

A new Cu^I(SCN) structural motif: synthesis of an uncharged three-dimensional co-ordination network

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The complex [Cu₂(SCN)₂(L)]_∞ (L = pyrazine) has been prepared and characterised by X-ray diffraction studies revealing a new uncharged three-dimensional co-ordination network consisting of undulating [Cu(SCN)]_∞ sheets bridged by pyrazine ligands.

There is intense current interest in the construction of channelled inorganic co-ordination polymers with chemical architectures that mimic some of the characteristics of zeolite and mineral materials.¹ We are using a building-block approach for the construction of three-dimensional co-ordination polymers;² however, in contrast to many researchers, we are attempting to incorporate the anion as an essential element of the framework. This strategy allows for the synthesis of uncharged architectures in which channels remain unblocked by anions and free for solvent inclusion. By following this approach we have identified the halides and pseudo-halides of copper(I) as effective building-blocks.³ A limited number of structural motifs are known for Cu^I(SCN) itself, including the three-dimensional α-⁴ and β-forms,⁵ as well as the anionic network in {[C₆H₅NH]⁺[Cu₂(SCN)₃]⁻]_∞, in which the pyridinium cations fill cavities.⁶ Simple step structures and one-dimensional chains have also been observed in Cu^I and mixed-valence Cu^I–Cu^{II} thiocyanate complexes.^{7,8} We report herein a different structural motif for Cu^I(SCN) and the first example of the use of Cu^I(SCN) in the construction of an inorganic co-ordination polymer. This electrically neutral, undulating [Cu^I(SCN)]_∞ sheet is used as a component in the formation of a new polymeric array.

The three-dimensional network [Cu₂(SCN)₂(L)]_∞ (L = pyrazine) was prepared as an orange powder by the addition of an ethanolic solution of pyrazine to a deoxygenated dilute aqueous ammoniacal solution of Cu^I(SCN).[†] Copper(I) thiocyanate has been used rarely in co-ordination chemistry due to its extreme insolubility in common solvents, and thiocyanates have not been widely used in the construction of inorganic polymeric networks,^{8,9} most systems involving terminal rather than bridging NCS⁻ ligands. Significantly, dilute aqueous ammonia can be used to dissolve polymeric Cu^I(SCN) which probably exists as [Cu(NH₃)₂]NCS or [Cu(NH₃)(NCS)] in solution.¹⁰ Importantly, using this procedure allowed us to avoid the isolation of

any Cu^{II} impurities, and single crystals of [Cu₂(SCN)₂(L)]_∞[‡] were grown by slow diffusion of layered solutions of Cu^I(SCN) in dilute aqueous ammonia and pyrazine in EtOH under an Ar atmosphere. This synthesis was found to be reproducible. Over a period of a week orange-yellow tablets formed at the solvent interface, while all attempts thus far to prepare compounds with a 1:1 Cu:L ratio always produced, in our hands, [Cu₂(SCN)₂(L)]_∞, but in lower yield.

The polymer [Cu₂(SCN)₂(L)]_∞ exists as a three-dimensional network consisting of sheets of [Cu^I(SCN)]_∞ linked by pyrazine bridges (Fig. 1). Within the [Cu^I(SCN)]_∞ sheets each copper(I) centre is co-ordinated by three (two μ-S and one μ-N) thiocyanate ligands. This arrangement leads to the formation of ten-membered Cu–S–Cu–NCS–Cu–SCN rings (Fig. 2). Because of the rigid rod-like nature of (SCN)⁻, each ten-membered ring adopts a pseudo-chair conformation and is fused to six other rings to give a honeycomb sheet. The rings are joined to each

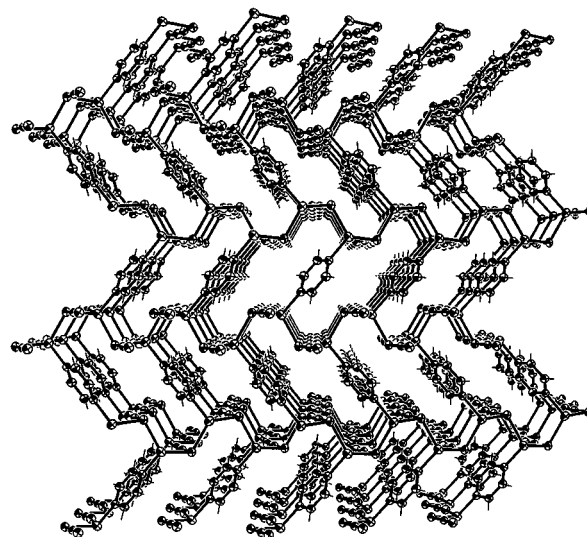


Fig. 1 A view of [Cu₂(SCN)₂(L)]_∞ down the *a* axis showing the small channels and herring-bone pattern of the pyrazine bridges. The *cis*-fusion of the [Cu^I(SCN)]_∞ sheets can also be seen

[†] Experimental: [Cu₂(SCN)₂(L)]_∞. Cu^I(SCN) (240 mg, 2.00 mmol) was dissolved in degassed dilute aqueous NH₃ (20 cm³) and a solution of pyrazine (L) (80 mg, 1.00 mmol) in ethanol (20 cm³) was added. The solution became slightly green and a bright orange solid precipitated out over 1 h. Yield 68% (Found: C, 21.71; H, 0.99; N, 17.02. Calc. for C₆H₄Cu₂N₄S₂: C, 22.28; H, 1.25; N, 17.33%). M.p. 270 °C (decomp.). IR (KBr)/cm⁻¹: 2923w, 2852w, 2123s, 1482w, 1419s, 1153m, 1123m, 1052m, 796m, 757m, 444w.

[‡] Crystal data for [Cu₂(SCN)₂(L)]_∞: C₆H₄Cu₂N₄S₂, *M* = 323.33, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 5.792(2), *b* = 13.877(4), *c* = 6.548(2) Å, β = 113.95(2)°, *U* = 481.0(3) Å³, *Z* = 2, *F*(000) = 316, *D*_c = 2.233 g cm⁻³, μ(Cu-Kα) = 9.195 mm⁻¹, *T* = 220(2) K. 818 Unique reflections (*R*_{int} = 0.0219) were collected. At final convergence *R*1 [802 data with *I* > 2σ(*I*)] = 0.0442, *wR*2 (all 817 data) = 0.1221 for 65 parameters. CCDC reference number 186/967. See <http://www.rsc.org/suppdata/dt/1998/1533/> for crystallographic files in .cif format.

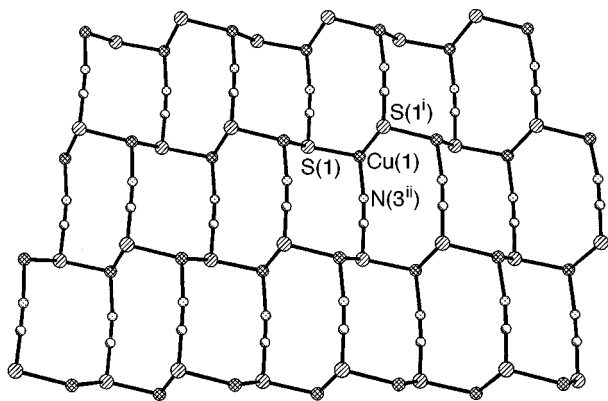


Fig. 2 A view of the $[\text{Cu}^{\text{I}}(\text{SCN})]_{\infty}$ sheet showing the ten-membered pseudo-cyclohexane rings, (Cu cross-hatched, S hatched). Selected bond lengths (Å) and angles ($^{\circ}$): Cu(1)–S(1) 2.349(2), Cu(1)–S(1ⁱ) 2.3377(15), Cu(1)–N(3ⁱⁱ) (N_{SCN}) 1.940(4), Cu(1)–N_{pyz} 2.047(4) (N_{pyz} not shown); N(3ⁱⁱ) (N_{SCN})–Cu–N_{pyz} 112.4(2), N(3ⁱⁱ) (N_{SCN})–Cu–S(1) 106.69(13), N_{pyz}–Cu–S(1) 109.31(11), N(3ⁱⁱ) (N_{SCN})–Cu–S(1) 107.96(14), N_{pyz}–Cu–S(1) 105.83(11), S(1)–Cu–S(1ⁱ) 114.75(5) (symmetry codes: i $x, \frac{1}{2} - y, \frac{1}{2} + z$; ii $1 + x, y, z$)

other in two different ways, *cis* and *trans*. In the direction of the *c* axis the rings are *trans*-fused to each other, while in the direction of the *a* axis they are *cis*-fused. The propagation of this *cis*-fusion gives rise to an undulating sheet (Fig. 1). This arrangement within the $[\text{Cu}^{\text{I}}(\text{SCN})]_{\infty}$ sheet in $[\text{Cu}_2(\text{SCN})_2(\text{L})]_{\infty}$ is analogous to that seen in the (011) set of lattice planes in zinc blende.¹¹ Although ten-membered rings exist in the α -⁴ and β -modifications⁵ of $\text{Cu}^{\text{I}}(\text{SCN})$ or $[\text{Cu}_2(\text{SCN})_3]^{-}$,⁶ the sheets formed in these structures are not the same as those observed in $[\text{Cu}_2(\text{SCN})_2(\text{L})]_{\infty}$. The remaining fourth co-ordination site of each tetrahedral Cu^{I} centre is occupied by a pyrazine ligand which bridges adjacent sheets (Fig. 1). For each $[\text{Cu}^{\text{I}}(\text{SCN})]_{\infty}$ sheet the available co-ordination sites are arranged such that on one side 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 pyrazine ligands in an axial–axial and equatorial–equatorial manner giving rise to a herring-bone pattern (Fig. 1) with channels running parallel to the *a* axis. These channels have interatomic dimensions of 12.2×3.6 Å and therefore, at first glance, appear to be of sufficient size to accommodate solvent molecules, and indeed, cavities with smaller interatomic dimensions have been claimed by other workers to be important as potential interchelation agents.¹² However, using interatomic dimensions to assess channel size can be deceptive. For example, in our case the unusual shape of the cavities and the orientation of the pyrazines in $[\text{Cu}_2(\text{SCN})_2(\text{L})]_{\infty}$ (L = pyrazine) actually prevents solvent inclusion for, when hydrogen atoms and van der Waal's radii are taken into account, the channels in $[\text{Cu}_2(\text{SCN})_2(\text{L})]_{\infty}$ are found to have no solvent-accessible volume.¹³

The structural motif observed in the complex $[\text{Cu}_2(\text{SCN})_2(\text{L})]_{\infty}$ represents both a new arrangement of polymeric $\text{Cu}^{\text{I}}(\text{SCN})$ and also a new three-dimensional network. We have shown that pseudo-halides can be used as bridging anions in the synthesis of uncharged three-dimensional co-ordination frameworks. The preparation of this compound illustrates a new and potentially versatile approach to the construction of uncharged inorganic co-ordination networks and we are currently pursuing this methodology towards the synthesis of new intercalation materials.

Acknowledgements

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