

An unprecedented 2-D CuSCN coordination network containing both regular and irregular $[\text{Cu}_3(\text{SCN})_3]$ rings supported by a tridentate N-donor ligand†

Shun-Ze Zhan,^a Rong Peng,^a Shi-Hong Lin,^a Seik Weng Ng^b and Dan Li^{*a}

Received 13th October 2009, Accepted 25th November 2009

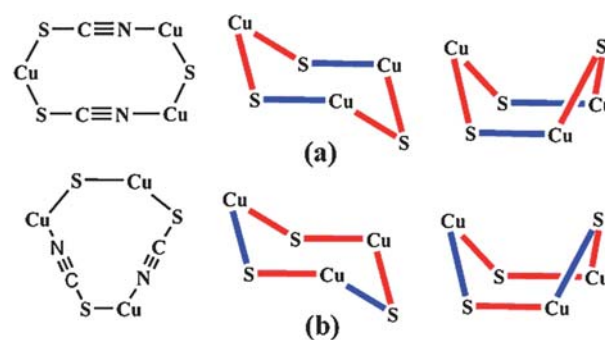
First published as an Advance Article on the web 17th December 2009

DOI: 10.1039/b921264g

A neutral 2-D $(\text{CuSCN})_\infty$ containing both regular and irregular $[\text{Cu}_3(\text{SCN})_3]$ six-membered rings supported by an asymmetrical tridentate ligand 3,5-bis(3-pyridyl)-1H-pyrazole (Hbppz) were prepared with the formula $[\text{Cu}_3(\text{SCN})_3(\text{Hbppz})]_\infty$. The compound gives strong green luminescence with an emission maximum at 536 nm.

There has been continuous research interest focused on copper(I) halide and pseudo-halide related compounds not only due to the strong affinity of halide and pseudo-halide anions with copper(I) that gives abundant structural diversity^{1–4} but also because of their promising luminescence properties.^{5–7} Many of these compounds represent a new kind of organic–inorganic polymeric hybrid material in which inorganic chains or sheets are linked by *exo*-bidentate organic N-donor ligands.^{2,3} CuSCN and CuCN have a strong ability for constructing 2-D and 3-D networks^{2–4} due to the linear geometry and various coordination modes of SCN^- and CN^- anions as soft bases and approximately trigonal planar or tetrahedral coordination geometry of the copper(I) center as a soft acid. Numerous neutral and anionic CuSCN and CuCN related complexes were synthesized by direct reactions of organic ligand and inorganic CuSCN or CuCN under room temperature or solvothermal (hydrothermal) conditions.^{2–4} Under solvothermal conditions, we discovered sulfur transformation reactions from inorganic SCN^- anions to organic products^{8,9} such as methyl mercaptide^{8a,b} and phosphine sulfide^{8c–f} resulting in pure $[\text{Cu}_x(\text{CN})_y]^{-(y-x)/8d,f}$ or hybrid $[\text{Cu}_x(\text{CN})_y(\text{SCN})_z]^{-(z+y-x)/8c–e}$ anionic networks.

Previous reports showed that polymeric CuSCN networks are considerably influenced by the steric properties of the ligand.² For example, the CuSCN motifs in the complexes $[\text{Cu}_2(\text{SCN})_2(\text{pyz})]$ and $[\text{Cu}_2(\text{SCN})_2(4,4'\text{-bpy})]$ exhibited similar 2-D honeycomb sheets with *cis*-fused and *trans*-fused SCNCu edges, while the CuSCN motifs in the compound $[\text{Cu}_2(\text{SCN})_2(\text{bpe})]$ showed a 1-D stair polymeric chain.^{2a,b} All three complexes are formed by similar linear N-donor ligands, pyrazine (pyz), 4,4'-bipyridine (4,4'-bpy) and 1,2-*trans*-(4-pyridyl)ethane (bpe) with CuSCN. In the 2-D neutral $(\text{CuSCN})_\infty$



Scheme 1 Two kinds of six-membered rings with the composition of $[\text{Cu}_3(\text{SCN})_2\text{S}]$ and their pseudo-chair or pseudo-boat conformation (blue: S–C–N–Cu edge, red: S–Cu edge). (a) regular rings: SCN^- on the *para*-edge, (b) irregular rings: SCN^- on the *meta*-edge.

honeycomb sheets, two kinds of ten-membered rings (Scheme 1) with the composition of $[\text{Cu}_3(\text{SCN})_2\text{S}]$ are mostly encountered.^{2a,b,3b–d} For convenience, we called herein the CuSCN rings six-membered rings when Cu atoms and S atoms are treated as nodes and the linear SCN^- or Cu–S bonds as edges. In each ring, two linear SCN^- edges are positioned on the *para*-edge along the same direction (regular ring, Scheme 1a) or on the *meta*-edge along the opposite direction (irregular ring, Scheme 1b). Both types of six-membered rings can adopt pseudo-chair or pseudo-boat conformations taking the tetrahedral coordination geometry of Cu(I) atoms and the tetrahedral sp^3 hybrid electron conformation of S atoms in SCN^- .^{2a,b} Each ring is fused to six other rings to give a honeycomb sheet with (6, 3) topology in *cis* or *trans* ways just observed in the two isomers of decahydronaphthalene. Taking the varieties of the types, the conformations and the fusing ways of the six-membered rings into account, we can speculate there exist numerous neutral 2-D $(\text{CuSCN})_\infty$ sheets with (6, 3) topology. However, only very few of them were reported consisting of the same six-membered rings, either regular or irregular, with different fusing ways,^{2,3} and none of them contained mixed regular and irregular rings.

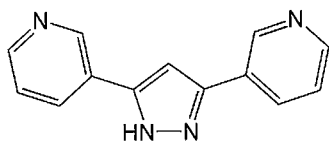
In our continuous investigation on CuSCN compounds,^{5,8} we obtained a new 3-D CuSCN coordination polymer $[(\text{CuSCN})_3(\text{Hbppz})]_\infty$ † with novel neutral 2-D CuSCN structural motifs supported by an asymmetrical tridentate N-donor ligand 3,5-bis(3-pyridyl)-1H-pyrazole (Hbppz) (Scheme 2). Hbppz was synthesized by a modified literature procedure from 3-acetylpyridine and methyl nicotinate as primary materials experiencing 1,3-bis(3-pyridyl)-1,3-propanedione mediate,¹⁰ and was characterized by IR, NMR and X-ray crystallography (Fig. S1, ESI†).

X-ray structure determination§ reveals that the compound crystallized in the chiral *PI* space group with the absence of any

^aDepartment of Chemistry, Shantou University, Guangdong, 515063, People's Republic of China. E-mail: dli@stu.edu.cn; Fax: + 86 754 8290-2767; Tel: + 86 754 8290-2741

^bDepartment of Chemistry, University of Malaya, Kuala Lumpur, 50603, Malaysia

† Electronic supplementary information (ESI) available: X-ray crystallographic file in cif for ligand and complex, synthesis procedure, IR, ¹H NMR and crystal data for ligand, XRPD and TGA data for complex. CCDC reference numbers 736108 & 736109. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b921264g



Scheme 2 The ligand 3,5-bis(3-pyridyl)-1H-pyrazole (Hbppz).

crystallographic symmetry elements. The asymmetrical unit of the complex consists of one neutral 3,5-bis(3-pyridyl)-1H-pyrazole ligand and three symmetry-independent CuSCN units. Each Cu center is surrounded by four different coordination atoms (two independent S atoms, one N atom from the SCN[−] anion and another N atom from the Hbppz ligand), as a consequence each Cu atom in a tetrahedral coordination geometry acts as a chiral center (Fig. 1). As usual the μ_3 -bridge (μ_2 -S and μ -N) ligands, thiocyanate anions, connect Cu atoms into neutral 2-D (CuSCN)_∞ sheets, which are parallel to the (010) crystallography plane (Fig. 2 and Fig. 3).

Hbppz ligand links the 2-D (CuSCN)_∞ sheets through N-pyridyl atoms and N-pyrazole atoms at the 2-position to generate a 3-D organic–inorganic hybrid framework. The IR spectral peak of 3402 cm^{−1} indicates the organic ligand remains undeprotonated, which leads to an asymmetrical ligand. It is notable that all the Hbppz ligands are positioned in the same direction. Bond angles and lengths centered by Cu atoms (Fig. 1) are comparable to the previous report.^{2,3}

One of the interesting features distinguishing the structure from other neutral inorganic (CuSCN)_∞ sheets and N-donor organic ligands^{2,3} is that both the regular and irregular six-membered rings exist in the structure. Within the 2-D neutral (CuSCN)_∞ sheet, each regular ring is fused to two other regular rings by two S2Cu2 bonds along the (100) direction and four irregular rings by S2Cu3, S1Cu2, S1C14N5Cu2 and S2C15N6Cu3 bonds directed in a *trans* way, and each irregular ring containing two S1 atoms or one S2 atom is fused to two regular rings by Cu2S1 and S1C14N5Cu2 bonds or Cu3S2 and S2C15N6Cu3 bonds in a *trans* way, four other irregular rings by two Cu1S1 bonds along the (100) direction in a *cis* way and Cu1S3, S3C16N7Cu1 bonds in a *trans* way, or by two Cu3S3 bonds along the (100) direction in a *cis* way and Cu1S3, S3C16N7Cu1 bonds in a *trans* way. Although the two analogues of six-membered rings

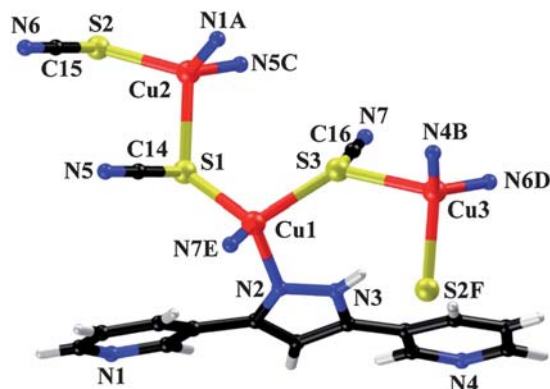


Fig. 1 Coordination environments in the compound. (Selected bond length: Cu1–N7E 1.908(5) Cu1–N2 2.072(6) Cu1–S1 2.314(2) Cu1–S3 2.360(2) Cu2–N5C 1.941(6) Cu2–N1A 2.043(5) Cu2–S2 2.318(2) Cu2–S1 2.422(2) Cu3–N6D 1.930(6) Cu3–N4B 2.010(5) Cu3–S2F 2.382(2) Cu3–S3 2.462(2) Symmetry codes: A +x, +y +1, +z B +x −1, +y +1, +z C +x +1, +y, +z D +x −1, +y, +z −1 E +x −1, +y, +z F +x, +y, +z −1).

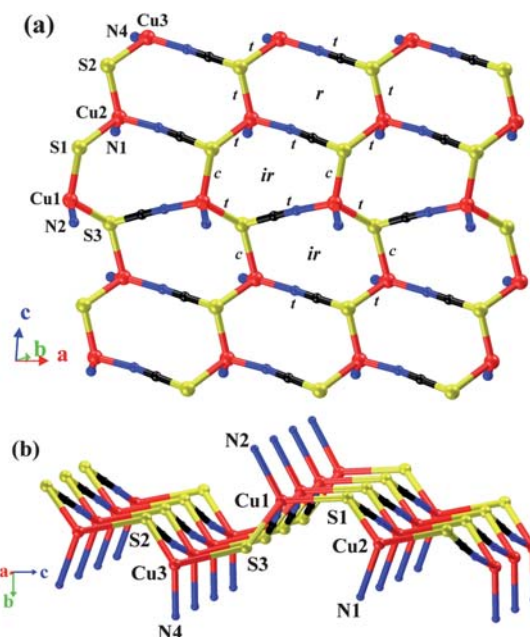


Fig. 2 Neutral 2-D CuSCN sheet consisting of regular (*r*) and irregular (*ir*) six-membered rings in *trans* (*t*) and *cis* (*c*) fusion modes along [010] (a) and [100] directions (b).

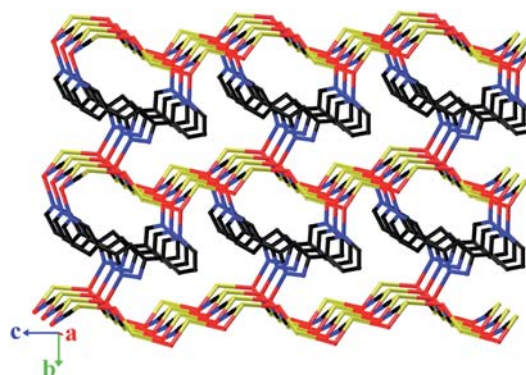


Fig. 3 3-D packing diagram of the complex along the [100] direction.

(or ten-membered rings) are ubiquitous in those CuSCN-related compounds, the layers formed by the fusion of both types of rings in the structure is rarely reported, which is dependent perhaps on the structural asymmetry of the ligand.

The other interesting feature is that the six-membered rings exhibit two different conformations viewing from the *a* axis: regular rings are pseudo-chair and irregular are pseudo-boat. These fusion ways between these different rings with different conformations result in an undulating layer mixed with regular chair rings and irregular boat rings in a 1 : 2 ratio. The remaining fourth coordination site of each tetrahedral Cu center is occupied by an N-pyridyl atom (Cu5–N1, Cu3–N4) or an N-pyrazole atom (Cu1–N2). As a result, adjacent sheets are linked from two sides by the asymmetric tridentate Hbppz ligand in *anti-anti* conformation giving rise to a kind of organic–inorganic hybrid material.

The complex is stable in air and insoluble in many common solvents. TGA (thermal-gravity analysis) indicated that it began to decompose at 280 °C and loses about 30% weight when heated to

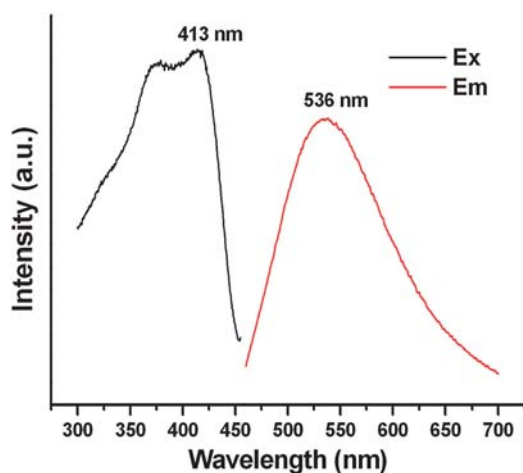


Fig. 4 Excitation and emission spectra of the complex in the solid state.

380 °C (Fig. S3, ESI†). According to previous literature, neutral N-heterocycle ligands are released at a lower temperature than the decomposition of SCN^- anions.^{3c,3f} We tentatively ascribe the mass loss to the release of part of the Hbppz ligands (about 79.4%) (the total Hbppz mass is about 37.8%).

Interestingly, the complex exhibits a strong green emission maximum at 536 nm upon an excitation maximum at 413 nm at room temperature in the solid state (Fig. 4). In this complex, the higher energy intra-ligand (IL) excited state and the lower energy metal-center (MC) excited state are excluded. On the basis of the photoluminescence of d^{10} metal complexes,^{5-7,11,12,3f,4f} the emission is tentatively ascribed to MLCT ($\text{Cu} \rightarrow \text{Hbppz}$) for its green emission mixed with XMCT ($\text{S} \rightarrow \text{Cu}$) for its residual emission as low as 600 nm, which is constant with the photoluminescence properties of heteroleptic Cu(I) complexes containing different ligands.^{7,11,12}

In conclusion, we have prepared a new complex with neutral 2-D (CuSCN) $_{\infty}$ sheets supported by an asymmetrical tridentate ligand 3,5-bis(3-pyridyl)-1H-pyrazole (Hbppz). In the complex, the neutral 2-D (CuSCN) $_{\infty}$ sheet consists of two kinds of six-membered ring [$\text{Cu}_3(\text{SCN})_3$] in *trans* and *cis* fusion modes, which were hardly reported in the previous literature though the similar (CuSCN) $_{\infty}$ sheets with only regular or irregular six-membered rings were numerous encountered. Photoluminescence experiments show that it is a good candidate for potential green emission material.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 20571050 and 20771072) and the National Science Foundation for Distinguished Young Scholars of China (Grant No. 20825102).

Notes and references

† Synthesis of complex: A mixture of Hbppz (44.4 mg, 0.2 mmol), CuSCN (73.2 mg, 0.6 mmol) and 10 mL acetonitrile was sealed in a 15-mL Teflon-lined reactor and heated in an oven at 140 °C for 72 h and slowly cooled to room temperature at a rate of 5 °C h⁻¹. The resulted yellow precipitate was washed by ethanol and soluted acetonitrile of NaSCN in order to remove residual reactants. A single crystal suitable for X-ray determination was separated from the filter residual, which is identical with the single crystal structure by X-ray Powder Determination

experiment (Fig. S2 ESI†). Yield: 71 mg, 37.82% based on Hbppz). Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{N}_7\text{S}_3\text{Cu}_3$: C 32.70, H 1.19, N 16.69%, Found: C 32.41, H 1.10, N 16.81%. IR data (KBr, cm^{-1}): 3402 s, 3170 w, 3047 w, 2101 vs, 1613 vs, 1585 s, 1474 m, 1437 m, 1210 m, 1066 m, 972 m, 808 s, 714 s.

§ Crystal data for complex: Triclinic, space group $P1$, $M_r = 587.11$, $a = 5.7798(6)$ Å, $b = 8.7059(9)$ Å, $c = 10.3704(11)$ Å, $\alpha = 83.700(2)^\circ$, $\beta = 84.555(2)^\circ$, $\gamma = 76.231(2)^\circ$, $V = 502.49(9)$ Å³, $Z = 1$, $\rho_c = 1.940$ g cm⁻³, $F(000) = 290.0$, $T = 293(2)$ K, 2653 reflections collected, 2128 unique with $[R_{\text{int}} = 0.0107]$, $R1[I > 2\sigma(I)] = 0.0341$, $wR_2 = 0.0873$, final (for all data) $R_1 = 0.0348$, $wR_2 = 0.0879$, GOF = 1.036.

- (a) M. Kabesova, M. Dunaj-Jurco, M. Serator, J. Gazo and I. Garja, *Inorg. Chim. Acta*, 1976, **17**, 161; (b) L. Smith and V. I. Saunders, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1982, **38**, 907; (c) B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 534; (d) M. Kabešová, R. Boča, M. Melnik, D. Valigura and M. Dunaj-Jurčo, *Coord. Chem. Rev.*, 1995, **140**, 115; (e) O. M. Yaghi and G. Li, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 207; (f) R. Peng, M. Li and D. Li, *Coord. Chem. Rev.*, 2010, **254**, 1.
- (a) A. J. Blake, N. R. Champness, M. Crew, L. R. Hanton, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 1533; (b) A. J. Blake, N. R. Brooks, N. R. Champness, M. Crew, L. R. Hanton, P. Hubberstey, S. Parsons and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1999, 2813; (c) A. J. Blake, N. R. Brooks, N. R. Champness, L. R. Hanton, P. Hubberstey and M. Schröder, *Pure Appl. Chem.*, 1998, **70**, 2351; (d) S. A. Barnett, A. J. Blake, N. R. Champness and C. Wilson, *CrystEngComm*, 2000, **2**, 36; (e) S. A. Barnett, A. J. Blake, N. R. Champness and C. Wilson, *Chem. Commun.*, 2002, 1640; (f) Q.-M. Wang, G.-C. Guo and T. C. W. Mak, *Chem. Commun.*, 1999, 1849.
- (a) O. A. Babich, V. N. Kokozay and V. A. Pavlenko, *Polyhedron*, 1996, **15**, 2727; (b) O. Teichert and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1860; (c) O. Teichert and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2196; (d) T. Kromp and W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 2003, **629**, 45; (e) C. Näther, I. Jeß and P. Kowalik, *Z. Anorg. Allg. Chem.*, 2003, **629**, 2144; (f) C. Näther, J. Greve, I. Jeß and C. Wickleder, *Solid State Sci.*, 2003, **5**, 1167.
- For examples: (a) G. A. Bowmaker, H. Hartl and V. Urban, *Inorg. Chem.*, 2000, **39**, 4548; (b) L. A. Kovbasyuk, O. A. Babich and V. N. Kokozay, *Polyhedron*, 1997, **16**, 161; (c) M. A. Beno, H. H. Wang, A. M. Kini, K. D. Carlson, U. Geiser, W. K. Kwok, J. E. Thompson, J. M. Williams, J. Ren and M. H. Whangbo, *Inorg. Chem.*, 1990, **29**, 1599; (d) M. A. S. Goher, N. A. Al-Salem and T. C. W. Mak, *Polyhedron*, 2000, **19**, 1465; (e) R. Dilshad, H. Boller and K. O. Klepp, *Solid State Sci.*, 2005, **7**, 1230; (f) M. A. S. Goher, Q. C. Yang and T. C. W. Mak, *Polyhedron*, 2000, **19**, 615.
- (a) R. Peng, T. Wu and D. Li, *CrystEngComm*, 2005, **7**, 595; (b) R. Peng, S.-R. Deng, M. Li, D. Li and Z.-Y. Li, *CrystEngComm*, 2008, **10**, 590; (c) W.-J. Shi, C.-X. Ruan, Z. Li, M. Li and D. Li, *CrystEngComm*, 2008, **10**, 778; (d) M. Li, Z. Li and D. Li, *Chem. Commun.*, 2008, 3390.
- T. H. Kim, Y. W. Shin, J. H. Jung, J. S. Kim and J. Kim, *Angew. Chem., Int. Ed.*, 2008, **47**, 685.
- S.-B. Ren, X.-L. Yang, J. Zhang, Y.-Z. Li, Y.-X. Zheng, H.-B. Du and X.-Z. You, *CrystEngComm*, 2009, **11**, 246.
- (a) D. Li and T. Wu, *Inorg. Chem.*, 2005, **44**, 1175; (b) D. Li, T. Wu, X.-P. Zhou, R. Zhou and X.-C. Huang, *Angew. Chem., Int. Ed.*, 2005, **44**, 4175; (c) X.-P. Zhou, D. Li, T. Wu and X. Zhang, *Dalton Trans.*, 2006, 2435; (d) X.-P. Zhou, W.-X. Ni, S.-Z. Zhan, J. Ni, D. Li and Y.-G. Yin, *Inorg. Chem.*, 2007, **46**, 2345; (e) J.-Z. Hou, M. Li, Z. Li, S.-Z. Zhan, X.-C. Huang and D. Li, *Angew. Chem., Int. Ed.*, 2008, **47**, 1711; (f) S.-H. Lin, X.-P. Zhou, D. Li and S. W. Ng, *Cryst. Growth Des.*, 2008, **8**, 3879.
- X.-M. Chen and M.-L. Tong, *Acc. Chem. Res.*, 2007, **40**, 162.
- (a) S.-Z. Zhan, D. Li, X.-P. Zhou and X.-H. Zhou, *Inorg. Chem.*, 2006, **45**, 9163; (b) S.-Z. Zhan, M. Li, J.-Z. Hou, J. Ni, D. Li and X.-C. Huang, *Chem.-Eur. J.*, 2008, **14**, 8916.
- (a) V. W. W. Yam and K. K. W. Lo, *Chem. Soc. Rev.*, 1999, **28**, 323; (b) P. C. Ford, E. Cariati and J. Bourassa, *Chem. Rev.*, 1999, **99**, 3625.
- T. M. Mark, K. G. Peter and B. K. Timothy, *J. Am. Chem. Soc.*, 1999, **121**, 4292.