Syntheses of supramolecular CuCN complexes by decomposing CuSCN: a general route to CuCN coordination polymers?

Xiao-Ping Zhou, Dan Li,* Tao Wu and Xuanjun Zhang

The solvothermal reaction of CuSCN with 1,2-bis(diphenylphosphino)ethane (dppe) yielded a coordination polymer, which was characterized to be a complex of CuCN and 1,2-bis(diphenylthiophosphinyl)ethane (dppeS$_2$): $[(CuCN)_2(dppeS_2)]_n$ (**1**). The identification of complex **1** reveals that CuSCN was decomposed and the sulfur was transferred to dppe, and represents a new example of the transformation of inorganic sulfur to organic sulfur. The weak coordination interactions between CuCN and dppeS$_2$ indicate that dppeS$_2$ may be substituted by ligands with strong coordination ability. The ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) was chosen as a substitute ligand. Three novel CuCN coordination polymers of tpt were synthesized and characterized: $[Cu_2(CN)_2(tpt)]_n$ (**2**) with a 3-D (10,3)-a network, $[Cu_2(CN)_2(tpt)]_n$ (**3**) and $[Cu_2(SCN)(CN)(tpt)]_n$ (**4**) both with a 2-D (6,3) network, and only complex **2** can be obtained from CuCN directly. Interestingly, compounds **2** and **3** are genuine high-dimensional supramolecular isomers. During the syntheses of **2–4**, single crystals of dppeS$_2$ were isolated, which indicates it was substituted by tpt ligand and also confirmed the transformation of sulfur from CuSCN to dppe. The transformation of sulfur can be observed only when the temperature is relative high (>160 °C). At 140 °C, complex **5** containing only CuSCN was attained and no dppeS$_2$ has been monitored in the resulting filtrate.

Introduction

Hydro(solvo)thermal techniques, which may promote some interesting inorganic and organic reactions such as metal redox, ligand substitution, hydroxylation, and cycloaddition, have been employed to generate coordination complexes with sophisticated architectures.[1] Many hydro(solvo)thermal reactions accompanied by new ligand generation, *in situ* syntheses, have been developed as a new approach to the crystal engineering of complexes.[2] Another advantage for *in situ* synthesis is that the process is apt to grow suitable crystals for structural characterizations.[2] Therefore, *in situ* synthesis in hydro(solvo)thermal conditions may be a good choice when the required single crystals are difficult to attain by direct syntheses. However, results of *in situ* syntheses are difficult to predict, especially for the black-box-like hydro(sovlo)thermal synthesis. Much work has been focused on changing hydro(sovlo)thermal conditions (such as solvents, time, temperature) to examine effects of conditions on the final products.[3]

We are interested in exploring the coordination chemistry of metal complexes of copper(I) halides and pseudohalides because of their intriguing coordination architectures and favorable photoluminescent properties.[4] As a part of our work, we examined the reaction of CuSCN with 2-bis(diphenylphosphino)ethane (dppe) under solvothermal conditions. Unexpectedly when the temperature was raised to 180 °C, CuSCN was decomposed and the sulfur of CuSCN was transferred to dppe forming 1,2-bis(diphenylthiophosphinyl)ethane (dppeS$_2$) which coordi-

nated copper(I) yielding a two-dimensional coordination polymer $[(CuCN)_2(dppeS_2)]_n$ (**1**). The single-crystal structure of **1** shows that the bond distance of Cu(I)–S [2.5263(13) Å] is obviously longer than common Cu(I)–S bond distances,[5] indicating that the ligand dppeS$_2$ weakly coordinates to Cu(I) and may be easily substituted by other ligands with stronger coordination ability. The solvothermal reaction which *in situ* yields weak coordinated dppeS$_2$ synchronously releasing CuCN may be feasible for the synthesis of some novel CuCN complexes which are difficultly to synthesize by direct reactions using CuCN as a reactant. To prove the feasibility of the tentative strategy, a ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) was chosen. Fortunately, we achieved three unprecedented Cu(I)–tpt coordination polymers. It is noteworthy that only one of them can be synthesized from CuCN directly. The compound 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) was used firstly as an analytical reagent for various metals,[6] and recently as a ligand for designing transition metal complexes such as Cu(II), Ru(II) and Rh(III) complexes.[7]

The phenomenon of carbon–sulfur bond cleavage including desulfuration has been observed in traditional solution reactions or critical solvothermal reactions.[4a,b,8] The sulfur in such desulfurized reactions has been transformed in two distinct ways: one was from organic sulfur (thiol) into inorganic sulfur (sulfate);[8] the other was from inorganic sulfur (CuSCN) into organic sulfur (methyl mercaptide).[4a,b] The transformation of inorganic sulfur into organic sulfur is of vital significance as such a process has been found under natural anoxic and geothermic conditions or in an organism catalyzed by anaerobic bacteria.[9] Hydro(solvo)thermal reactions creating high-pressure and high-temperature conditions that simulate natural geothermic environments, may provide a new way for understanding the nature of sulfur transformation.

Department of Chemistry, Shantou University, Guangdong, 515063, P.R. China. E-mail: dli@stu.edu.cn

Experimental

Materials and methods

All reagents were commercially available and used as received. Solvents acetonitrile and *n*-hexane, cyclohexane and benzene were analytical grade and were used without further purification. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000–400 cm^{-1}. Elemental analyses of C, H and N were determined with a Perkin-Elmer 2400C elemental analyzer. Thermal analysis (TG) was carried out in a nitrogen stream using Seiko Extar 6000 TG/DTA equipment with a heating rate of 10 °C min^{-1}.

[(CuCN)$_2$(dppeS$_2$)]$_n$, 1. A mixture of CuSCN (0.0488 g, 0.40 mmol), dppe (0.0796 g, 0.20 mmol) and acetonitrile–*n*-hexane (8.0 mL 3 : 1, v/v) was sealed in a 15-mL Teflon-lined reactor and heated in an oven at 180 °C for 60 h and slowly cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block-like crystals were collected and dried in air (yield 67%). Anal. Calc. for C$_{28}$H$_{24}$N$_2$Cu$_2$P$_2$S$_2$: C, 52.41; H, 3.75; N, 4.36. Found: C, 52.43; H, 3.74; N, 4.35%. IR (v/cm^{-1}): 3051w, 2896w, 2132s, 1629w, 1482w, 1433s, 1401w, 1307w, 1172m, 1098s, 1021w, 996w, 730s, 690m, 604m, 493s.

[(CuCN)$_2$(tpt)]$_n$, 2. A mixture of CuSCN (0.0122 g, 0.10 mmol), tpt (0.0156 g, 0.05 mmol), dppe (0.0398 g, 0.10 mmol) in acetonitrile (8.0 mL) was sealed in a 15-mL Teflon-lined reactor and heated in an oven at 180 °C for 60 h and slowly cooled to room temperature at a rate of 5 °C h^{-1}. The resulting mixture of solid and yellow liquor was separated by filtration and black stick-like crystals were collected and dried in air (yield 60%). Anal. Calc. for C$_{20}$H$_{12}$Cu$_2$N$_8$: C, 48.83; H, 2.24; N, 22.78. Found: C, 48.80; H, 2.25; N, 22.76%. IR (v/cm^{-1}): 3064w, 2116s, 1519s, 1462w, 1368s, 1258m, 1151w, 1094m, 1000m, 853w, 771s, 661m.

[Cu$_2$(CN)$_2$(tpt)]$_n$, 3. The preparation was carried out with a method similar to that for the preparation of **2** using acetonitrile–*n*-hexane (1 : 1, v/v) instead of acetonitrile. The resulting mixture of solid and yellow liquor was separated by filtration and black block-like crystals were collected and dried in air (yield 48%). Anal. Calc. for C$_{20}$H$_{12}$Cu$_2$N$_8$: C, 48.83; H, 2.24; N, 22.78. Found: C, 48.84; H, 2.20; N, 22.80%. IR (v/cm^{-1}): 3051w, 2116s, 1625w, 1515s, 1462w, 1364s, 1254m, 1151w, 1094m, 1041m, 763s, 665m.

[Cu$_2$(SCN)(CN)(tpt)]$_n$, 4. The preparation was carried out with a method similar to that for the preparation of **2** using acetonitrile–cyclohexane or acetonitrile–benzene (1 : 1, v/v) instead of acetonitrile. The resulting mixture of solid and orange liquor was separated by filtration and black hexagonal crystals were collected and dried in air (yield 56%). Anal. Calc. for C$_{20}$H$_{12}$Cu$_2$N$_8$S: C, 45.88; H, 2.29; N, 21.40. Found: C, 45.90; H, 2.26; N, 21.36%. IR (v/cm^{-1}): 3039w, 2116s, 2050s, 1511s, 1364s, 1258m, 1094w, 996m, 845w, 759s, 665m.

[(CuSCN)(tpt)]$_n$, 5. The preparation was carried out with a method similar to that for the preparation of **2** using acetonitrile–benzene (1 : 1, v/v) instead of acetonitrile and the reaction temperature was set to 140 °C. Black needle-like crystals were collected and dried in air (yield 47%). Anal. Calc. for C$_{20}$H$_{12}$N$_8$Cu$_2$S$_2$: C, 43.23; H, 2.17; N, 20.16. Found: C, 43.22; H, 2.19; N, 20.14%.

IR (v/cm^{-1}): 2921w, 2843w, 2116s, 1638w, 1511s, 1462w, 1368s, 1249w, 1082w, 1045w, 996, 759s, 661w.

1,2-Bis(diphenylthiophosphinyl)ethane, dppeS$_2$. Compound dppeS$_2$ was obtained synchronously during the syntheses of **2–4**, and characterized by crystallography.[10] The filtrate of **2**, **3** or **4** was left standing at room temperature. Colorless column-like crystals were obtained after several days. Anal. Calc. for C$_{26}$H$_{24}$P$_2$S$_2$: C, 67.51; H, 5.18. Found: C, 67.52; H, 5.16%. IR (v/cm^{-1}): 3048w, 2884w, 1568w, 1482w, 1429s, 1368s, 1307w, 1168s, 1102s, 996w, 743s, 686s, 608s.

Crystal structure determinations

Suitable crystals of **1–5** were mounted with glue at the end of a glass fiber, respectively. Data collections were performed on a Bruker-AXS SMART CCD area detector diffractometer at 293(2) K using ω rotation scans with a scan width of 0.3° and Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal parameters and experimental details of the data collection are summarized in Table 1. Empirical absorption corrections were carried out utilizing SADABS routine. The structures were solved by direct methods and refined by full-matrix least squares refinements based on F^2. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were added geometrically and refined with a riding model, structure solutions, refinements, and graphics were performed with the SHELXL-97 package.[11] Selected bond lengths and angles for the complexes are given in Table 2.

CCDC reference numbers 293329–293333.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517969f

Results and discussion

Synthesis and sulfur transformation

Our earlier reports[4a,b] found that in the presence of acetonitrile, sulfur in CuSCN can transfer to CH$_3$OH forming frameworks containing CuCN and methyl mercaptide. In the present work, solvothermal treatment of CuSCN and dppe in the mixed solvent acetonitrile–*n*-hexane affords complex **1**, which was composed of CuCN and dppeS$_2$. The result not only confirms the decomposition of CuSCN but also presents another example of the transformation from inorganic sulfur to organic sulfur.[4a,b] It has been reported that compound dppeS$_2$ can be obtained by the reaction of elemental sulfur and dppe in benzene.[12] Based on our observations that heating Cu(NO$_3$)$_2$·3H$_2$O, NaSCN, CH$_3$OH and *m*-phenylenediacetonitrile in a sealed reactor at 180 °C produced crystals of S$_8$,[4b] it is possible that CuSCN was decomposed generating CuCN and elemental sulfur, and then dppe captures sulfur to give organic dppeS$_2$. On the other hand, it seems that temperature is critical for the transformation. The transformation of sulfur can be observed only when the temperature is relative high. At 140 °C, complex **5** containing only CuSCN was obtained and no dppeS$_2$ has been monitored in the resulting filtrate.

Previous studies reveal that the redox reaction of Cu(II) and thiocyanate generates Cu(I) and cyanide.[13] Single-crystal structural determination (see structure description section) proves that the decomposition CuSCN occurs and the coordination interaction between CuCN and dppeS$_2$ in **1** is weak. We speculated that the

Table 1 Summary of the crystal data and structure refinement parameters for **1–5**

| Parameters	1	2	3	4	5
Empirical formula	$C_{28}H_{24}Cu_2N_2P_2S_2$	$C_{20}H_{12}Cu_2N_8$	$C_{20}H_{12}Cu_2N_8$	$C_{20}H_{12}Cu_2N_8S$	$C_{20}H_{12}Cu_2N_8S_2$
M_r	641.63	491.46	491.46	523.52	555.58
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_12_12_1$	$C2/c$	$P2_1$	$P\bar{1}$
$a/\text{Å}$	10.0561(13)	8.4743(5)	8.6163(8)	6.9991(16)	3.814(3)
$b/\text{Å}$	15.461(2)	13.1830(8)	15.7573(14)	18.333(4)	16.187(11)
$c/\text{Å}$	9.5055(12)	17.4013(11)	14.2116(14)	8.3381(18)	17.468(12)
$\alpha/°$	90	90	90	90	113.292(10)
$\beta/°$	107.044(2)	90	95.956(2)	112.652(4)	92.875(12)
$\gamma/°$	90	90	90	90	95.627(11)
$V/\text{Å}^3$	1413.0(3)	1944.0(2)	1919.1(3)	987.4(4)	981.2(12)
Z	2	4	4	2	2
$D_c/\text{g cm}^{-3}$	1.508	1.679	1.701	1.761	1.881
μ/mm^{-1}	1.786	2.213	2.242	2.286	2.409
Reflns collected	7321	10161	4983	5066	7077
Indep. reflns	2483	3411	1700	2678	3448
R_{int}	0.0237	0.0204	0.0252	0.0263	0.0301
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0409$	$R_1 = 0.0281$	$R_1 = 0.0989$	$R_1 = 0.0711$	$R_1 = 0.0614$
	$wR_2 = 0.1009$	$wR_2 = 0.0703$	$wR_2 = 0.2152$	$wR_2 = 0.1835$	$wR_2 = 0.1507$
Final R indices (all data)	$R_1 = 0.0539$	$R_1 = 0.0307$	$R_1 = 0.1182$	$R_1 = 0.0749$	$R_1 = 0.0803$
	$wR_2 = 0.1092$	$wR_2 = 0.0715$	$wR_2 = 0.2289$	$wR_2 = 0.1879$	$wR_2 = 0.1717$
max., min. $\Delta\rho/\text{e Å}^{-3}$	0.670, −0.398	0.447, −0.365	1.892, −1.661	2.080, −0.520	0.946, −0.780

^{a} $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

reaction can be used to synthesize some CuCN complexes which may be difficult to synthesize directly from CuCN. A ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) with strong coordination ability was chosen to verify this strategy. To date, no structural report of Cu(I) complex with this ligand was reported. Fortunately, three air-stable CuCN complexes of tpt with the same black color but different shapes were obtained under different solvent conditions (**2–4**, Scheme 1), and dppeS$_2$ crystals were also isolated.[10] Crystallographic studies showed that **2** and **3** are genuine supramolecular isomers bearing a fixed stoichiometry of CuCN : tpt = 2 : 1, and **3**, **4** are topologically isostructural with different space groups $C2/c$ and $P2_1$. Surprisingly, complex **4** contains both SCN$^-$ and CN$^-$, which indicates that CuSCN was only partially decomposed

during the generation of **4**. The existence of SCN$^-$ or/and CN$^-$ groups is further confirmed by the IR spectra of the complexes. In the IR spectrum of **4**, there are two absorptions at 2116 and 2050 cm^{-1}, assigned to the ν(C≡N) stretching vibrations of CuCN and CuSCN, respectively. In the spectra of **2** and **3**, only the CN$^-$ (2116 cm^{-1}) characteristic absorption exists.

Comparative experiments in which CuSCN was replaced by CuCN or CuSCN–CuCN (for **4**) in the syntheses of the corresponding complexes were carried out. Unfortunately, although the solvothermal conditions were varied, only complex **2** was synthesized successfully.

On the other hand, a rational deduction is that the CuSCN–CuCN containing complex **4** may possibly be further desulfurized
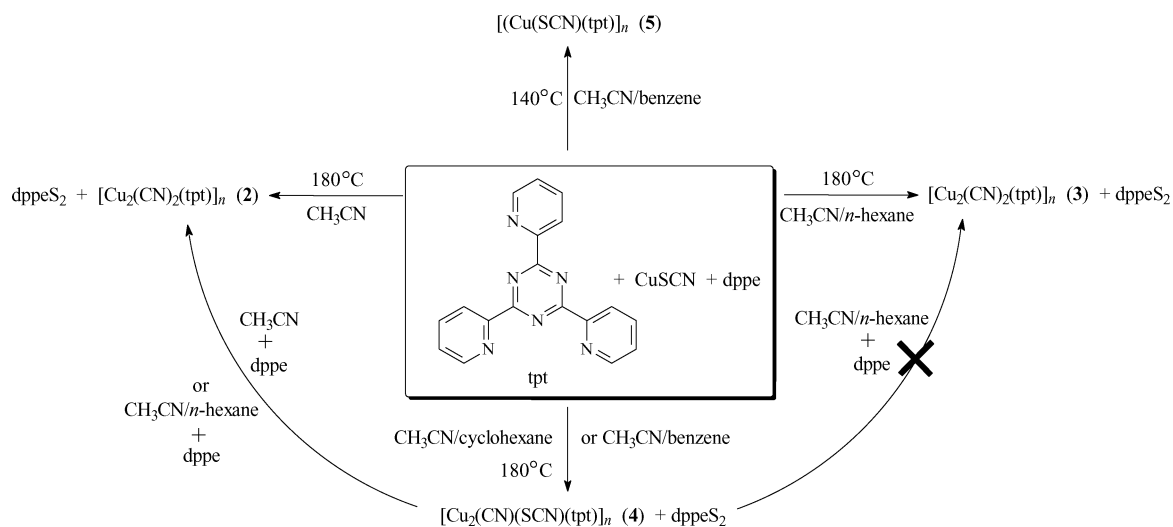
Scheme 1

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1–5**

Complex 1			
Cu(1)–N(1)	1.887(4)	Cu(1)–C(1A)	1.860(3)
Cu(1)–S(1)	2.5263(13)	P(1)=S(1)	1.9630(13)
N(1)–Cu(1)–C(1A)	106.89(12)	N(1)–Cu(1)–S(1)	106.89(12)
C(1A)–Cu(1)–S(1)	100.29(13)		
Complex 2			
Cu(1)–N(1)	2.326(3)	Cu(1)–N(2)	2.219(2)
Cu(1)–N(8)	1.936(3)	Cu(1)–C(19A)	1.921(3)
Cu(2)–N(5)	2.426(2)	Cu(2)–N(6)	2.105(3)
Cu(2)–N(7)	1.937(3)	Cu(2)–C(20B)	1.893(3)
C(19)–N(7)	1.119(4)	C(20)–N(8)	1.127(4)
N(1)–Cu(1)–N(2)	70.91(9)	N(1)–Cu(1)–N(8)	101.29(11)
N(1)–Cu(1)–C(19A)	98.51(11)	N(2)–Cu(1)–N(8)	125.23(10)
N(2)–Cu(1)–C(19A)	100.81(10)	N(8)–Cu(1)–C(19A)	133.62(11)
N(5)–Cu(2)–N(6)	73.61(8)	N(5)–Cu(2)–N(7)	112.82(10)
N(5)–Cu(2)–C(20B)	91.94(10)	N(6)–Cu(2)–N(7)	106.36(10)
N(6)–Cu(2)–C(20B)	114.19(11)	N(7)–Cu(2)–C(20B)	137.14(13)
Complex 3			
Cu(1)–N(1)	2.191(7)	Cu(1)–N(2)	2.232(6)
Cu(1)–X(1)	1.919(8)	Cu(1)–X(2)	1.902(7)
X(1)–X(1B)	1.143(15)	X(2)–X(2C)	1.125(14)
N(1)–Cu(1)–N(2)	75.5(2)	N(1)–Cu(1)–X(1)	109.8(3)
N(1)–Cu(1)–X(2)	113.9(3)	N(2)–Cu(1)–X(1)	101.2(3)
N(2)–Cu(1)–X(2)	118.1(3)	X(1)–Cu(1)–X(2)	126.6(3)
Complex 4			
Cu(1)–N(1)	2.322(9)	Cu(1)–N(5)	2.399(8)
Cu(1)–N(6)	2.085(7)	Cu(1)–N(8A)	1.909(10)
Cu(1)–S(1)	2.362(3)	Cu(2)–N(2)	2.404(7)
Cu(2)–N(3)	2.017(7)	Cu(2)–N(7B)	2.011(9)
Cu(2)–C(20)	1.867(9)	N(8)–C(20)	1.142(12)
N(1)–Cu(1)–N(5)	145.3(3)	N(1)–Cu(1)–N(6)	74.0(3)
N(1)–Cu(1)–N(8A)	102.8(4)	N(1)–Cu(1)–S(1)	102.6(2)
N(2)–Cu(2)–N(3)	74.5(3)	N(2)–Cu(2)–N(7B)	90.3(4)
N(2)–Cu(2)–C(20)	121.6(3)	N(3)–Cu(2)–C(20)	119.5(4)
N(3)–Cu(2)–N(7B)	107.6(3)	N(5)–Cu(1)–N(6)	72.2(3)
N(5)–Cu(1)–N(8A)	100.6(4)	N(5)–Cu(1)–S(1)	92.9(2)
N(6)–Cu(1)–N(8A)	146.0(3)	N(6)–Cu(1)–S(1)	103.4(2)
N(7B)–Cu(2)–C(20)	127.9(4)	N(8A)–Cu(1)–S1	110.2(3)
Complex 5			
Cu(1)–N(1)	2.371(5)	Cu(1)–N(2)	2.089(5)
Cu(1)–N(3)	2.358(5)	Cu(1)–S(1)	2.2949(19)
Cu(1)–S(1A)	2.339(2)	Cu(2)–N(7)	1.921(5)
Cu(2)–N(8B)	1.977(5)	Cu(2)–S(2)	2.466(2)
Cu(2)–S(2C)	2.449(2)		
N(1)–Cu(1)–N(2)	72.39(17)	N(1)–Cu(1)–N(3)	145.18(16)
N(1)–Cu(1)–S(1)	95.85(13)	N(1)–Cu(1)–S(1A)	96.94(13)
N(2)–Cu(1)–N(3)	73.27(18)	N(2)–Cu(1)–S(1)	139.66(14)
N(2)–Cu(1)–S(1A)	108.92(14)	N(3)–Cu(1)–S(1)	106.63(13)
N(3)–Cu(1)–S(1A)	99.38(13)	S(1)–Cu(1)–S(1A)	110.78(8)
N(7)–Cu(2)–N(8B)	125.7(2)	N(7)–Cu(2)–S2	110.87(16)
N(7)–Cu(2)–S(2C)	111.04(16)	N(8B)–Cu(2)–S2	102.23(17)
N(8B)–Cu(2)–S(2C)	102.42(16)	S(2)–Cu(2)–S(2A)	101.82(8)

Symmetry codes: **1**: A: x, $−y + 1/2$, $z + 1/2$; B: $−x + 1$, $−y + 1$, $−z + 2$; C: x, $−y + 1/2$, $z − 1/2$. **2**: A: $x − 1/2$, $−y + 3/2$, $−z + 2$; B: $−x + 2$, $y + 1/2$, $−z + 3/2$; C: $x + 1/2$, $−y + 3/2$, $−z + 2$; D: $−x + 2$, $y − 1/2$, $−z + 3/2$. **3**: A: $−x + 2$, y, $−z + 3/2$; B: $−x + 1$, y, $−z + 3/2$; C: $−x + 3/2$, $−y + 1/2$, $−z + 2$. **4**: A: $−x + 1$, $y + 1/2$, $−z + 1$; B: $x − 1$, y, z; C: $x + 1$, y, z; D: $−x + 1$, $y − 1/2$, $−z + 1$. **5**: A: $x − 1$, y, z; B: $−x + 1$, $−y$, $−z$; C: $x + 1$, y, z.

under similar solvothermal conditions and transformed to the pure CuCN containing complexes **2** and **3**, or other new CuCN complexes. To investigate the possibility, we used complex **4** as a precursor to proceed with solvothermal reactions in CH_3CN or the mixed solvent CH_3CN–*n*-hexane in the presence of dppe. Interestingly, products obtained in both reactions were characterized as complex **2**. These phenomena allow us speculate that cyclohexane or benzene may prevent the further decomposition of CuSCN by the formation of a metastable complex **4** in this system.

In comparison with our previous work[4a,b] on the transformation from inorganic sulfur into organic sulfur, where methanol traps sulfur forming methyl mercaptide, dppe in this work acts as a sulfur capture agent to complete the sulfur transformation.

Structure description

Complex **1** adopts a two-dimensional structure, in which each Cu(I) atom is three-coordinated by one sulfur atom from dppeS$_2$, one carbon and one nitrogen atom from two different CN$^-$ in a distorted T-type geometry [C(1A)–Cu(1)–N(1) 152.80(18), C(1A)–Cu(1)–S(1) 100.29(13), N(1)–Cu(1)–S(1) 106.89(12)°], as shown in Fig. 1(a). The two-dimensional layers contain inversion centres at the mid-point of the C–C bond linking the P atoms. The Cu(1)–S(1) bond distance of 2.5263(13) Å is obvious longer than normal Cu(I)–S distances,[5] indicating a weak coordination interaction between CuCN and dppeS$_2$. The Cu–N/C bond distances ranging from 1.860(3) to 1.887(4) Å are within typical Cu–N/C bond distances of CuCN.[14] The Cu(I) cations are bridged by CN$^-$ anions forming infinite zigzag like chains (Fig. 1(b)), and the CuCN chains are extended to a two-dimensional (6,3) brickwall-like structure through the dppeS$_2$ bridges (Fig. 1(c)). The dppeS$_2$ in complex **1** adopts an *anti*-conformation, with the P=S bond distance of 1.9630(13) Å similar to the bond distances in free dppeS$_2$.[15]

In the asymmetric unit of **2**, each Cu(I) atoms is four-coordinated by two nitrogen atoms from the same tpt ligand and one nitrogen, one carbon atoms from two different CN$^-$ in a distorted tetrahedral geometry (Fig. 2(a)). The Cu(1)–N(1) and Cu(2)–N(5) distances [2.326(3) and 2.426(2) Å] are obviously longer than the distances of Cu(1)–N(2) and Cu(2)–N(6) [2.219(2) and 2.105(3) Å], suggesting that two of the Cu–N bonds are weaker. The copper centered angles in each tetrahedron vary from 70.91(9) to 137.14(13)°, forming a heavily distorted geometry around the both copper atoms. The Cu(I) atoms are linked by CN$^-$ anions into an infinite helical CuCN chain along a 2$_1$ screw axis in the *c* direction, as shown in Fig. 2(b). Notably, all CuCN chains crystallize in a right-handed fashion, and are extended to a three-dimensional (3-D) chiral network through the bis-bidentate tpt ligand bridges (Fig. 2(c)). In the CuCN chains of **2**, the bond lengths appear reasonable [Cu–C/N 1.893(3)–1.937(3) Å, C≡N 1.119(4)–1.127(4) Å], and are in good agreement with those found in [Cu$_2$(CN)$_2$(bpym)] (bpym = 2,2′-bipyrimidine).[16] However, the C–Cu–N bond angles [133.62(11)–137.14(13)°] are significantly smaller than the bond angles in a low temperature polymorph of CuCN [176.7(3)–179.0(5)°],[14] which is due to the bite angle of the tpt ligand chelating the Cu(I) forming a distorted tetrahedral geometry.

Topological analysis shows that **2** is a non-interpenetrating, neutral, and chiral (10,3)-a net with a vertex symbol (10$_5$,10$_5$,10$_5$),
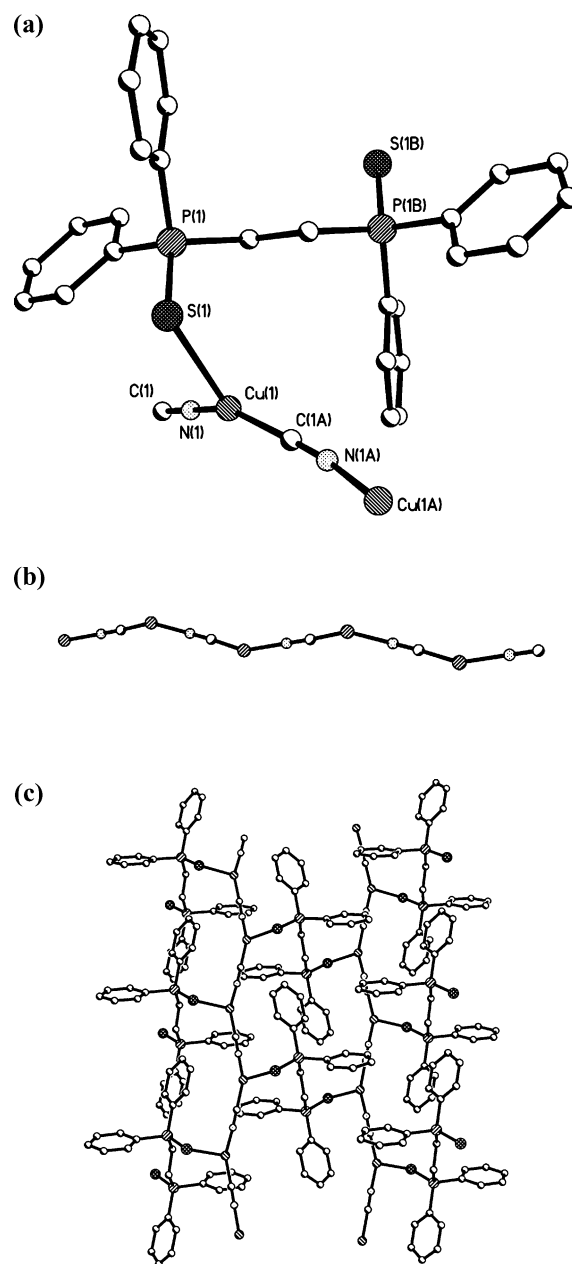
Fig. 1 Complex **1**: (a) coordination environment; (b) view of the zigzag CuCN chain; (c) brickwall-like 2-D structure. Symmetry codes: A: *x*, −*y* + 1/2, *z* + 1/2; B: −*x* + 1, −*y* + 1, −*z* + 2.

when the tpt ligand and CN$^-$ are considered as spacers and Cu atoms as nodes, as shown in Fig. 2(d). The (10,3)-a net as a whole is chiral containing fourfold helices with the same handedness.[17] The only 2$_1$ screw axis exists in **2** with a chiral space group $P2_12_12_1$, which may be because that the different linkers in the network destroy the symmetry. The phenomenon has been observed in the report of Liu and coworkers,[18] where the manganese/alternating EO–EE azido chains run around and cross two parallel axes forming a *meso*-helix with a space group C2/c. The (10,3)-a net is in principle capable of interpenetrating not only an identical net of the same handedness, but also a net of the opposite handedness.[17] Therefore in most cases the resultant crystals are racemic.[4c,19] The non-interpenetrating and neutral (10,3)-a net is really rare,[20] which
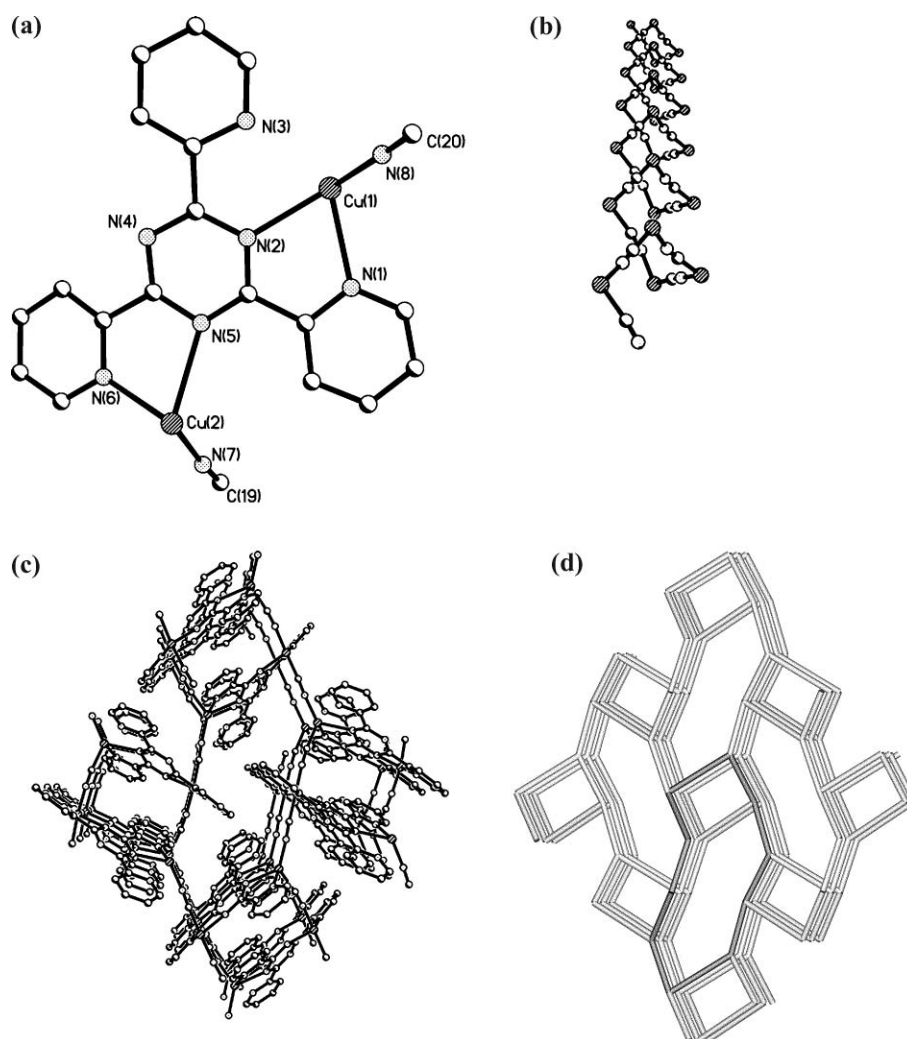
Fig. 2 Complex **2**: (a) representation of the asymmetric unit; (b) view of the right-handed 2_1 helical CuCN chain; (c) 3-D structure along the *a* axis; (d) (10,3)-a topological network.

required the shorter length of spacer or the effective space filling of the network voids/channels from the ligand or solvent and anionic ligand to balance the positive charge of the metal cation. In **2**, the tpt ligand has an uncoordinated pyridyl group, which can be used to fill the voids, and the CN⁻ provides the anion to neutralize the Cu(I) cation. The example of **2** offers a new way to construct the non-interpenetrating neutral (10,3)-a network.

Complex **3** adopts a two-dimensional structure, in which the coordination environments found for both distorted tetrahedral Cu(I) and bis-bidentate tpt ligand are similar to **2** (Fig. 3(a)). However, the unsymmetrical unit in **3** is only half that of **2**. The N(3) atom resides on the twofold symmetry axis with site occupancy 0.5. The N(4) and C(9) of the uncoordinated pyridyl are site occupancy disordered. The two indistinguishable C/N atoms in the cyanide group occupy the same sites, and thus are labeled as X1, X2. The Cu(1)–N(1) and Cu(1)–N (2) distances are 2.191(7) and 2.232(6) Å, respectively, slightly longer than common Cu–N distances. The Cu–X distances are 1.919(8) and 1.902(7) Å, which are similar to those found in **2**. As in **2**, the copper centred angles in **1** vary from 75.5(2) to 126.6(3)°, resulting in the copper atom possessing a highly distorted tetrahedral geometry.

Unlike the situation in compound **3**, where the CuCN chains are infinite helical chains with 2_1 screw axis, in complex **3** the CuCN chains run around and cross two parallel axes forming *meso*-helices (Fig. 3(b)). Then, the CuCN chains are extended to a two-dimensional (6,3) network through the bis-bidentate tpt bridging ligand (Fig. 3(c)).

Supramolecular isomerism is of particular importance for crystal engineering because the difference in suprastructure between isomers will lead to remarkably different application as solid materials.[3b,c,21] However, most reported examples in coordination networks are pseudopolymorphic for they contain different solvent molecules in the structures.[22] The two compounds **2** and **3**, in which the local connectivity of both the metals and ligands are the same, represent high-dimensional supramolecular isomers bearing a fixed stoichiometry of CuCN : tpt = 2 : 1. The use of tpt as ligand and CN⁻ as coordinated anion is likely a key to the formation of supramolecular isomers because the tpt can chelate two metal atoms forming two stable five-membered rings and CuCN can extend in varied chains with fixed stoichiometry of Cu : CN⁻ = 1 : 1, such as zigzag, helical and *meso*-helical chain. Therefore, we believe that the infinite assembly of tpt with CuCN
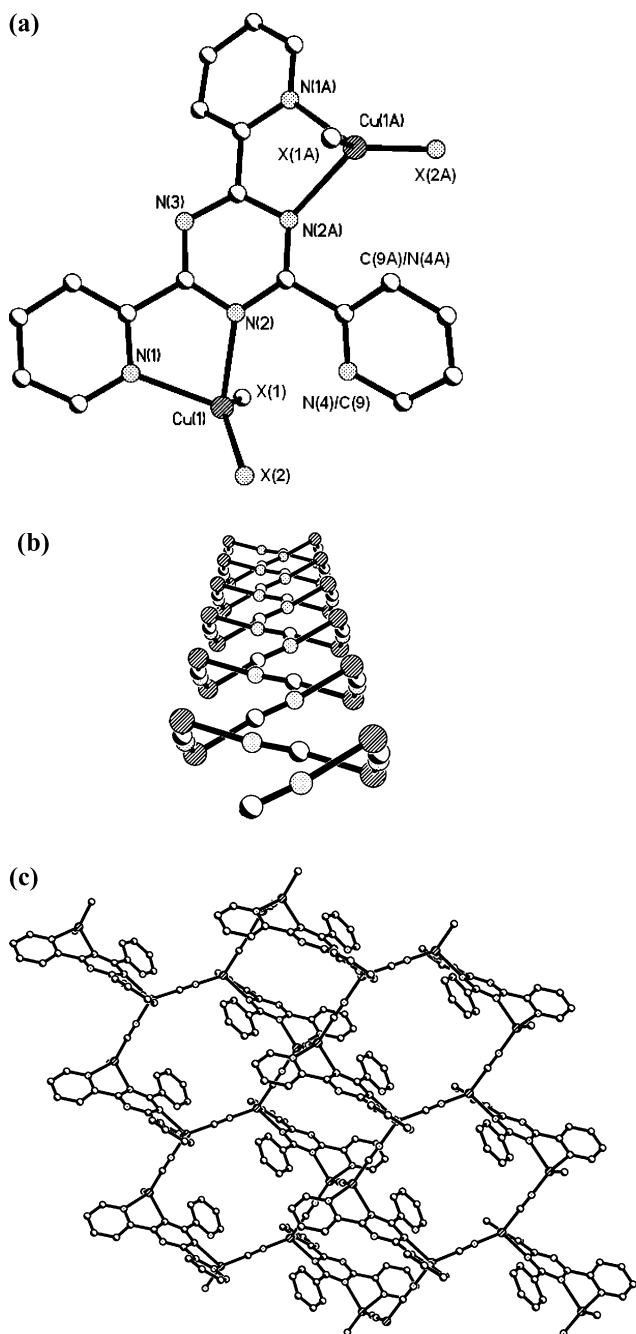
Fig. 3 Complex **3**: (a) coordination environment; (b) view of the *meso*-helical CuCN chain; (c) 2-D structure. Symmetry code: A: $-x + 2$, y, $-z + 3/2$.

could possibly afford a variety of supramolecular isomers owing to the stable coordination mode of tpt and competition in varied CuCN chains.

The crystal structure of **4** contains one tpt ligand, one non-decomposed CuSCN and one CuCN co-existing in the asymmetric unit, as illustrated in Fig. 4(a). The coordination geometry of the five-coordinated Cu(1) atom is approximately square pyramidal with three N donors of the chelating tpt and another N donor [N(8A)] of the CN⁻ occupying the basal sites and a S donor of SCN⁻ occupying the vertex site, similar to that in our previous terpyridine compound.[23] The Cu(1)–N(1) and Cu(1)–
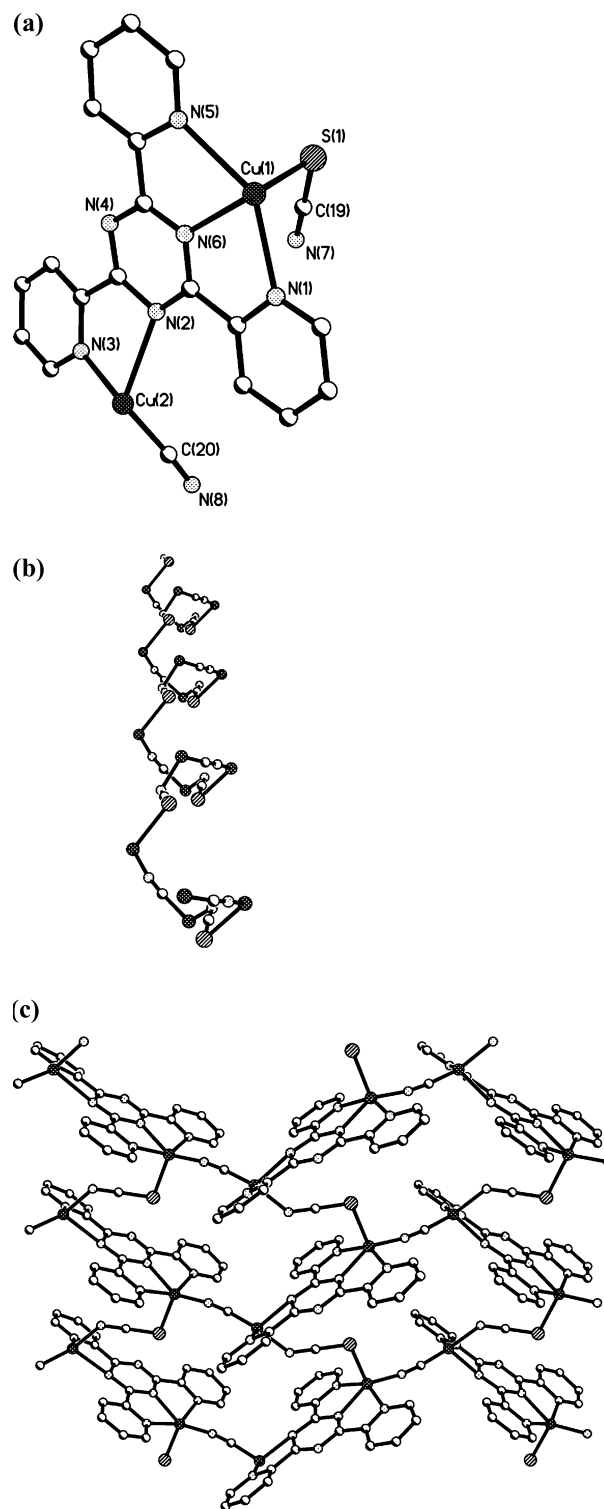
Fig. 4 Complex **4**: (a) representation of the asymmetric unit; (b) view of the right-handed 2_1-helical CuCN–CuSCN chain; (c) 2-D structure.

N(5) distances of 2.322(9) and 2.399(8) Å are obviously longer than common Cu–N distances. The other Cu(1)–donor bond distances [Cu(1)–N(6) 2.085(7), Cu(1)–N(8A) 1.909(10), Cu(1)–S(1) 2.362(3) Å] are normal. The highly distorted tetrahedral coordination environment of Cu(2) is similar to that in **2** and

3 with Cu–N distances ranging from 2.011(9) to 2.404(7) Å, copper centred bond angles ranging from 90.3(4) to 127.9(4)°. It is noteworthy that the Cu(I) atoms are linked by CN⁻ and SCN⁻ anions into infinite helical CuCN–CuSCN chains along a 2₁ screw axis in right-handed fashion (Fig. 4(b)). As far as we are aware, this is the first example of mixed CuSCN–CuCN chains existing in a 2-D structure. The two-dimensional chiral (6,3) network containing extended CuCN–CuSCN chains and bis-bidentate tpt ligand bridges is topologically identical with that of **3** (Fig. 4(c)).

In the asymmetric unit of complex **5**, there are two crystallo-graphically independent copper(I) atoms which adopt different co-ordination geometries, as shown in Fig. 5(a). The coordination geometry of five-coordinated Cu(1) atom is approximately trigonal-bipyramidal with three N donors from the chelating tpt ligand and two S donor from two SCN⁻ ligands. Like Cu(1) with five-coordination geometry in **4**, there are two obviously long Cu(1)–N bond distances [Cu(1)–N(1) 2.371(5), Cu(1)–N(3) 2.358(5) Å] in **5**. The Cu(1)–S bond distances [Cu(1)–S(1) 2.2949(19), Cu(1)–S(1A) 2.339(2) Å] in **5** are also close to the Cu(1)–S(1) bond distance [2.362(3) Å] in **4**. The Cu(2) adopts a distorted tetrahedral geometry and coordinates with two S donors and two N donors from four SCN⁻ ligands. The Cu(2)–N distances [Cu(2)–N(7) 1.921(5),Cu(2)–N(8B) 1.977(5) Å] are common for CuSCN, and the Cu(2)–S distances [Cu(2)–S(2C) 2.449(2), Cu(2)–S(2) 2.466(2) Å] are longer than the Cu(1)–S distances in other reports.[24] Interestingly, the SCN⁻ anions bridging Cu(I) form a tri-ladders-like [CuSCN]ₙ ribbon (Fig. 5(b)), which is severed by tpt ligands (Fig. 5(c)). Within the ribbons, each thiocyanate coordinates three copper(I) and adopts a μ₃ bridge (two μ-S and one μ-N). Unusually, the arrangement leads to the formation of two types of rings (ten-membered ring: Cu–SCN–Cu–S–Cu–SCN, eight-membered ring: Cu–SCN–Cu–SCN). Unlike the reported ten-membered ring[24a] adopting a pseudo-chair conformation, the ten-membered ring in **5** adopts a boat conformation. On the other hand, the eight-membered ring adopts the pseudo-chair conformation.

Thermogravimetric characterization

Thermogravimetric analyses of complexes **1–5** are given in Fig. 6. Complex **1** is stable until around 160 °C and a total weight of 73.8% is lost from 160 to 360 °C, which corresponds to the removal of all dppeS₂ ligands (calculated 72.0%). The thermal degradation behaviors of complexes **2** and **3** are similar. Their structural skeletons remain stable until 320 °C. The thermogravimetric curves of **2** and **3** give abrupt weight losses of *ca.* 20.3, 26.4%, respectively, from 320 to 430 °C. These may be caused by yielding more stable carbon nitride through the degradation of triazine of tpt ligand. Such a phenomenon has been observed in an analogous triazine-compound (trichloromelamine).[25] In contrast, complex **4** began to lose weight at a lower temperature around 200 °C, and then a total weight loss of 55.2% through three abrupt weight losses from 200 to 400 °C, which almost corresponds to the removal of the tpt ligands (calculated 59.6%) to yield CuSCN–CuCN. Complex **5** began to lose mass at about 270 °C, and a total weight loss of 38.9% through an abrupt loss from 270 to 400 °C, similar to complexes **2** and **3** which only lose total weights of 20.3, 26.4%, respectively.
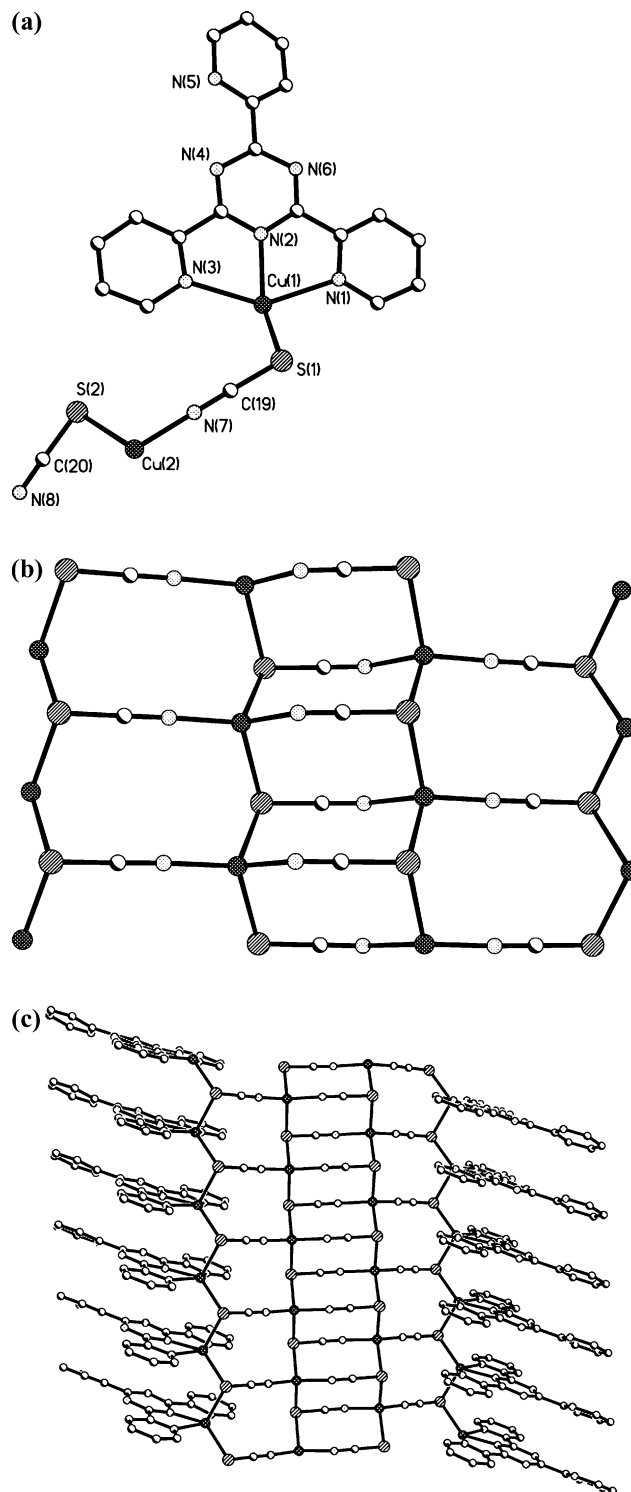
Fig. 5 Complex **5**: (a) representation of the asymmetric unit; (b) view of the tri-ladder-like [CuSCN]ₙ chain; (c) 1-D structure.

Conclusion

In summary, the sulfur transfer from CuSCN to dppe forming dppeS₂ under solvothermal conditions has been observed and determined by the characterization of complex **1** and isolation of dppeS₂, which represents another example of the transformation from inorganic sulfur to organic sulfur. With the CuSCN
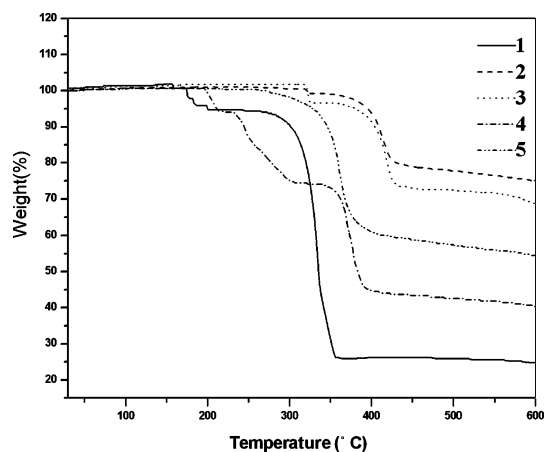
Fig. 6 Thermogravimetry curves of complexes **1–5**.

decomposition reactions, we successfully synthesized three novel polymeric CuCN-tpt complexes, including two genuine high-dimensional supramolecular isomers. Such a circuitous route for yielding CuCN by decomposition CuSCN provides a new avenue for constructing CuCN containing frameworks, which may be difficult to obtain from CuCN directly. Synthesis of **2** represents a new way to construct a non-interpenetrated and neutral (10,3)-a net by different linkers. The decomposition reactions of CuSCN seem to be temperature- and solvent-dependent.

Acknowledgements

References

1 (a) J.-K. Cheng, Y.-G. Yao, J. Zhang, Z.-J. Li, Z.-W. Cai, X.-Y. Zhang, Z.-N. Chen, Y.-B. Chen, Y. Kang, Y.-Y. Qin and Y.-H. Wen, *J. Am. Chem. Soc.*, 2004, **126**, 7796; (b) X.-M. Zhang, M.-L. Tong and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2002, **41**, 1029; (c) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B. F. Abrahams and Z.-L. Xue, *Angew. Chem., Int. Ed.*, 2002, **41**, 3800; (d) J.-P. Zhang, S.-L. Zheng, X.-C. Huang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2004, **43**, 206.
2 X.-M. Zhang, *Coord. Chem. Rev.*, 2005, **249**, 1201.
3 (a) D. Sun, Y. Ke, T. M. Mattox, B. A. Ooro and H.-C. Zhou, *Chem. Commun.*, 2005, 5447; (b) X.-C. Huang, J.-P. Zhang, Y.-Y. Lin and X.-M. Chen, *Chem. Commun.*, 2005, 2232; (c) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *Dalton Trans.*, 2005, 3681; (d) X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li, Z.-M. Su and L. Carlucci, *Angew. Chem., Int. Ed.*, 2005, **44**, 5824.
4 (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) D. Li, W.-J. Shi and L. Hou, *Inorg. Chem.*, 2005, **44**, 3907; (d) T. Wu, D. Li and S. W. Ng, *CrystEngComm*, 2005, **7**, 514; (e) L. Hou, D. Li, W.-J. Shi, Y.-G. Yin and S. W. Ng, *Inorg. Chem.*, 2005, **44**, 7825; (f) R. Peng, T. Wu and D. Li, *CrystEngComm*, 2005, **7**, 595.
5 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
6 (a) W. A. Embry and G. H. Ayres, *Anal. Chem.*, 1968, **40**, 1499; (b) M. J. Janmohamed and G. H. Ayres, *Anal. Chem.*, 1972, **44**, 2263; (c) R. S. Vagg, R. N. Warrener and E. C. Watton, *Aust. J. Chem.*, 1969, **22**, 141.
7 (a) T. Glaser, T. Lügger and R. Fröhlich, *Eur. J. Inorg. Chem.*, 2004, 394; (b) F. P. Pruchnik, P. Jakimowicz, Z. Ciunik, J. Zarkrzewska-Czerwinska, A. Opolski, J. Wietrzyk and E. Wojdat, *Inorg. Chim. Acta*, 2002, **334**, 59; (c) P. Paul, B. Tyagi, M. M. Bhadbhade and E. Suresh, *J. Chem. Soc., Dalton Trans.*, 1997, 2273.
8 (a) J.-L. Song, Z.-C. Dong, H.-Y. Zeng, W.-B. Zhou, T. Naka, Q. Wei, J.-G. Mao, G.-C. Guo and J.-S. Huang, *Inorg. Chem.*, 2003, **42**, 2136; (b) J.-K. Cheng, Y.-B. Chen, L. Wu, J. Zhang, Y.-H. Wen, Z.-J. Li and Y.-G. Yao, *Inorg. Chem.*, 2005, **44**, 3386.
9 (a) M. E. L. Kohnen, J. S. S. Damsté, H. L. ten Haven and J. W. de Leeuw, *Nature*, 1989, **341**, 640; (b) D. P. Kelly, *Nature*, 1987, **326**, 830; (c) J. S. S. Damst, S. G. Wakeham, M. E. L. Kohnen, J. M. Hayes and J. W. de Leeuw, *Nature*, 1993, **362**, 827; (d) R. P. Kiene and B. F. Taylor, *Nature*, 1988, **332**, 148.
10 *Crystal data* for dppeS₂ at 293(2) K: monoclinic, space group, $C2/c$, $a = 15.805(3)$, $b = 8.9531(18)$, $c = 17.435(4)$ Å, $\beta = 107.964(4)°$, $V = 2346.9(8)$ Å³.
11 G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, Göttingen University, Göttingen, Germany, 1997.
12 S. S. Sandhu and T. Singh, *Transition Met. Chem.*, 1976, **1**, 155.
13 (a) X.-M. Zhang and R.-Q. Fan, *Inorg. Chem.*, 2005, **44**, 3955; (b) X.-M. Zhang, R.-Q. Fan and H.-S. Wu, *J. Am. Chem. Soc.*, 2005, **127**, 7670.
14 S. J. Hibble, S. G. Eversfield, A. R. Cowley and A. M. Chippindale, *Angew. Chem., Int. Ed.*, 2004, **43**, 628.
15 (a) A. L. Rheingold and G. P. A. Yap, personal communication, 1996; (b) A. Shaver, B. E. Mouatassim and A. M. Lebuis, personal communication, 2001 (CCDC 165284).
16 E. Colacio, J. M. Domínguez-Vera, F. Lloret, J. M. M. Sánchez, R. Kivekäs, A. Rodríguez and R. Sillanpää, *Inorg. Chem.*, 2003, **42**, 4209.
17 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.
18 C.-M. Liu, S. Gao, D.-Q. Zhang, Y.-H. Huang, R.-G. Xiong, Z.-L. Liu, F.-C. Jiang and D.-B. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 990.
19 (a) B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 1313; (b) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393; (c) X.-H. Bu, K. Biradha, T. Yamaguchi, M. Nishimura, T. Ito, K. Tanaka and M. Shionoya, *Chem. Commun.*, 2000, 1953.
20 (a) B. F. Abrahams, P. A. Jackson and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 2656; (b) X.-H. Bu, W. Chen, M. Du, K. Biradha, W.-Z. Wang and R.-H. Zhang, *Inorg. Chem.*, 2002, **41**, 437.
21 (a) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (b) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *Cryst. Growth Des.*, 2006, **6**, 519; (c) J.-P. Zhang, Y.-Y. Lin, X.-C. Huang and X.-M. Chen, *Chem. Commun.*, 2005, 1258; (d) S. Masaoka, D. Tanaka, Y. Nakanishia and S. Kitagawa, *Angew. Chem., Int. Ed.*, 2004, **43**, 2530; (e) N. Masciocchi, S. Bruni, E. Cariati, F. Cariati, S. Galli and A. Sironi, *Inorg. Chem.*, 2001, **40**, 5897.
22 (a) T. Wu, B.-H. Yi and D. Li, *Inorg. Chem.*, 2005, **44**, 4130; (b) B. Chen, F. R. Fronczek and A. W. Maverick, *Chem. Commun.*, 2003, 2166; (c) B. Rather, B. Moulton, R. D. B. Walsh and M. J. Zaworotko, *Chem. Commun.*, 2002, 694.
23 Q. Feng, D. Li, Y.-G. Yin, X.-L. Feng and J.-W. Cai, *Acta Chim. Sinica*, 2000, **60**, 2167.
24 (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) Q.-M. Wang, G.-C. Guo and T. C. W. Mak, *Chem. Commun.*, 1999, 1849.
25 D. R. Miller, J. Wang and E. G. Gillan, *J. Mater. Chem.*, 2002, **12**, 2463.