DALTON
FULL PAPER

Two- and three-dimensional CuSCN co-ordination networks including new CuSCN structural motifs

Alexander J. Blake,[a] Neil R. Brooks,[a] Neil R. Champness,*[a] Marcello Crew,[a] Lyall R. Hanton,[b] Peter Hubberstey,[a] Simon Parsons[c] and Martin Schröder*[a]

[a] *School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD*
[b] *Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand*
[c] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

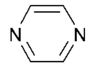
Received 22nd April 1999, Accepted 30th June 1999

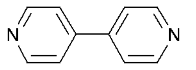
The reaction of CuSCN with linear bridging N-donor ligands afforded two- and three-dimensional networks depending on the ligand used. Reaction of two equivalents of CuSCN with one equivalent of pyrazine in ethanol and aqueous ammonia afforded the three-dimensional network $[Cu_2(SCN)_2(pyz)]_\infty$. Replacing pyrazine with 4,4′-bipyridyl under the same conditions gave a different three-dimensional network $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$. In contrast two-dimensional sheets of $[Cu_2(SCN)_2(bpe)]_\infty$ (bpe = 1,2-*trans*-(4-pyridyl)ethene) were isolated from the reaction of CuSCN with bpe in a 2:1 ratio. The structures of both $[Cu_2(SCN)_2(pyz)]_\infty$ and $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$ are constructed from $(CuSCN)_\infty$ layers linked in a herringbone fashion by the bridging N-donor ligands to afford three-dimensional networks. The complex $[Cu_2(SCN)_2(bpe)]_\infty$, however, shows two-dimensional sheets which are formed from $(CuSCN)_\infty$ stair-polymers bridged by bpe ligands.

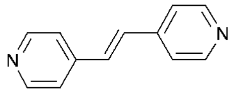
The development of inorganic supramolecular architectures is a rapidly developing area of research that has implications for the rational design of functional materials.[1,2] This work has been driven by the diversity of network topologies that can be accessed by exploiting the variety of co-ordination geometries adopted by transition metal centres. The structural motifs formed by these supramolecular arrays can, to a certain extent, be predicted and this has led to the development of a wide variety of architectures including adamantoid,[3,4] cubic,[5] ladder,[6] honeycomb[7] and helical staircase.[8,9] Although the structure is predominantly controlled by the co-ordination preferences of the transition metal and the ligand building blocks, more subtle effects such as anion control[8,10] and the use of π–π stacking[4] have been seen to have a profound effect upon network topology.

We are using a building-block approach for the construction of co-ordination polymers illustrating both the importance of metal-ion geometry and the effect that variation of ligand backbone can have on network construction.[2] This has been illustrated in copper(I) adamantoid networks in which the degree of interpenetration can be controlled by varying the length and bulk of the bridging ligand.[3,4] We have also demonstrated that the counter anion present can have a remarkable effect on the topology of the system. This has been clearly demonstrated by the helical staircase motif formed by $\{[Ag(4\text{-pytz})]NO_3\}_\infty$ [4-pytz = 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine] which contrasts with the linear chains observed for the BF_4^- and PF_6^- analogues.[8] Bearing in mind the dependence of network topology on anion, we have been investigating the use of strongly co-ordinating anions within extended networks.[11,12] This in effect incorporates the anion as an essential structural element of the network frame. This strategy will ultimately lead to uncharged arrays in which channels remain unblocked by anions and free for guest inclusion. Upon considering their rich structural chemistry, particularly suitable building-blocks for this approach are Cu^IX (X = Cl, Br or I),[7,13] Cu^ISCN and Cu^ICN.[13]

We have recently reported a three-dimensional network based on CuSCN which incorporates a new undulating layer motif for CuSCN.[11] Simple step structures and one-dimensional chains have been observed in complexes of CuSCN.[14,15] A limited number of structural motifs are known for CuSCN itself, including the three-dimensional α[16] and β[17] forms, as well as the $\{[Cu_2(SCN)_3]^-\}_\infty$ anionic lattice.[18] We report herein the synthesis of two- and three-dimensional lattices formed between CuSCN and bridging bipyridyl ligands. Variation of ligand length gives rise to different CuSCN motifs and network topologies. The structure of $[Cu_2(SCN)_2(pyz)]_\infty$ **1** (pyz = pyrazine) has been previously communicated.[11]


pyrazine (pyz)


4,4′-bipyridine (4,4′-bipy)


1,2-*trans*-(4-pyridyl)ethene (bpe)

Results and discussion

The complexes $[Cu_2(SCN)_2(L)]_\infty$ {L = pyz **1**, 4,4′-bipy **2** or *trans*-1,2-bis(4-pyridyl)ethene (bpe) **3**} were prepared as orange powders by the addition of a deoxygenated solution of the ligand in EtOH to a deoxygenated dilute aqueous ammoniacal solution of CuSCN. The products are insoluble in all common organic solvents and stable in air for periods of months. In order to determine the long-range structure and network topology, single-crystal X-ray diffraction studies were undertaken. Single crystals of all the compounds investigated were grown by slow diffusion of layered solutions of CuSCN in dilute aqueous ammonia and the ligand in EtOH under an argon atmosphere. Over a period of a week orange tablets formed at the solvent interface. Attempts to prepare com-

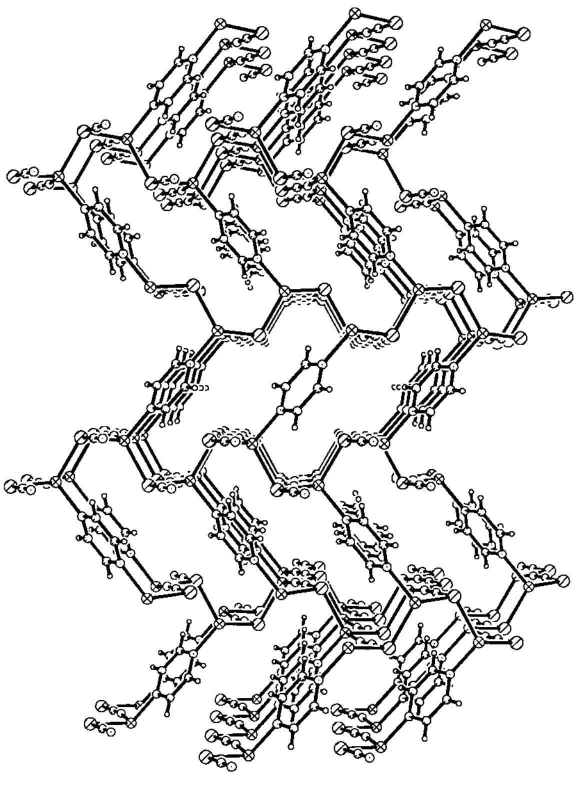
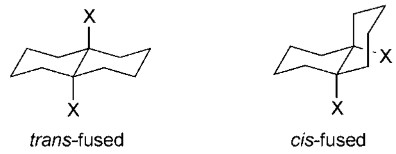


Fig. 1 A view of the structure of $[Cu_2(SCN)_2(pyz)]_\infty$ **1** showing the herringbone pattern of the pyrazine bridges.

pounds with a 1 : 1 Cu : L ratio produced only $[Cu_2(SCN)_2(L)]_\infty$ but in lower yield.

Structures of $[Cu_2(SCN)_2(pyz)]_\infty$ 1 and $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$ 2

The complexes $[Cu_2(SCN)_2(pyz)]_\infty$ **1** and $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$ **2** exist as three-dimensional networks consisting of $(CuSCN)_\infty$ layers linked by N-donor bridges (Figs. 1 and 2 respectively). In both cases each copper(I) centre is co-ordinated by three (μ-S, N) thiocyanate ligands and an aromatic N-donor ligand (Fig. 3a and 3b respectively). Selected bond lengths and angles are shown in Table 1. This arrangement leads to the formation of ten-membered Cu–S–Cu–NCS–Cu–SCN rings. Assuming the rigid rod-like SCN^- ligand to be a single centre, each ring can be considered to adopt a pseudo-chair conformation. Rings are fused to give a honeycomb layer analogous to that observed in black phosphorus. The rings are joined to each other in two different ways, *cis* or *trans*, just as observed for the two-fused cyclohexane rings in the two isomers of decalin (Scheme 1). The nature of the fusion between adjacent ten-membered rings is different between compounds **1** and **2**. In $[Cu_2(SCN)_2(pyz)]_\infty$ **1** the rings are *cis*-fused through the SCNCu "edges" (Fig. 4a) whereas in $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$ **2** the rings are *trans*-fused through the SCNCu "edges" (Fig. 4b). In both cases the propagation of this fusion gives rise to an undulating layer (Figs. 1 and 2). Although ten-membered rings exist in the α-[12] and β-modifications[13] of CuSCN or $\{[Cu_2(SCN)_3]^-\}_\infty$[14] the layers formed in these structures are not the same as those observed in $[Cu_2(SCN)_2(L)]_\infty$. The remaining fourth co-ordination site of each tetrahedral copper(I) centre is occupied by pyrazine (in **1**) or 4,4′-bipy (in **2**) which bridge adjacent sheets (Figs. 1 and 2). For each $(CuSCN)_\infty$ layer the available co-ordination sites are arranged such that on one face all the sites are axial with respect to the ten-membered ring while on the other they are all equatorial. Adjacent sheets are linked by the N-donor ligands in an axial–axial and equatorial–equatorial manner giving rise to a herringbone pattern (Figs. 1 and 2).



Scheme 1 The *cis* and *trans* fusion as observed between six-membered rings in decalin.

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1**–**3**

	1	**2**	**3**
Cu–S(1)	2.349(2)	2.3549(13)	2.5171(9)
Cu–S(1^{i})	2.338(2)	2.3549(13)	2.4203(8)
Cu–N(4)	1.940(4)	2.057(5)	1.999(2)
Cu–N(3^{ii})	2.047(4)	1.944(5)	1.9362(13)
N(3^{ii})–Cu(1)–N(4)	112.4(2)	107.4(2)	130.53(6)
N(3^{ii})–Cu(1)–S(1)	106.69(13)	117.04(8)	102.05(5)
N(3^{ii})–Cu(1)–S(1^{i})	107.96(14)	117.04(8)	104.04(5)
N(4)–Cu(1)–S(1)	109.31(11)	108.2(2)	100.01(5)
N(4)–Cu(1)–S(1^{i})	105.83(11)	99.9(2)	109.42(6)
S(1)–Cu(1)–S(1^{i})	114.75(5)	105.72(8)	109.33(3)

Symmetry transformations: **1**, i x, $1\frac{1}{2} - y$, $\frac{1}{2} + z$; ii $x - 1$, y, z; **2**, i x, y, $z + 1$; ii $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z + \frac{1}{2}$; **3**, i $-x$, $-y$, $-z$; ii $-x + 1$, $-y$, $-z$.

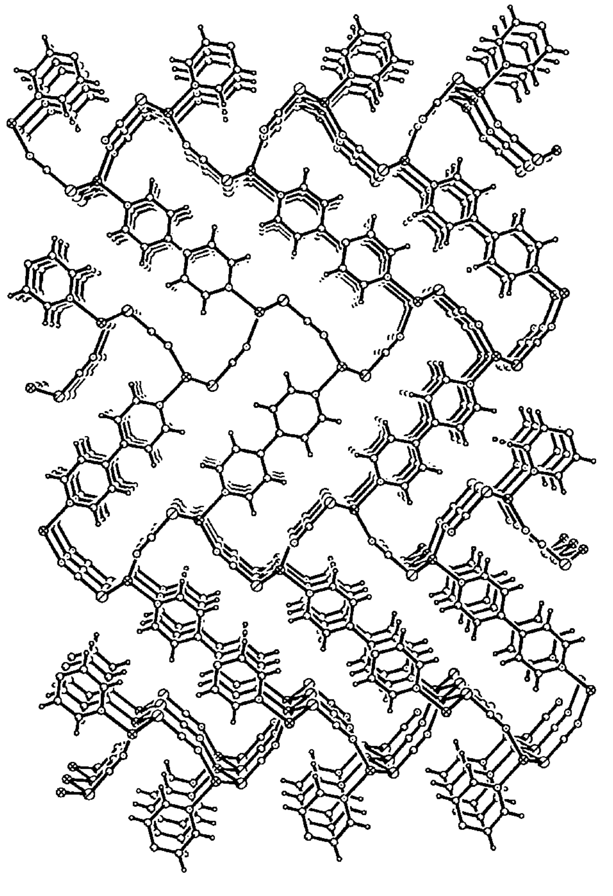


Fig. 2 A view of the structure of $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$ **2** contrasting the undulating nature of the $[CuSCN]_\infty$ sheet with that observed in $[Cu_2(SCN)_2(pyz)]_\infty$ **1**.

The structures of complexes **1** and **2** are related to that of $[Cu(SCN)(py)]_\infty$[19] which consists of $(CuSCN)_\infty$ layers capped by pyridine donor ligands. The $(CuSCN)_\infty$ layers in $[Cu(SCN)(py)]_\infty$ also consist of ten-membered Cu–S–Cu–NCS–Cu–SCN rings, but the layer adopts the conformation that is observed in β-CuSCN.[17] This results in all the vacant co-ordination sites on the copper(I) centres lying on the same face of the $(CuSCN)_\infty$ layer. This is in contrast to the structures of **1** and **2** where the

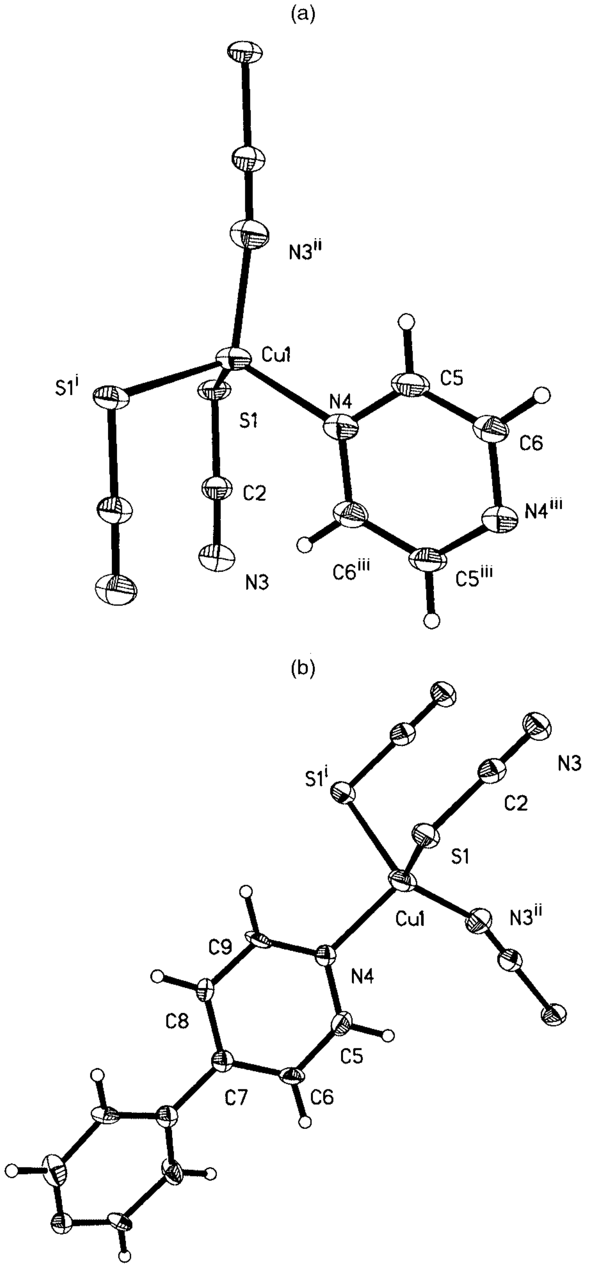


Fig. 3 Views of the copper(I) co-ordination environment in (a) [Cu$_2$(SCN)$_2$(pyz)]$_\infty$ **1**, illustrating the numbering scheme used. (Displacement ellipsoids are drawn at the 50% probability level; symmetry codes i x, 1½ − y, ½ + z; ii x − 1, y, z; iii 2 − x, 1 − y, 1 − z) and (b) [Cu$_2$(SCN)$_2$(4,4′-bipy)]$_\infty$ **2** (symmetry codes i x, y, 1 + z; ii x − ½, ½ − y, ½ + z).

(CuSCN)$_\infty$ layers are arranged so that the vacant copper(I) co-ordination sites are arranged on opposing faces of every (CuSCN)$_\infty$ unit so that the N-donor ligands may link adjacent layers. This results in the unusual conformations of the (CuSCN)$_\infty$ layers observed in **1** and **2** which appear to be a direct result of the bridging nature of the pyrazine and 4,4-bipy ligands.

Structure of [Cu$_2$(SCN)$_2$(bpe)]$_\infty$ 3

In contrast to complexes **1** and **2**, [Cu$_2$(SCN)$_2$(bpe)]$_\infty$ **3** forms two-dimensional sheets in the solid state (Fig. 5). These sheets are formed by [Cu(SCN)]$_\infty$ stair-polymers which are linked by bridging bpe ligands. As in **1** and **2** each copper(I) centre in **3** is co-ordinated by three (μ-S, N) thiocyanate ligands and by one pyridyl donor (Fig. 6). See Table 1 for selected bond lengths and angles. Adjacent sheets are closely packed with the shortest distance being an inter-sheet S · · · H separation of 2.935 Å and are staggered so that the [Cu(SCN)]$_\infty$ stair-polymers sit perpendicularly above bpe ligands in adjacent sheets and are stacked diagonally along the b axis. The structure of the [Cu$_2$(SCN)$_2$(bpe)]$_\infty$ two-dimensional sheet is related to that observed for copper(I) halides with pyrazine[20] or 4,4′-bipyridyl related ligands in which copper(I) halide stair-polymers are also observed.[12,21,22]

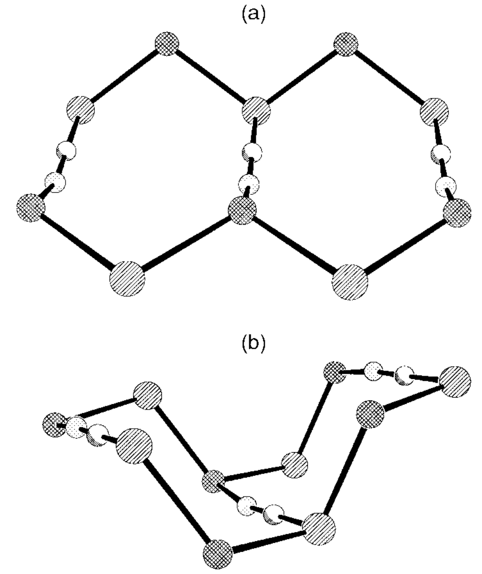


Fig. 4 Cu–S–Cu–NCS–Cu–SCN Rings *cis*-fused through the SCNCu "edges" in [Cu$_2$(SCN)$_2$(pyz)]$_\infty$ **1** (a) and *trans*-fused in [Cu$_2$(SCN)$_2$(4,4′-bipy)]$_\infty$ **2** (b) (copper, cross-hatched; sulfur, hatched; nitrogen, dotted; carbon, plain).

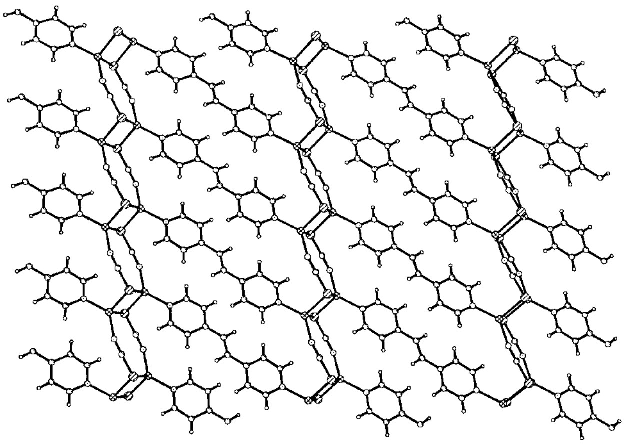


Fig. 5 A view of the two-dimensional sheet formed by [Cu$_2$(SCN)$_2$(bpe)]$_\infty$ **3** showing the [CuSCN]$_\infty$ step-polymers linked by the bpe ligands (copper, cross-hatched; sulfur, hatched; nitrogen, dotted; carbon, plain).

The stair-polymer arrangement observed in this complex has been observed before for [Cu(SCN)(NC$_5$H$_4$Me-2)]$_\infty$[14] and [Cu(SCN)(NC$_9$H$_7$)]$_\infty$ (NC$_9$H$_7$ = quinoline).[15] The bond lengths and angles at the copper(I) centre in **3** are typical of the values expected for a stair-polymer[14,15] but it can be seen that there are slight differences to those observed for **1** and **2**. In particular there is a significant lengthening of the Cu–S bond lengths from 2.338(2), 2.349(2) Å in **1**, 2.3549(13) Å in **2**, to 2.4203(8), 2.5172(8) Å in **3**. This is indicative of increased strain in the (CuSCN)$_\infty$ stair-polymer of **3** compared to the (CuSCN)$_\infty$ layers in **1** and **2**. This can be accounted for by the presence of fused four-membered Cu–S–Cu–S rings and eight-membered Cu–NCS–Cu–NCS rings, necessitated by the stair-polymer, compared with less strained ten-membered Cu–S–Cu–NCS–Cu–SCN rings observed in the (CuSCN)$_\infty$ layers.

Copper(I) halides exhibit a wide range of different forms

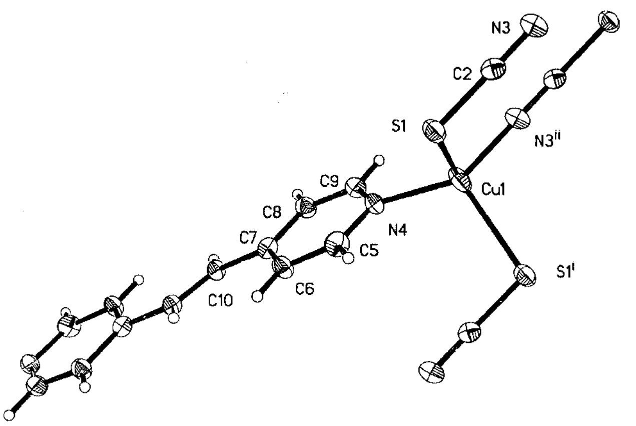


Fig. 6 A view of the copper(I) co-ordination environment in $[Cu_2(SCN)_2(bpe)]_\infty$ **3**, illustrating the numbering scheme used. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: i $-x, -y, -z$; ii $1-x, -y, -z$.

including $(CuX)_2$ dimers, $(CuX)_4$ cubanes and step structures, stair- and split-stair polymers.[12] It has been previously noted that the balance between the different forms of copper(I) pseudo-halide or halide is extremely subtle.[23] Although steric arguments have been used to explain the variation between the forms of Cu^ISCN observed in previously reported complexes[15] this cannot be the reason for the differences observed in the structures of **1**–**3** as all the ligands have similar steric properties. Therefore, we can only attribute the variations in structures to the packing effects within the crystal lattice.

From viewing Figs. 1 and 2 it may appear that compounds **1** and **2** have channels within their networks. However when taking into account hydrogen atoms and van der Waals radii these channels are found to have no solvent accessible volume.[24] Similarly **3** has no solvent accessible volume between the adjacent sheets.[24]

The infrared spectra of compounds **1**–**3** show intense absorptions at *ca.* 2100 cm^{-1} assigned to ν_{C-N}. The wavenumbers of these vibrations are all lower than that of the corresponding stretch in β-CuSCN (2170 cm^{-1}) reflecting the weaker co-ordination of the S-donor in **1**–**3**. The wavenumbers of this vibration in **1** (2123 cm^{-1}) and **2** (2129 cm^{-1}) are consistent with that observed for $[Cu(SCN)(py)]_\infty$[19] (2120 cm^{-1}) reflecting the related $(CuSCN)_\infty$ structural motif. The ν_{C-N} vibration in **3** (2104 cm^{-1}) is similar to those observed in [1,6-bis(5-methylimidazol-4-yl)-2,5-dithiahexane]trithiocyanatodicopper][25] (2104, 2080 cm^{-1}) which has both $Cu(SCN)_2Cu$ double bridges and Cu–SCN–Cu single bridges, and $[Cu(SCN)(py)_2]_\infty$[19] (2099 cm^{-1}) which exhibits a $(CuSCN)_\infty$ chain (or split staircase) motif. The shift to lower wavenumbers in $[Cu_2(SCN)_2(bpe)]_\infty$ reflects the change in $(CuSCN)_\infty$ structural motif from the $(CuSCN)_\infty$ layers in **1**,**2** to the stair-polymer chain in **3**. Solid-state diffuse reflectance UV/vis/nir spectra of compounds **1**–**3** show broad absorptions between 300 and 600 nm which are assigned as copper(I)–ligand charge transfer transitions.[22]

Conclusion

We have shown that pseudo-halides can be used as bridging anions in the synthesis of uncharged three-dimensional co-ordination frameworks. The structural motifs observed in the complexes $[Cu_2(SCN)_2(L)]_\infty$ [L = pyz **1** or 4,4′-bipy **2**] represent not only new arrangements of polymeric CuSCN but also remarkable three-dimensional networks. The two-dimensional sheet formed by $[Cu_2(SCN)_2(bpe)]_\infty$ **3** is a surprising contrast to the three-dimensional networks **1** and **2**. The preparation of these compounds illustrate a potentially versatile approach to the construction of uncharged inorganic co-ordination networks and we are currently pursuing this methodology in the synthesis of new intercalation materials.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer (FTIR, samples in KBr discs), UV/vis/nir spectra on a Perkin-Elmer Lambda-9 spectrophotometer using a 60 mm MgO coated integrating sphere diffuse reflectance attachment on samples diluted with $BaSO_4$. Elemental analytical data were obtained by the microanalytical service (Perkin-Elmer 240B analyser) at the University of Nottingham. Melting points were measured on a Gallenkamp apparatus and are uncorrected. The compound CuSCN and ligands were purchased from Aldrich Chemicals and used without further purification.

Preparations

$[Cu_2(SCN)_2(py)]_\infty$ 1. The compound CuSCN (24.4 mg, 2.00 mmol) was dissolved in degassed dilute aqueous NH_3 (20 cm^3) and a solution of pyrazine (81.1 mg, 1.00 mmol) in EtOH (20 cm^3) added. The solution became slightly green and a bright orange solid precipitated over 1 h. Yield 68% (Found: C, 21.70; H, 1.00; N, 17.00. Calc. for $C_3H_2CuN_2S$: C, 22.30; H, 1.25; N, 17.35%), mp 270 °C (decomp.). IR (KBr)/cm^{-1}: 2923w, 2852w, 2123s, 1482w, 1419s, 1153m, 1123m, 1052m, 796m, 757m and 444w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 22940s (br), 20370 (sh), 5980w, 4590w, 4550w, 4470w, 4410w, 4360w, 4300w, 4230w, 4170w and 4110w.

The complex $[Cu_2(SCN)_2(4,4'\text{-bipy})]_\infty$ **2** was prepared similarly. Yield 81% (Found: C, 36.25; H, 1.95; N, 14.35. Calc. for $C_6H_4CuN_2S$: C, 36.10; H, 2.00; N, 14.65%), mp 335 °C (decomp.). IR (KBr)/cm^{-1}: 3074w, 3044w, 3025w, 2129s, 1602m, 1530w, 1411m, 807s, 749w, 630w and 500w. UV/vis/nir ($BaSO_4$)/cm^{-1}: 26300s (br), 25000s (br), 5990w, 4920w, 4690w, 4590w, 4480w, 4385w, 4270w and 4115w.

The complex $[Cu_2(SCN)_2(bpe)]_\infty$ **3** was also prepared similarly. Yield 85% (Found: C, 39.75; H, 1.95; N, 13.15. Calc. for $C_7H_5CuN_2S$: C, 39.50; H, 2.35; N, 13.15%), mp 300 °C (decomp.). IR (KBr)/cm^{-1}: 3048w, 3035w, 2104s, 1604s, 1497w, 1425m, 981m, 829s, 761w and 556s. UV/vis/nir ($BaSO_4$)/cm^{-1}: 26310s (br), 5990w, 5155w, 5000w, 4650w, 4590w, 4490w, 4350w, 4250w and 4115w.

Crystallography

All single crystal X-ray experiments were performed on a Stoë Stadi-4 four-circle diffractometer equipped with a Oxford Cryosystems open flow cryostat[26] (graphite monochromated Cu-Kα (λ = 1.54184 Å) **1** or Mo-Kα radiation (λ = 0.71073Å) (**2** and **3**); ω–θ scans). Absorption corrections, for **1** and **3**, were performed by Gaussian integration following refinement of the crystal morphology and dimensions against a set of ψ scans.[27] For **2** a numerical correction was applied. Other details of crystal data, data collection and processing are given in Table 2. The single-crystal structures of complexes **1** and **2** were both solved by direct methods using SHELXS 97[28] and all non-H atoms were located using subsequent Fourier-difference methods.[29] The single-crystal structure of **3** was solved by identifying the positions of the heavy atoms using Patterson methods (DIRDIF).[30] In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Compounds **2** and **3** both exhibited disorder in the ligand pyridyl rings. For **2** the atoms of the pyridyl ring, N4–C9, were each modelled over two equally occupied sites related by a mirror plane. They were modelled isotropically and the ligand restrained to have C_{2v} symmetry. For **3** the atoms of the pyridyl ring, N4–C9, were found to be disordered over two unequally occupied sites (80 and 20%); the lower occupancy component was modelled isotropically, with the pyridine ring treated as a rigid hexagon. The disordered C=C bonds were restrained to have equal lengths.

CCDC reference number 186/1544.

See http://www.rsc.org/suppdata/dt/1999/2813/ for crystallographic files in .cif format.

Table 2 Crystallographic data summary

	1	**2**	**3**
Empirical formula	$C_6H_4Cu_2N_4S_2$	$C_{12}H_8Cu_2N_4S_2$	$C_{14}H_{10}Cu_2N_4S_2$
M	323.33	399.42	425.46
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	*Pnnm*	$P\bar{1}$
a/Å	5.792(2)	8.257(3)	5.728(2)
b/Å	13.877(4)	21.694(8)	7.049(2)
c/Å	6.548(2)	3.7543(17)	9.861(3)
α/°	—	—	100.80(2)
β/°	113.95(2)	—	103.34(2)
γ/°	—	—	101.62(2)
U/Å^3	481.0(3)	672.5(5)	367.9(2)
Z	2	2	1
T/K	220(2)	220(2)	220(2)
μ/mm^{-1}	9.915[a]	3.464[b]	3.172[b]
Reflections collected	2048	5137	3465
Unique reflections (R_{int})	802 (0.0219)	702 (0.1879)	1307 (0.0169)
Final $R1$ [$F > 4\sigma(F)$]	0.0442	0.0391	0.0229
$wR2$ (all data)	0.1221	0.0788	0.0538

[a] Cu-Kα. [b] Mo-Kα.

Acknowledgements

We thank the Nuffield Foundation, University of Otago (L. R. H.) and EPSRC for support.

References

1 S. R. Batten and R. Robson, *Angew. Chem.*, 1998, **110**, 1558; *Angew. Chem., Int. Ed.*, 1998, **37**, 1461; T. Iwamoto, S. Nishikiori, T. Kitazawa and H. Yuge, *J. Chem. Soc., Dalton Trans.*, 1997, 4127; C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431; N. R. Champness and M. Schröder, *Curr. Opin. Solid State Mater. Sci.*, 1998, **3**, 419.

2 A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder and M. A. Withersby, *Coord. Chem. Rev.*, 1999, **183**, 117.

3 A. J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1005; K. A. Hirsch, S. R. Wilson and J. S. Moore, *Chem. Eur. J.*, 1997, **3**, 765; L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun*, 1994, 1325.

4 A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1339.

5 B. F. Hoskins, R. Robson and D. A. Slizys, *Angew. Chem.*, 1997, **109**, 2861; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2752.

6 A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2027; P. Losier and M. J. Zaworotko, *Angew. Chem.*, 1996, **108**, 2957; *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779; M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287; M. A. Withersby, A. J. Blake, N. R. Champness, P. A. Cooke, P. Hubberstey and M. Schröder, *Inorg. Chem.*, 1999, **38**, 2259.

7 O. M. Yaghi and G. Li, *Angew. Chem.*, 1995, **107**, 232; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 207.

8 M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Angew. Chem.*, 1997, **109**, 2421; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2327.

9 S. R. Batten, B. F. Hoskins and R. Robson, *Angew. Chem.*, 1997, **109**, 652; *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 636.

10 K. A. Hirsch, S. R. Wilson and J. S. Moore, *Inorg. Chem.*, 1997, **36**, 2960; L. Ballester, I. Baxter, P. C. M. Duncan, D. M. L. Goodgame, D. A. Grachvogel and D. J. Williams, *Polyhedron*, 1998, **17**, 3613; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem.*, 1995, **107**, 2037; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895.

11 A. J. Blake, N. R. Champness, M. Crew, L. R. Hanton, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 1533.

12 A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey and M. Schröder, *Pure Appl. Chem.*, 1998, **70**, 2351.

13 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 534.

14 P. C. Healy, C. Pakawatchai, R. I. Papasergio, V. A. Patrick and A. H. White, *Inorg. Chem.*, 1984, **23**, 3769.

15 P. C. Healy, B. W. Skelton, A. F. Waters and A. H. White, *Aust. J. Chem.*, 1991, **44**, 1049.

16 M. Kabesova, M. Dunaj-Jurco, M. Serator, J. Gazo and I. Garja, *Inorg. Chim. Acta*, 1976, **17**, 161.

17 D. L. Smith and V. I. Saunders, *Acta Crystallogr., Sect. B*, 1982, **38**, 907.

18 C. L. Raston, B. Walter and A. H. White, *Aust. J. Chem.*, 1979, **32**, 2757.

19 H. Krautsheid, N. Emig, N. Klaassen and P. Seringer, *J. Chem. Soc., Dalton Trans.*, 1998, 3071.

20 S. Kawata, S. Kitagawa, H. Kumagai, S. Iwabuchi and M. Katada, *Inorg. Chim. Acta*, 1998, **267**, 143.

21 M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1727.

22 M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Honda and S. Kitagawa, *J. Chem. Soc., Dalton Trans.*, 1994, 2771.

23 For example see: A. Camus, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1975, **12**, 23; G. A. Bowmaker, Effendy, R. D. Hart, J. D. Kildea and A. H. White, *Aust. J. Chem.*, 1997, **50**, 653.

24 PLATON, A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, C34.

25 E. Bouwman, W. L. Driessen and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1988, 1337.

26 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

27 X-SHAPE, crystal optimisation for absorption correction, Stoë & Cie, Darmstadt, 1996.

28 G. M. Sheldrick, SHELXS 97, University of Göttingen, 1997.

29 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.

30 P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, The DIRDIF 96 program system, Crystallography Laboratory, University of Nijmegen, 1996.

Paper 9/03218E