text{-L}$] ($n = 1$ or 0) free of $\{\text{Cu}_2(\mu\text{-CN})_2\}$ fragments will be described, too.

2. Preparation of the coordination polymers 2–5

Two different routes have turned out to be useful for the generation of single crystals suitable for X-ray crystallography. The first one resembles strongly the preparation of **1** [7], in that an aqueous solution of either authentic or in-situ-prepared $\text{K}_3[\text{Cu}(\text{CN})_4]$ is added to a solution of the bipodal organic base L and Me_3SnCl in water–acetonitrile. The start from a clear solution resulting from CuCN and KCN (1:3) seems to help circumventing the formation of various earlier reported, Me_3Sn -free products (e.g. of $[(\text{CuCN})_2\cdot\text{bpy}]$ [11,12], $[(\text{CuCN})_7\cdot(\text{bpy})_2]$ [12] and $[(\text{CuCN})_2\cdot\text{bpe}]$ [12], respectively), which were obtained at least in the absence of Me_3SnCl . In pure acetonitrile, Zubieta et al. had arrived constantly at mixtures of crystals of both $[(\text{CuCN})_2\cdot\text{bpy}]$ and $[(\text{CuCN})_7\cdot(\text{bpy})_2]$ [12].

The second route makes use of the very slow transfer of Me_3SnCl molecules from the gas phase above a sample of solid Me_3SnCl (or of a concentrated aqueous solution) into an aqueous solution of $\text{K}_3[\text{Cu}(\text{CN})_4]$, the bipodal base L and a small quantity of MeCN [14,15]. A third, rather promising route, which has, however, not yet been applied for the preparation of organotin-containing species, is the so-called ‘thiosulfate-assisted’ method which is carried out in aqueous solution [9]. It is, moreover, worth emphasizing that occasionally route 1 and 2 may lead to assemblies of the slightly modified composition $[\text{CuCN}\cdot\text{R}_3\text{SnCN}\cdot\mu\text{-L}]$, which is richer in L and therefore inappropriate for the formation of $\{\text{Cu}(\mu\text{-CN})_2\}$ rhombs (vide supra). In such cases, either distorted-diamondoid frameworks [16] or layered structures based upon strongly corrugated sheets [17] with constantly four-coordinate $\text{Cu}(\text{I})$ result. In the following, we wish to present for comparison also the structures of the two new coordination polymers $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot\text{cpy}]$ (**4**; disordered diamondoid; cpy = 4-cyanopyridine) and $[\text{CuCN}\cdot\text{pdvb}]$ (**5**; corrugated sheets; pdvb = bis(4-pyridyl)-*trans*-1,4-divinylbenzene).

3. Crystal structures of 2 and 3

Significant crystal data of **2** and **3** are listed in Table 1, and the corresponding asymmetric units which clearly display the $\{\text{Cu}_2(\mu\text{-CN})_2\}$ building blocks mentioned in the Introduction are shown in Fig. 1. While the CN bridges of most polymeric copper cyanides devoid of other metal ions may be considered as disordered, mainly owing to quite similar $\text{Cu}-\text{C}$ and $\text{Cu}-\text{N}$ distances, the structures of **1**, **2** and **3** turn out to be

free of any disorder. The $\text{Sn}-\text{X}$ distances—X denoting here the atoms in axial positions of the trigonal bipyramidal (tbp) $\{\text{Me}_3\text{SnX}_2\}$ units present in **1**, **2** and **3**—compare well with the $\text{Sn}-\text{N}$ distances of authentic $\{\text{Me}_3\text{Sn}(\text{NC})_2\}$ building blocks present in numerous earlier reported super-Prussian blue derivatives [18]. $\text{Sn}-\text{C}(\text{axial})$ distances in tbp-configured $\{\text{R}_3\text{SnXX}'\}$ units are, on the other hand shorter than 2.2 \AA [19,20]. Thus, it seems more reasonable to assume that the carbon ends of both cyanide groups of **1–3** point towards the copper ions. Although the atomic numbering schemes (see Fig. 1) also follow this view, it should be kept in mind that at present no unambiguous method to distinguish $\{\text{Cu}_2(\mu\text{-CN})_2\}$ fragments with direct carbon bridges from those with corresponding nitrogen bridges is available. The recently described 3-D framework of the coordination polymer $[\text{Cu}_2(\text{CN})_2\cdot\text{pip}]$ (pip = piperazine) even seems to involve $\mu_4\text{-CN}$ units, i.e. here both the carbon and the nitrogen atom must be assumed to connect two copper ions [9].

Notable deviations of the metrical parameters of the two Cu-centred fragments: $\{\text{Cu1}(\text{C1},\text{C3},\text{N7})\}$ and $\{\text{Cu2}(\text{C2},\text{C4},\text{N6})\}$ of **2** and **3** from data required for ideal trigonal planarity (see Table 3) suggest that the comparatively long distances $\text{Cu1}-\text{C4}$ and $\text{Cu2}-\text{C1}$ (Table 2) may still be associated with some non-negligible metal-carbon interaction. Cyanide bridges of this particular type have therefore occasionally been addressed as ‘bifurcated’ [5]. The $\text{Cu1}\cdots\text{Cu2}$ distances of **2** and **3** are likewise longer than e.g. in the archetype of all systems involving a rhombic $\{\text{Cu}_2(\mu\text{-CN})_2\}$ fragment (i.e. the 2D polymer $[\text{CuCN}\cdot\text{NH}_3]$; $\text{Cu}\cdots\text{Cu} = 2.417 \text{ \AA}$ [1]), but, according to recent theoretical studies [22], still shorter than for copper pairs with weak, but non-negligible $\text{Cu}\cdots\text{Cu}$ interaction (vide infra).

Four of the then imaginable $\{\text{Cu}_2(\mu\text{-CN})_2(\text{CN})_2\}^{2-}$ anions and four $\{\text{Me}_3\text{Sn}^+\}$ cations of either **2** or **3** are, as in the structure of **1** [7], fused to a 24-atomic ring. However, while in **1** all four $\text{Cu}_2(\mu\text{-C})_2$ minicycles adopt *exo*-positions of the macrocycle (Fig. 2a), the notably longer bipodal spacers L of **2** and **3** cause one $\text{Cu}_2(\mu\text{-C})_2$ ring to switch into an *endo*-position (Fig. 2b). In consequence, the macrocycles of **2** and **3** can no longer aggregate to infinite sheets (as in the structure of **1**), but expand instead as infinite ribbons. In Fig. 3a the projection of two adjacent ribbons of **2** along the crystallographic *a* axis is shown. While just one complete macrocycle is indicated in the right hand ribbon by bold faced lines and spheres, projections of the dpe spacers (extending perpendicular to the bc-plane) are seen to originate from all copper atoms. The dpe molecules (and also the dpeH₂ spacer of **3**) interconnect the stapled ribbons to infinite (double-) layers (Fig. 3b). Thus, both in **2** and **3** layers result only in cooperation with the organic base, whereas in the

Table 1
Crystal data and structure refinement parameters for **2**, **3**, **4** and **5**

	2	3	4	5
Empirical formula	C ₂₂ H ₂₈ Cu ₂ N ₆ Sn ₂	C ₂₂ H ₃₀ Cu ₂ N ₆ Sn ₂	C ₁₁ H ₁₃ CuN ₄ Sn	C ₂₁ H ₁₆ CuN ₃
Formula weight M_r (g mol ⁻¹)	740.96	742.98	383.48	373.91
Temperature (K)	153(2)	153(2)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions				
<i>a</i> (Å)	14.4868(10)	14.41166(11)	13.2501(11)	6.4709(3)
<i>b</i> (Å)	10.5419(7)	10.8141(8)	11.2014(9)	27.5229(13)
<i>c</i> (Å)	18.0390(12)	17.8373(13)	19.5229(15)	9.6059(4)
α (°)	90	90	90	90
β (°)	90	90	90	101.5450(10)
γ (°)	90	90	90	90
<i>V</i> (Å ³)	2754.9(3)	2780.9(4)	2897.6(4)	1676.18(13)
<i>Z</i>	4	4	8	4
ρ_{calc} (Mg m ⁻³)	1.786	1.775	1.758	1.482
Absorption coefficient (mm ⁻¹)	3.335	3.304	3.176	1.310
<i>F</i> (000)	1440	1448	1488	768
Reflections collected/unique	39044/9504	72913/10097	17873/3303	24408/5848
<i>R</i> _{int}	0.0533	0.0689	0.0583	0.0362
Data/restraints/parameters	9504/1/295	10097/1/296	3303/0/157	5848/0/226
Goodness-of-fit on <i>F</i> ²	0.896	1.003	0.854	0.992
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁ / <i>wR</i> ₂	0.0349/0.0599	0.0333/0.0731	0.0298/0.0519	0.0381/0.1008
<i>R</i> indices (all data)	0.0458/0.0620	0.0365/0.0738	0.0542/0.0558	0.0509/0.1099
Largest difference peak and hole (e Å ⁻³)	1.555; -1.062	4.128; -0.746	0.669; -0.501	0.732; -0.377

structure of **1** bpy-free sheets exist. A perspective view of two adjacent layers of **3** (which strongly resembles that of **2**) is depicted in Fig. 4. Notably wide, infinite channels which host the tin-bonded methyl groups are seen to traverse the layers both along *a* and *c*. Nevertheless, the porous layers do not mutually interpenetrate, whereas interpenetration of two independent 3D frameworks of **1** takes place as a void-reducing phenomenon [7].

The structures of **2** and **3** may also be compared with those of two formal ‘congeners’ described as [(CuCN)₂·μ-L] with L = bpy and bpe, respectively, which contain again {Cu₂(μ-CN)₂} fragments, but instead of the CNSn(Me₃)NC bridge in **1–3** a CNCuNC (or CNCuCN) bridge of similar length [12]. The central Cu(I) ion of this bridge is, however, three-coordinate, owing to additional anchoring of an extra L molecule. Interestingly, again 24-membered macrocycles exist in

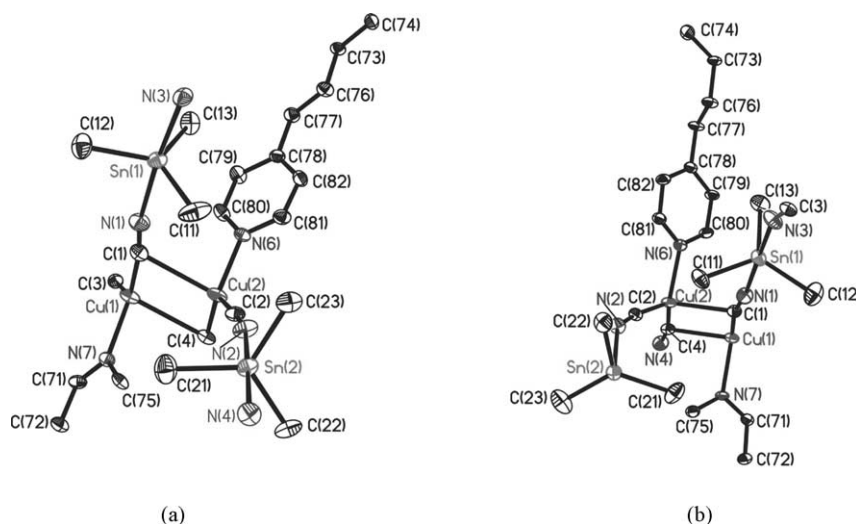


Fig. 1. ORTEP plots (50% probability) of the asymmetric units of **2** (a) and **3** (b).

Table 2
Selected interatomic distances (Å) of the compounds **2** and **3**

Distance (Å)	2 (L = dpe)	3 (L = dpeH ₂)
Cu1–C1	1.922(4)	1.944(3)
Cu1–C3	1.927(4)	1.919(3)
Cu1–C4	2.617(3)	2.462(3)
Cu2–C1	2.599(3)	2.461(3)
Cu2–C2	1.916(4)	1.924(3)
Cu2–C4	1.927(4)	1.928(3)
C–N	1.138(5)–1.153(5)	1.141(4)–1.155(4)
Sn1–N1	2.313(3)	2.324(3)
Sn1–N3	2.390(3)	2.358(3)
Sn2–N2	2.358(3)	2.361(3)
Sn2–N4	2.309(3)	2.319(3)
Cu1–N7	2.042(3)	2.051(2)
Cu1–Cu2	2.7579(6)	2.6335(5)

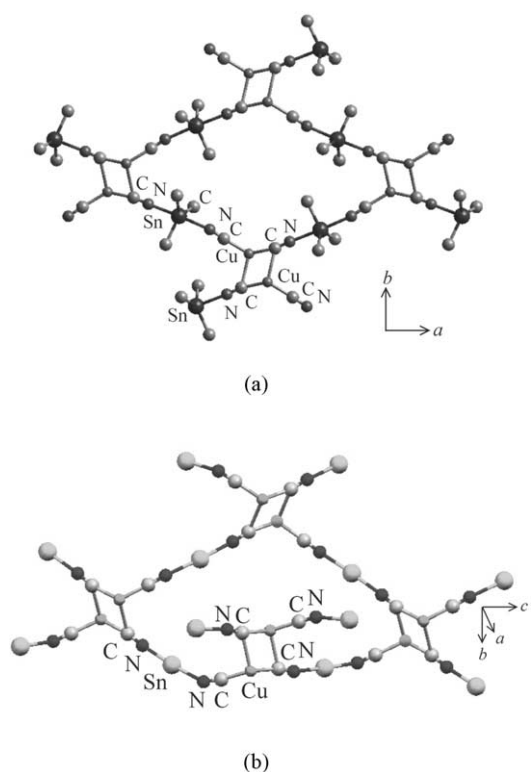


Fig. 2. Comparison of the 24-atomic rings (secondary building blocks) of **1** (a) and **2** (b). Tin-bonded methyl carbon atoms have been omitted for clarity.

these tin-free assemblies, which differ, however, once more from those realized in **1**, **2** and **3**.

4. Crystal structures of **4** and **5**

Application of the shorter (than e.g. bpy, bpe and bpeH₂) bipodal ligand μ -L = 4-cyanopyridine (cpy) afforded the new assembly $[\text{CuCN} \cdot \text{Me}_3\text{SnCN} \cdot \text{cpy}] = {}^3_\infty[\text{Cu}^I\{\mu\text{-CNSn}(\text{Me}_3)\text{NC}\}\{\mu\text{-cpy}\}]$ (**4**) with

strictly four-coordinate Cu(I). Optimal, yellow single crystals resulted from route 2, but also the polycrystalline precipitate obtained along route 1 turned out to be identical with the product of route 2. The experimental X-ray powder diffractogram (XRD) of the precipitate was practically coincident with the XRD simulated from data of the single-crystal X-ray study. From the filtrate of route 1, well shaped single crystals orange in colour resulted after several days, which were identified by X-ray crystallography [23] as the earlier reported [24] 3D assembly $[\text{CuCN} \cdot \text{cpy}] = {}^3_\infty[\text{Cu}^I(\mu\text{-CN})(\mu\text{-cpy})]$.

The crystal structure of **4** resembles strongly that of $[\text{CuCN} \cdot \text{Me}_3\text{SnCN} \cdot \text{pyz}]$ (pyz = pyrazine [16]), in that both assemblies form distorted-diamondoid frameworks. In accordance with the longer separation of two cpy-bridged copper ions ($\text{Cu} \cdots \text{Cu} = 9.484$ Å; $\text{Cu} \cdots \text{Cu}$ with μ -pyz: 7.142 Å [16]), four equivalent and independent frameworks interpenetrate in the lattice of **4** (Fig. 5a), whereas $[\text{CuCN} \cdot \text{Me}_3\text{SnCN} \cdot \text{pyz}]$ consists only of three interlocking frameworks. A corresponding situation holds for the tin-free assembly $[\text{CuCN} \cdot \text{cpy}]$ (three interlocking frameworks; see Fig. 5b) when compared with $[\text{CuCN} \cdot \text{pyz}]$ and $[\text{CuCN} \cdot \text{Mepyz}]$, respectively (two interlocking frameworks [27,10]). Interestingly, $[\text{CuCN} \cdot \text{cpy}]$ crystallizes, like $[\text{CuCN} \cdot \text{Mepyz}]$, in the chiral space group $P2_12_12_1$. In spite of the space-reducing, multiple self-catenation, none of the coordination polymers considered here displays inter-framework $\text{Cu} \cdots \text{Cu}$ distances comparable with those of the $\{\text{Cu}_2(\mu\text{-CN})_2\}$ building blocks of **1–3**. The shortest inter-framework $\text{Cu} \cdots \text{Cu}$ distances of **4**, $[\text{CuCN} \cdot \text{Me}_3\text{SnCN} \cdot \text{pyz}]$ and $[\text{CuCN} \cdot \text{cpy}]$ are 5.606, 5.842 and 5.365 Å, respectively.

Application of the considerably longer, again potentially bipodal, ligand bis(4-pyridyl)-*trans*-1,4-divinylbenzene (pdvb) resulted, in spite of the presence of Me_3SnCl (route 1), exclusively in the formation of the tin-free assembly $[\text{CuCN} \cdot \text{pdvb}] = {}^2_\infty[\text{Cu}^I(\mu\text{-CN})(\mu\text{-pdvb})]$ (**5**). Unlike for, e.g. ${}^3_\infty[\text{CuCN} \cdot \text{cpy}]$, the two drastically different intra-chain $\text{Cu} \cdots \text{Cu}$ separations (via μ -CN: 4.804 Å; via pdvb: 20.366 Å) seem to be more favourable for the formation of strongly corrugated, stapled sheets (shortest inter-sheet $\text{Cu} \cdots \text{Cu}$ separation: 6.471 Å). Each sheet consists of parallel running, infinite $-\text{[Cu-pd vb]}-$ zigzag chains that are tied together by the shorter CN bridges (Fig. 6).

Stapled, corrugated sheets seem to be an attractive alternative of distorted-diamondoid frameworks. Thus, also two tin-containing assemblies of the type $[\text{CuCN} \cdot \text{R}_3\text{SnCN} \cdot \mu\text{-L}]$ were found to adopt the sheet motif (R = Et, L = bpy; R = Me, L = pyrimidine (pym) [17]). The hydrazine complex $[\text{CuCN} \cdot \text{N}_2\text{H}_4]$ [25] can be considered as the ‘archetype’ of the sheet motif. While neither a diamondoid isomer nor a species $[\text{CuCN} \cdot 0.5\text{N}_2\text{H}_4]$ with $\{\text{Cu}_2(\mu\text{-CN})_2\}$ building blocks is known, both ${}^3_\infty[\text{CuCN} \cdot \text{Mepyz}]$ [10] (isostructural with ${}^3_\infty[\text{CuCN} \cdot \text{pyz}]$

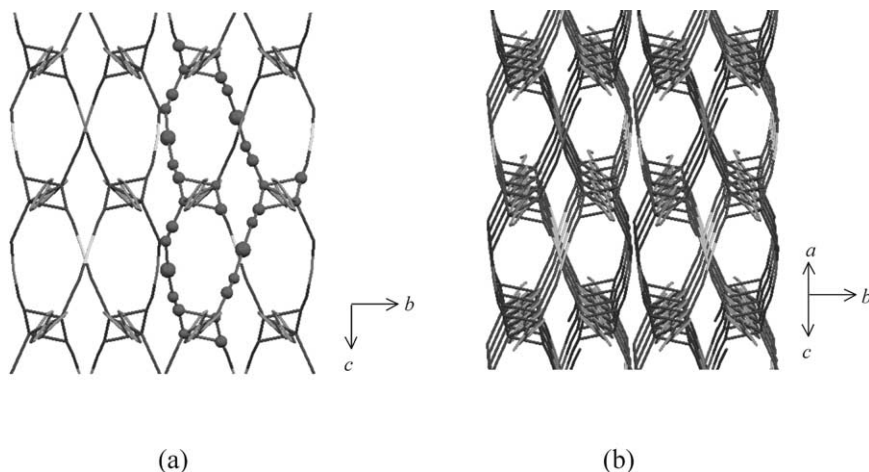


Fig. 3. Projection of two adjacent ribbons of **2**, built up of the building blocks depicted in Fig. 2. (a): One secondary building block is indicated by bold-faced spheres and lines. (b) More perspective view, demonstrating the connection of stapled (along *b*) ribbons to (double-) sheets.

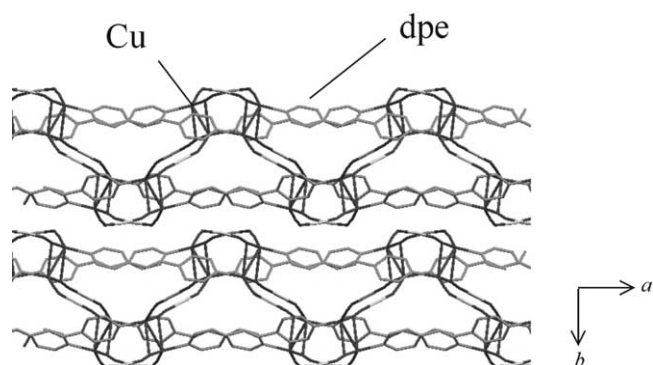


Fig. 4. Perspective view of two adjacent (double-) layers of **2** expanding along *c*. Methyl groups have been omitted. Green: dpe molecules, blue: $\text{Cu}_2(\text{CN})_4$ fragments, yellow: tin atoms.

[27]) and ${}^3_\infty[\text{CuCN}\cdot 0.5\text{Mepyz}]$ [10,12] have been reported. In the latter assembly, puckered sheets similar to those realized in $[\text{CuCN}\cdot\text{NH}_3]$ [1] are stacked via μ -Mepyz bridges to a 3D framework.

5. Space demand and supramolecular architecture

The space required by extended framework structures typical of numerous coordination polymers is expected to depend primarily on the coordination properties of the metal ion (the ‘node’) and the size of the usually bipodal, bridging ligands (the metal ‘connectors’). Since, according to experimental experience, isomeric or quasi-isomeric assemblies are not uncommon (see e.g. the pairs *D/E* and *R/S*, respectively, of Table 4), a well-accessible quantity helpful to assess the individual space demand of a framework structure is strongly desirable. In Table 4, the formula volume $V_f = 0.602 V/Z = M_r/\rho_{\text{calc}}$ of a number of supramolecular assemblies ${}^n_\infty[\text{Cu}^1(\mu\text{-L}^{(1)})_p(\mu\text{-L}^{(2)})_q]$ ($n=2$ or 3 ; $p+q\leq 2$) is listed for comparison. Members of the family of the formally more related species *D*, *E* and *K–M* with p and $q=1$ contain all one negatively charged, five-atomic metal connector $\text{L}^{(1)}$ (i.e. either NCNCN^- , $\text{CNSn}(\text{Me}_3)\text{NC}^-$ or CNCuCN^-) and an uncharged nitrogen base $\text{L}^{(2)}$ the

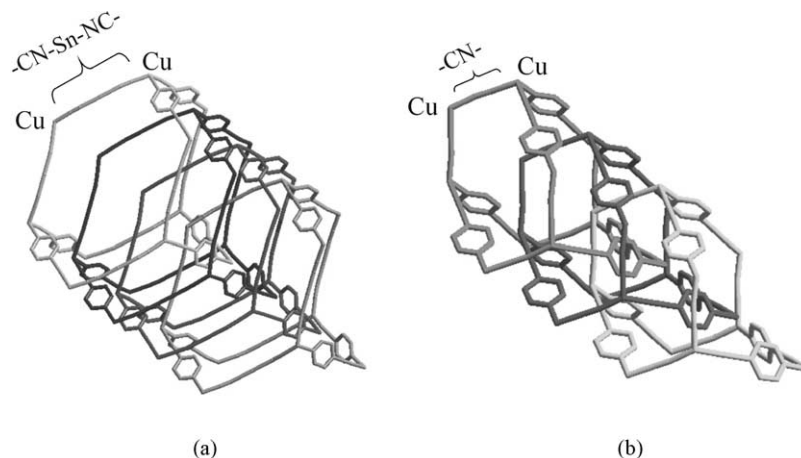


Fig. 5. (a) Four interpenetrating, distorted-adamandoid cages of **4**; (b) three interpenetrating, distorted-adamandoid cages of ${}^3_\infty[\text{CuCN}\cdot\text{cpy}]$ [24]. In (a), all $\text{CN-Sn}(\text{Me}_3)\text{-NC}$ bridges are simplified to linear rods.

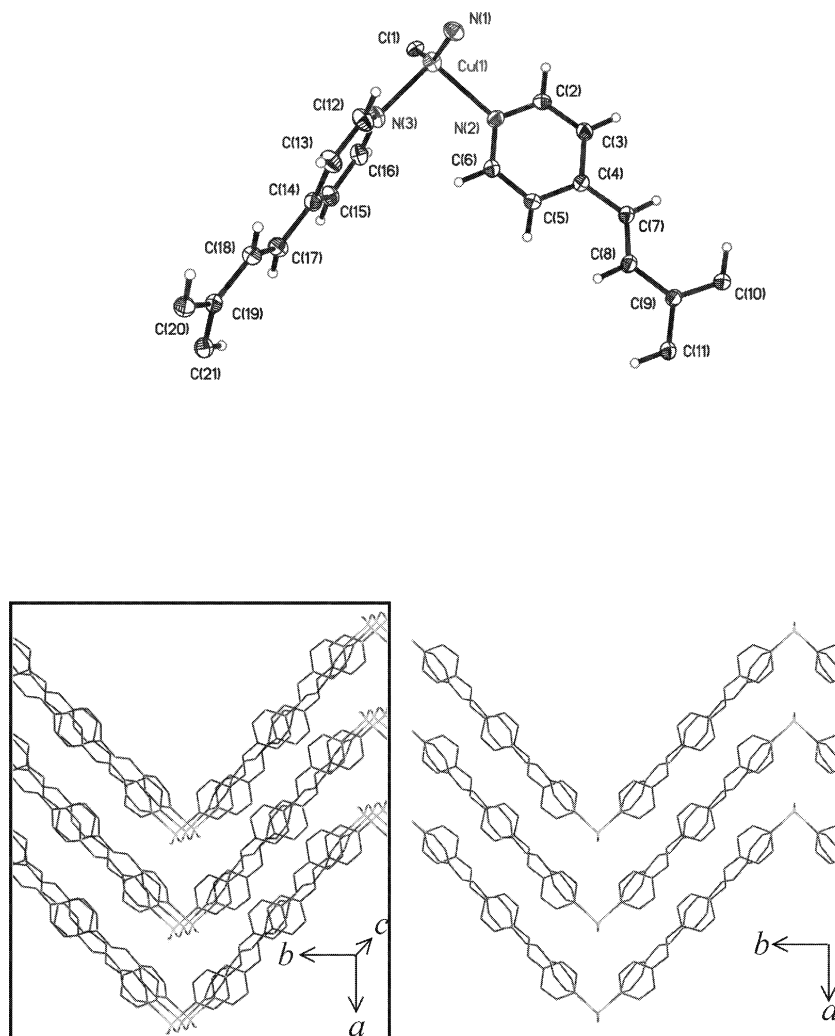


Fig. 6. Top: asymmetric unit of **5**; bottom: view along *c* parallel to the strongly corrugated sheets. The left-hand side presents the layers in a slightly more perspective view.

spatial expansion of which ranges from bpe down to pym (pyrimidine). Quite surprisingly, V_f values around 200 \AA^3 result not only for this particular family, but also for assemblies of the composition ${}^\infty[\text{Cu}^{\text{I}}(\mu_3\text{-L}^{(1)})(\mu_2\text{-L}^{(2)})_{0.5}]$ (including thus the sub-group *F–J*), wherein $\text{L}^{(1)}$ contains one bifurcated cyanide group. It is worth noting that V_f values of again constantly ca. 200 \AA^3 are arrived at, although within the slightly larger manifold *D–J* an impressive variety of different supramolecular architectures is realized.

When, on the other hand, $\text{L}^{(1)}$ becomes a common (i.e. ‘linear’) cyanide bridge, the V_f value turns out to be definitely lower than 150 \AA^3 (see the manifold *N–S*). Interestingly, the V_f value of the host/guest system ${}^\infty[2\text{bpy} \leftarrow \text{CuCN} \cdot \text{bpy}]$ (devoid of self-catenation [11]) is as high as 423 \AA^3 , whereas for the hypothetical, guest-free assembly ${}^\infty[\text{CuCN} \cdot \text{bpy}]$ with three interpenetrating frameworks $V_f = 140$ would be expected (alternative: $V_f = 105$ for $\text{NF} = 4$). The notably larger (than ca. 200 \AA^3) V_f values of the series *A–C* seem to indicate that

also a departure from the comparatively slim five-atomic connectors $\text{L}^{(1)}$ (vide supra) results in a considerable increase of the space demand, although the $\text{Cu} \cdots \text{Cu}$ distance with $\mu\text{-L}^{(1)} = \text{bpy}$ as spacer exceeds that with $\text{L}^{(1)} = \text{CNSn}(\text{Me}_3)\text{NC}$ only by ca. 0.3 \AA .

6. Concluding remarks: evidence of cuprophilicity?

The discussion of the data presented in Table 4 (vide supra) might suggest that the frequently resulting V_f value of about 200 \AA^3 reflects, for the comparatively large group of compounds *D–M*, throughout particularly favourable packing conditions. However, compounds of the sub-group *F–J* of the stoichiometry $[\text{Cu}(\mu_3\text{-L}^{(1)})(\mu_2\text{-L}^{(2)})_{0.5}]$ could, in principle, adopt structures with slightly lower V_f values if (as is in fact the case for the species *C* and *N*) strictly three-coordinate $\text{Cu}(\text{I})$ were realized. Driving forces different from optimal ‘molecular’ packing are therefore more likely to explain

Table 3
Selected bond angles (°) of the compounds **2** and **3**

Angle (°)	2 (L = dpe)	3 (L = dpeH ₂)
Cu1–C1–Cu2	73.45(11)	72.36(10)
Cu1–C4–Cu2	72.95(10)	72.55(10)
C3–Cu1–N7	114.87(13)	113.20(12)
C2–Cu2–N6	116.12(13)	113.06(12)
Cu1–C1–N1	170.4(3)	165.0(3)
Cu2–C4–N4	168.2(3)	167.3(3)
C1–N1–Sn1	168.1(3)	172.1(3)
C4–N4–Sn2	173.9(3)	167.1(3)
N1–Sn1–N3	174.01(11)	176.39(11)
N4–Sn2–N2	176.52(12)	175.20(11)
Sn1–N3–C3	150.8(3)	161.6(3)
Sn2–N2–C2	166.8(3)	147.6(3)
N3–C3–Cu1	173.0(3)	176.0(3)
N2–C2–Cu2	175.6(3)	171.8(3)

the preference for {Cu₂(μ-CN)₂} building blocks as displayed by the manifold *F–J*, wherein the coordination number may be considered as intermediate between 3 and 4.

In view of the presently lively discussion of cuprophilic interactions [30–32], one might also argue that the

formation of a {Cu₂(μ-CN)₂} rhomb could be triggered primarily by some weak, but non-negligible Cu···Cu attraction. Since, according to a detailed quantum chemical study [22] focused on pairs of Cu^IXY systems (with a coordination number of 2), faint Cu···Cu attraction (about three times weaker than aurophilic forces) seems to be realistic, the potential cuprophilicity also of Cu^IXYZ pairs (coordination number 3) deserves increasing interest. So far, the Cu···Cu distance found in {Cu₂(μ-CN)₂} rhombs ranges from 2.307 Å (every Cu(I) ion being here also chelated by a tetramethylethylenediamine ligand [9]) to 2.758 Å in compound **2** (vide supra). The longer of the Cu–C distances within the rhomb varies between 2.129 Å (in [CuCN·NH₃] [1]) and 2.617 Å in **2**.

As the experimentally confirmed Cu···Cu distances of established examples in favour of cuprophilic attraction are usually longer than 2.7 Å [30–32] it might be counter-argued that the usually shorter Cu···Cu distances in the {Cu₂(μ-CN)₂} rhombs are ‘obviously’ due to efficient bridging. However, the unsymmetrical CN bridges of **1**, **2** and **3** (see Tables 2 and 3) differ strongly e.g. from the practically symmetric aryethylnyl bridge between two Cu(I) centres (for Ar = C₆H₅, Cu–C =

Table 4
Formula volume, *V_f*, of coordination polymers with diverse layered or 3D framework structures of the general type $n_c[\text{Cu}^{\text{I}}(\mu\text{-L}^{(1)})_p(\mu\text{-L}^{(2)})_q]$ ($p+q \leq 2$)

Compound ^a	<i>V_f</i> (Å ³)	NF ^b	<i>n</i> D	Node	Ref.
<i>A</i> [Cu(bpe) ₂ (BF ₄)·0.5CH ₂ Cl ₂]	392	5	3D	Cu(I) ^c	[28]
<i>B</i> [Cu(bpy) ₂ (PF ₆)]	319	4	3D	Cu(I) ^c	[29]
<i>C</i> [Cu(bpy) _{1.5} (NO ₃)·1.25H ₂ O]	241	6	3D	Cu(I) ^c	[21]
<i>D</i> α-[Cu(dca)(bpe)] ^f	206	2	2D	Cu(I) ^c	[26]
<i>E</i> β-[Cu(dca)(bpe)] ^f	201	5	3D	Cu(I) ^c	[26]
<i>F</i> [CuCN·Me ₃ SnCN·0.5bpeH ₂] ^g (3)	209	–	2D	Cu(I)-pair ^d	This work
<i>G</i> [CuCN·Me ₃ SnCN·0.5bpe] ^g (2)	207	–	2–D	Cu(I)-pair ^d	This work
<i>H</i> [(CuCN) ₂ ·bpe] ^h	206	2	3D	Cu(I)-pair ^d	[12]
<i>I</i> [CuCN·Me ₃ SnCN·0.5bpy] ^g (1)	210	2	3D	Cu(I)-pair ^d	[7]
<i>J</i> [(CuCN) ₂ ·bpy] ^h	183	2	3D	Cu(I)-pair ^d	[11,12]
<i>K</i> [CuCN·Me ₃ SnCN·cpy] ^g (4)	218	4	3D	Cu(I) ^c	This work
<i>L</i> [CuCN·Me ₃ SnCN·pyz] ^{g,i}	199	3	3D	Cu(I) ^c	[16]
<i>M</i> [CuCN·Me ₃ SnCN·pym] ^{g,i}	200	–	2D	Cu(I) ^c	[17]
<i>N</i> [Cu(pyz) _{1.5} (SiF ₆) ⁱ	138	2	2D	Cu(I) ^c	[29]
<i>O</i> [CuCN·cpy]	104	3	3D	Cu(I) ^c	[24]
<i>P</i> [CuCN·Mepyz] ^{ij}	103	2	3D	Cu(I) ^c	[10]
<i>Q</i> [CuCN·0.5Mepyz] ⁱ	67	–	3D	Cu(I)-pair ^d	[10,12]
<i>R</i> [CuCN·N ₂ H ₂]	51	–	2D	Cu(I) ^c	[25]
<i>S</i> [CuCN·NH ₃]	46	–	2D	Cu(I)-pair ^c	[1]

^a To avoid confusion, formulae as found in the literature have been retained in the table; for the specification of the less comprehensively formulated metal connectors (L⁽¹⁾) see the following footnotes.

^b Number of interpenetrating frameworks.

^c With coordination number (CON) four (exceptions with CON 3: species C and N only).

^d Six-connected [Cu₂(μ-CN)₂] building blocks.

^e Four-connected [Cu₂(μ-CN)₂] unit.

^f dca = dicyanamide anion.

^g Containing the anionic –CNSn(Me₃)NC– bridge.

^h Containing the anionic CNCuCN[–] bridge.

ⁱ pyz = pyrazine, pym = pyrimidine, Mepyz = methylpyrazine, cpy = 4-cyanopyridine.

^j For L⁽²⁾ = pyz [27], *V_f* = 96 Å³. For L⁽²⁾ = 2,5-Me₂pyz [12], *V_f* = 68 Å³.

2.014 and 2.022 Å, Cu...Cu = 2.386 Å [33]). Even within the $\{M\text{Cu}^I(\mu\text{-CCR})_2\}$ core of so-called ‘ π -tweezer’ complexes, the coordinative Cu- η^2 -C₂ bond is much stronger (with Cu...C distances $\ll 2.3$ Å) than in **1–3** [34]. Interestingly, a $\{\text{Cu}_2(\mu\text{-C})_2\}$ rhomb is also realized in the dimeric complex $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{CCSiMe}_3)(\text{CCCu})_2]$ [35]. Here, two Ti-CC-Cu fragments are fused together instead of two Sn-NC-Cu entities as in **1–3**, however, the pronounced dihapto coordination of each Cu(I) ion in the tweezer derivative (Cu...C: 2.107 and 2.161 Å) prevents that the two Cu(I) ions come close together (Cu...Cu: 2.998 Å).

Actually, the ‘nonlinear’ (or ‘bifurcated’) cyanide bridge is hardly met outside assemblies involving dinuclear $\{\text{Cu}_2(\mu\text{-CN})_2\}$ fragments, and it might be speculated somewhat provocatively that the asymmetric CN bridge would be rather a consequence of cuprophilicity than the primary cause of comparatively short Cu...Cu distances. Theoretical studies would probably be most promising to answer those still open questions, and the meanwhile rich collection of structural data on crystallographically established $\{\text{Cu}_2(\mu\text{-CN})_2\}$ rhombs [1–13] could be helpful, e.g. for the gauging of distinct exploratory steps in a series of model calculations.

7. Experimental

All preparative and analytical work was carried out under normal atmosphere. Elemental analyses were conducted on a Heraeus CHN-O-Rapid analyser. Infrared spectra were run on a Perkin Elmer IR-683 spectrometer (KBr pellets) and the X-ray powder diffractogram of polycrystalline **4** on a Bruker Advance D 8 diffractometer (Cu-K_α source and Ni filter).

7.1. Preparation of $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{dpe}]$ (**2**)

Under exclusion of light, a solution of 90 mg (0.31 mmol) of K₃[Cu(CN)₄] in 10 ml of H₂O was added, under gentle stirring (for ca. 1 h), to a solution of 189 mg (0.95 mmol) of Me₃SnCl and 57.5 mg (0.31 mmol) of *trans*-1,2-bis(4-pyridyl)-ethene (bpe) in ca. 20 ml of hot acetonitrile. After 2 weeks, both yellow needles and a smaller portion of orange crystals had resulted. After filtration, subsequent washing with small portions of water and overnight drying at room temperature (r.t.), about 60 mg of the yellow crystalline product were obtained (yield referred to K₃[Cu(CN)₄]: 52.3%). Anal. Calc. for C₁₁H₁₄CuN₃Sn: C, 35.66; H, 3.809; N, 11.34. Found C, 35.77; H, 3.98; N, 11.47%. IR spectrum (cm⁻¹): 2105s (νCN), 552s (νSnC). Characteristic bands of dpe (cm⁻¹): 2997m, 1604s, 1499m, 1426s, 819s, 782s.

7.2. Preparation of $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot 0.5\text{dpeH}_2]$ (**3**)

The same procedure as for the preparation of **2** (although without exclusion of light) was adopted. K₃[Cu(CN)₄]: 180 mg (0.63 mmol) in 10 ml of H₂O; Me₃SnCl: 378 mg (1.9 mmol) and 1,2-bis(4-pyridyl)-ethane (bpeH₂): 116 mg (0.63 mmol) in 20 ml of acetonitrile. Already after some days, white crystals started growing from the initially clear solution. After filtration, washing with small, cold quantities of H₂O and MeCN and overnight drying, 144 mg (yield referred to K₃[Cu(CN)₄]: 61.5%) of the white crystals were obtained. Anal. Calc. for C₁₁H₁₅CuN₃Sn: C, 35.56; H, 4.07; N, 11.31. Found C, 35.71; H, 4.33; N, 11.55%. IR spectrum (cm⁻¹): 2102s (νCN), 550s (νSnC). Bands of dpeH₂: 2999m, 1610s, 1450m, 1425s, 827s, 785s.

7.3. Preparation of $[\text{CuCN}\cdot\text{Me}_3\text{SnCN}\cdot\text{cpy}]$ (**4**)

A clear solution of 392 mg (1.960 mmol) of Me₃SnCl and 102 mg (0.983 mmol) of 4-cyanopyridine (cpy) in ca. 2.2 ml of H₂O was added to a solution of 187 mg (0.655 mmol) of K₃[Cu(CN)₄] in ca. 2 ml of H₂O. After intense stirring (ca. 10 min), filtration, washing (cold H₂O) and drying at r.t., 70 mg of a yellow polycrystalline product (yield: 30% referred to K₃[Cu(CN)₄] were isolated. Anal. Calc. for C₁₁H₁₃CuN₄Sn: C, 34.45; H, 3.417; N, 14.61. Found C, 34.04; H, 3.45; N, 14.43%. IR (cm⁻¹): 2119s, 2105vs, 2066s (νCN), 556 (νSnC). From the filtrate, well-shaped orange crystals (identified as [CuCN·cpy] by X-ray crystallography) deposited at room temperature after 4 weeks.

7.4. Preparation of $[\text{CuCN}\cdot\text{pdvb}]$ (**5**)

A solution of 45 mg (0.158 mmol) of K₃[Cu(CN)₄] in 10 ml of H₂O was added to a mixture of 45 mg (0.158 mmol) of bis(4-pyridyl)-*trans*-1,4-divinylbenzene (pdvb) and 95 mg (0.475 mmol) of Me₃SnCl dissolved in 55 ml of warm acetonitrile. To dissolve the nitrogen base completely, part of the solvent (45 ml of MeCN) was briefly heated up to its boiling point. The finally clear, yellow solution was kept at r.t. for 10 days. Deep brown crystals could then be isolated after filtration, washing with small quantities of cold H₂O–MeCN and overnight drying at r.t. Anal. Calc. for C₂₁H₁₆CuN₃: C, 67.45; H, 4.313; N, 11.23. Found C, 67.16; H, 4.46; N, 11.26%. IR spectrum (cm⁻¹): 2095s (νCN), 452s (νCuC); vibrational modes of pdvb: 3047m, 2988m, 1598s, 1531s, 1480s, 1427s, 728s, 694s. All crystallization experiments according to route 2 (vide supra) were conducted as described earlier [14,15].

Crystal structure determinations of **2–5** and [CuCN·cpy] were performed using a Bruker axis Smart-CCD diffractometer (Mo-K_α source and graphite monochromator). Absorption correction based on symmetry

equivalent reflections using the SADABS program were accounted for instantaneously by the Smart-CCD diffractometer. All structures were solved and refined with SHELXTL (for Windows). For structure visualizations, either the CERIUS² V 4.0 or the Mercury 1.1 software was applied.

8. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 207242, 207241, 207244 and 207243 for compounds **2**, **3**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

Part of this work has been a spin-off resulting from the DFG-supported Priority Programme on Nanostructured Host/Guest Systems (1997–2002). The authors are grateful to Mrs. S. Samba for valuable technical assistance.

References

- [1] D.T. Cromer, A.C. Larson, R.B. Roof, Jr, *Acta Crystallogr.* 19 (1965) 192.
- [2] J.D. Kildea, B.W. Skelton, A.H. White, *Aust. J. Chem.* 38 (1985) 1329.
- [3] S.-H. Peng, D.-S. Liaw, *Inorg. Chim. Acta* 113 (1986) L11.
- [4] J. Cernák, K. Györyová, S. Sabolová, M. Dunaj-Jurco, *Inorg. Chim. Acta* 185 (1991) 119.
- [5] S.-I. Nishikiori, T. Iwamoto, *Chem. Lett.* (1994) 1199.
- [6] M. Schwarten, J. Chomic, J. Cernák, D. Babel, *Z. Anorg. Allg. Chem.* 622 (1996) 1449.
- [7] A.M.A. Ibrahim, E. Siebel, R.D. Fischer, *Inorg. Chem.* 37 (1998) 3521.
- [8] H. Yuge, T. Iwamoto, *J. Incl. Phenom. Mol. Recogn. Chem.* 26 (1996) 119.
- [9] F.B. Stocker, T.D. Staeva, C.M. Rienstra, D. Britton, *Inorg. Chem.* 38 (1999) 984.
- [10] O. Teichert, W.S. Sheldrick, *Z. Anorg. Allg. Chem.* 625 (1999) 1860.
- [11] O. Teichert, W.S. Sheldrick, *Z. Anorg. Allg. Chem.* 626 (2000) 1509.
- [12] D.C. Chesnut, D. Plewak, J. Zubieta, *J. Chem. Soc. Dalton Trans.* (2001) 2567.
- [13] C.P. Cui, P. Lin, W.-X. Du, L.-M. Wu, Z.-Y. Fu, J.-C. Dai, S.M. Hu, X.-T. Wu, *Inorg. Chem. Commun.* 4 (2001) 444.
- [14] R. Eckhardt, R.D. Fischer, *Inorg. Chem. Commun.* 3 (2000) 433.
- [15] R. Eckhardt, H. Hanika-Heidl, R.D. Fischer, *Chem. Eur. J.* 9 (2003) 1795.
- [16] E. Siebel, A.M.A. Ibrahim, R.D. Fischer, *Inorg. Chem.* 38 (1999) 2530.
- [17] E. Siebel, Doctoral dissertation, University of Hamburg, Germany, 1998.
- [18] R.D. Fischer, H. Hanika-Heidl, R. Eckhardt, in: F. Laeri, F. Schüth, U. Simon, M. Wark (Eds.), *Nanoporous Crystals*, Ch. 12, Wiley-VCH, Weinheim, 2003.
- [19] J.T.B.H. Jastrzebski, G. van Koten, *Adv. Organomet. Chem.* 35 (1993) 241.
- [20] P.G. Harrison, T.J. King, K.C. Molloy, *J. Organomet. Chem.* 185 (1980) 199.
- [21] O.M. Yaghi, H. Li, *J. Am. Chem. Soc.* 117 (1995) 10401.
- [22] H.L. Hermann, G. Boche, P. Schwerdtfeger, *Chem. Eur. J.* 7 (2001) 5333.
- [23] Crystallographic data for [CuCN·cpy]: C₇H₄CuN₃, *M_r* = 193.67, orthorhombic, space group *P*2₁2₁2₁, *a* = 6.0867(2), *b* = 8.4309(3), *c* = 13.4760(5) Å; *V* = 691.54(4) Å³, *Z* = 4, *ρ*_{calc} = 1.860 g cm⁻³, *R*₁ for *I* ≥ 2σ(*I*): 0.0311, *wR*₂ = 0.0955, *T* = 153 K.
- [24] D.T. Cromer, A.C. Larson, *Acta Crystallogr. Ser. B* 28 (1972) 105.
- [25] D.T. Cromer, A.C. Larson, R.B. Roof, Jr, *Acta Crystallogr.* 20 (1966) 279.
- [26] S.R. Batten, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell, *J. Chem. Soc. Dalton Trans.* (2000) 3829.
- [27] R. Kuhlmann, G.L. Schimek, J.W. Kolis, *Polyhedron* 18 (1999) 1379.
- [28] A.J. Blake, N.R. Champness, S.S.M. Chung, W.-S. Li, M. Schröder, *J. Chem. Soc. Chem. Commun.* (1997) 1005.
- [29] L.R. McGillivray, S. Subramanian, M.J. Zaworotko, *J. Chem. Soc. Chem. Commun.* (1994) 1325.
- [30] G. Boche, F. Bosold, M. Marsch, K. Harms, *Angew. Chem.* 110 (1998) 1778; *Angew. Chem. Int. Ed. Engl.* 37 (1998) 1684.
- [31] C.-M. Che, Z. Mao, V.M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D.L. Phillips, K.-H. Leung, *Angew. Chem.* 112 (2000) 4250; *Angew. Chem. Int. Ed. Engl.* 39 (2000) 4084.
- [32] R.D. Köhn, G. Seifert, Z. Pan, M.F. Mahon, G. Koziok-Köhn, *Angew. Chem.* 115 (2003) 818; *Angew. Chem. Int. Ed. Engl.* 42 (2003) 793.
- [33] F. Olbrich, U. Behrens, E. Weiss, *J. Organomet. Chem.* 472 (1994) 365.
- [34] H. Lang, D.S.A. George, G. Rheinwald, *Coord. Chem. Rev.* 206-207 (2000) 101.
- [35] M.D. Janssen, M. Herres, L. Zsolnai, D.M. Grove, A.L. Spek, H. Lang, G. van Koten, *Organometallics* 14 (1995) 1098.