Crystal Structures and Characterizations of Bis(pyrrolidinedithiocarbamato) Cu(II) and Zn(II) Complexes

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The structures of $[Cu(S_2CN(CH_2)_4)_2]$ (1) and $[Zn_2(S_2CN(CH_2)_4)_4]$ (2) have been determined by X-ray crystallography analysis. They are all isomorphous and triclinic, space group of $P\bar{1}$, with $Z=1$. The lattice parameters of compound 1 is: a = 0.63483(2) nm, b = 0.74972(3) nm, c = 0.78390(1) nm, α = 75.912(2)°, β = 78.634(2)° and γ = 86.845(2)°; compound 2: a = 0.78707(6) nm, b = 0.79823(6) nm, c = 1.23246(9) nm, α = 74.813(2)°, β = 73.048(2)° and γ = 88.036(2)°. The copper atom is located on a crystallographic inversion center and zinc atom lies across centers of symmetry. The Cu(II) ion has a square-planar geometry while Zn(II) has a distorted tetrahedral geometry. The thermal gravity (TG) data indicate that no structural transitions in the two compounds were observed and the decomposition products can adsorb gas. Also they all have a high thermal stability.

Keywords X-ray, dithiocarbamate(dtc), thermal gravity(TG), copper(II) and zinc(II) complexes

Introduction

The ability of dithiocarbamate(dtc) binding to metals has been known for many years. It forms chelates with virtually all transition metals.[1] The bidentate anion is also well known as a bridge between two transition metal centers.[2] Water-soluble dialkyldithiocarbamate complexes are known to be tested in various medical applications.[3] Dialkyl-dithiocarbamate sodium salts are good extracting agents for many transition metals,[4] and are good floating agents of flotation concentrate for novel metal ores and copper ores.[5] Some of dialkyl-substituted dithiocarbamate salts have also shown interesting biological effects which include *anti*-alkylation[6] or *anti*-HIV properties.[7] They are also used for the effective antidotes for cadmium intoxication.[8,9] In this paper, the crystal structures and the characterization of bis(pyrrolidinedithiocarbamato) Cu(II) and Zn(II) complexes were reported.

Experimental

Materials

All chemicals were obtained from commercial sources and used without further purification.

Preparation of N-pyrrolidinedithiocarbamato sodium $[NaS_2CN(CH_2)_4]$

To a solution of pyrrolidine (7.0 mL, 0.05 mol) in ethanol (5 mL) were added carbon disulfide (3.1 mL, 0.052 mol) and sodium hydroxide (50% aqueous solution, 4 mL) with stirring at a temperature below 4 ℃. After stirring for 5 h, evaporation of the volatiles was performed without heating. The white pure $[NaS_2CN(CH_2)_4]$ crystal (7.30 g) was obtained by recrystallization from ethanol. Yield 86.7%. Anal. calcd for $[NaS_2CN(CH_2)_4]\cdot 3H_2O$: C 26.91, H 6.28, N 6.28; found C 27.12, H 5.85, N 6.04; IR: ν (OH) 3380sh, ν(CN) 1470s, ν(CS) 970s cm^{-1}.

Preparation of the complex

To a heated aqueous solution of $NaS_2CN(CH_2)_4$ (4%, 5 mL) was added an EtOH solution of copper perchlorate $[Cu(ClO_4)_2\cdot 6H_2O$, 0.08 g, 0.5 mmol] for **1** or zinc perchlorate $[Zn(ClO_4)_2\cdot 6H_2O$, 0.08 g, 0.5 mmol] for **2** with stirring. The brown precipitate for **1** and white precipitate for **2** were formed, respectively. Upon collection by filtration, the deposit was washed with water and dried overnight in air. The deep brown plate-like crystals were obtained by recrystallization from the solution of ethyl-acetate for **1**, and the colorless prism crystals were obtained by recrystallization from the acetonitrile solution for **2**. They were all collected, dried and

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Received January 30, 2002; revised July 9, 2002; accepted September 19, 2002.

Project supported by the Key Project of Educational Administration of Shandong Province (No. J01C05) and the Outstanding Adult-Young Scientific Research Encouraging Foundation of Shandong Province (No. 01BS18).

submitted for elemental analysis. Anal. calcd for $C_{10}H_{16}N_2CuS_4$ (**1**): C 33.70, H 4.49, N 7.87; found C 33.65, H 4.44, N 7.83. Anal. calcd for $C_{10}H_{16}N_2ZnS_4$ (**2**): C 33.61, H 4.48, N 7.84; found C 33.58, H 4.43, N 7.80.

Physical measurements

Elemental analysis for carbon, hydrogen and nitrogen was performed on a Perkin-Elmer 240C analysis instrument. Infrared spectra were recorded in the range of 4000—300 cm^{-1} on a Perkin-Elmer 467 spectrometer using KBr pellets. Thermal gravity (TG) and differential analysis (DTA) were recorded on an SDT 2980 simultaneously for the samples of *ca*. 10 mg under a nitrogen atmosphere (150 mL/min) at a heating rate of 20 ℃/min.

Crystallographic study

A summary of the key crystallographic information is given in Table 1. Reflection data and reflections for the unit cell determination were measured at 20 ℃ using Mo Kα radiation ($\lambda = 0.071073$ nm) with a graphite monochromator. The technique used was ω-scan with θ limits $2.45° < \theta < 27.49°$ for $[Cu(S_2CN(CH_2)_4)_2]$ (**1**) and $2.69° < \theta < 27.50°$ for $[Zn_2(S_2CN(CH_2)_4)_4]$ (**2**), respectively. Empirical absorption correction was carried out by using the SADABS[10] program.

Both the structures of $[Cu(S_2CN(CH_2)_4)_2]$ (**1**) and $[Zn_2(S_2CN(CH_2)_4)_4]$ (**2**) were solved by direct methods and refined by least squares on F^2_{obs} by using the SHELXTL[11] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. For $[Cu(S_2CN(CH_2)_4)_2]$ (**1**), final conventional $R(F) = 0.0756$ and $wR(F^2) = 0.1765$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[(\sigma^2(F_o^2) + (0.1115P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. For $[Zn_2(S_2CN(CH_2)_4)_4]$ (**2**), the corresponding $R(F) = 0.0674$ and $wR(F^2) = 0.1622$ for $I > 2\sigma(I)$ with weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0890P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics were plotted using SHELXTL.[11] Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-Ray Crystallography*.[12] The final position parameters of non-hydrogen atoms of compounds **1** and **2** are given in Tables 2 and 3, respectively.

Table 1 Crystal data and structure refinement for the title compounds **1** and **2**

	Compound **1**	Compound **2**
Formula	$C_{10}H_{16}CuN_2S_4$	$C_{20}H_{32}N_4S_8Zn_2$
Formula weight	356.03	715.72
Temperature (K)	183(2)	183(2)
Wavelength (nm)	0.071073	0.071073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (nm, deg)	$a = 0.63483(2)$, $\alpha = 75.912(2)$	$a = 0.78707(6)$, $\alpha = 74.813(2)$
	$b = 0.74972(3)$, $\beta = 78.634(2)$	$b = 0.79823(6)$, $\beta = 73.048(2)$
	$c = 0.78390(1)$, $\gamma = 86.845(2)$	$c = 1.23246(9)$, $\gamma = 88.036(2)$
Volume (nm^3)	0.35476(2)	0.71405(9)
Z, Calculated density ($Mg \cdot m^{-3}$)	1, 1.666	1, 1.664
Absorption coefficient (mm^{-1})	2.106	2.283
$F(000)$	183	368
Crystal size (mm^3)	$0.50 \times 0.12 \times 0.02$	$0.20 \times 0.14 \times 0.08$
θ range for data collection (°)	2.73 to 25.00	1.79 to 25.00
Limiting indices	$-7 \leqslant h \leqslant 7$, $-8 \leqslant k \leqslant 8$, $-5 \leqslant l \leqslant 9$	$-9 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 9$, $-8 \leqslant l \leqslant 14$
Reflections collected/unique	2058/1238 [R(int) = 0.0615]	4126/2501 [R(int) = 0.0905]
Completeness to $\theta = 25.00$	99.3%	99.2%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9591 and 0.4190	0.8384 and 0.6581
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1238/0/80	2501/0/154
Goodness-of-fit on F^{-2}	1.013	0.960
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0756$, $wR_2 = 0.1765$	$R_1 = 0.0674$, $wR_2 = 0.1622$
R indices (all data)	$R_1 = 0.0892$, $wR_2 = 0.1842$	$R_1 = 0.1028$, $wR_2 = 0.1982$
Extinction coefficient	0.005(8)	—
Largest diff. peak and hole ($e \cdot nm^{-3}$)	1626 and −1390	1290 and −1862

Table 2 Atomic coordinates (× 10^4) and equivalent disotropic displacement parameters (× 10 nm^2) for **1**

Atom	*x*	*y*	*z*	U_{eq} [a]
Cu(1)	0	0	5000	23(1)
S(1)	3056(3)	1773(2)	4419(2)	34(1)
S(3)	-1070(2)	2761(2)	3411(2)	32(1)
N(1)	2159(8)	5149(6)	2549(7)	23(1)
C(1)	1467(9)	3465(8)	3343(7)	23(1)
C(2)	830(10)	6582(8)	1641(9)	30(2)
C(3)	2237(11)	8291(8)	1018(9)	38(2)
C(4)	4481(11)	7564(10)	1020(11)	52(2)
C(5)	4290(10)	5829(9)	2461(10)	38(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Atomic coordinates (× 10^4) and equivalent disotropic displacement parameters (× 10 nm^2) for **2**

Atom	*x*	*y*	*z*	U_{eq} [a]
Zn(1)	539(1)	5740(1)	3367(1)	18(1)
S(1)	-166(3)	3344(3)	2783(2)	19(1)
S(2)	2121(3)	6448(3)	1221(2)	18(1)
S(3)	2563(3)	5148(3)	4518(2)	17(1)
S(4)	-929(3)	8195(3)	3734(2)	18(1)
N(1)	1687(9)	3633(8)	560(6)	16(2)
N(2)	3299(8)	1988(9)	4205(6)	15(2)
C(1)	1275(11)	4364(11)	1417(7)	17(2)
C(2)	2893(11)	4430(10)	-626(7)	15(2)
C(3)	3023(12)	3005(11)	-1303(8)	26(2)
C(4)	2512(15)	1336(12)	-337(9)	37(3)
C(5)	1116(12)	1828(10)	661(8)	21(2)
C(6)	2343(10)	2845(9)	4920(7)	10(2)
C(7)	4597(11)	2807(11)	3060(7)	19(2)
C(8)	5269(16)	1258(12)	2543(10)	47(3)
C(9)	3975(15)	-187(12)	3204(9)	43(3)
C(10)	3016(12)	73(11)	4395(8)	20(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Structures of title compounds

Figs. 1 and 2 show perspective views of the complexes of $[Cu(S_2CN(CH_2)_4)_2]$ (**1**) and $[Zn_2(S_2CN(CH_2)_4)_4]$ (**2**) with the atomic numbering scheme, respectively. Fig. 3 shows a perspective view of the crystal packing in the unit cell for **1**. Selected bond distances and angles of **1** and **2** are listed in Tables 4 and Table 5.

In the crystal of the compound **1**, the asymmetric unit contains a pair of independent half-molecules of the complex $[Cu(S_2CN(CH_2)_4)_2]$. The Cu(II) ions of these crystallographically independent molecules lie on the inversion centre.

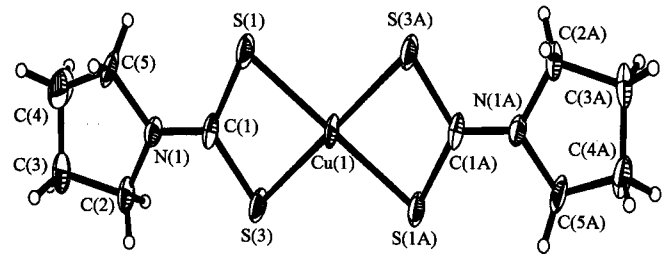

Fig. 1 Molecular structure for $Cu(S_2CNC_2H_4)_2$ with the atomic numbering scheme.

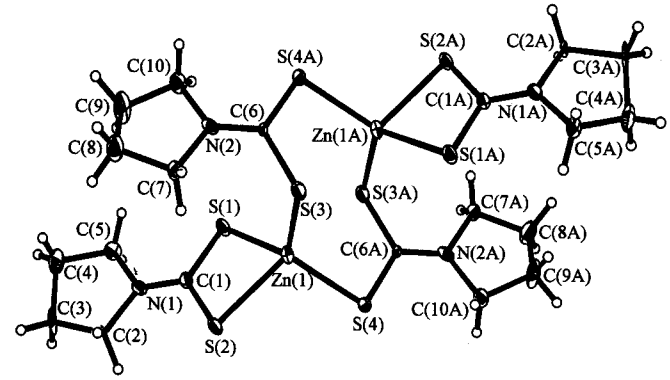

Fig. 2 Molecular structure for $Zn_2(S_2CNC_2H_4)_4$ with the atomic numbering scheme.

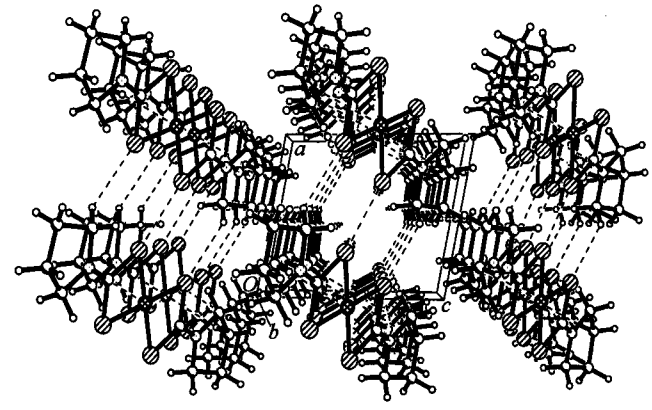

Fig. 3 Packing digagram of the unit cell of $Cu(S_2CNC_2H_4)_2$ (**1**) along the *b*-axis.

The two dithiocarbamate ligands coordinate to copper ion through the S atoms, which forms a four-membered chelate ring. The copper ion will adopt a square-planar geometry. The dimensions within each ligand are normal. The atoms in pyrrolidine ring are nearly within a plane, with the maximum deviation of 0.395(1) nm. The CuS_4 entities with pyrrolidine ring are almost coplanar. The dihedral angles between the CuS_4 plane and pyrrolidine ring are 6.5(3)°. The structure of compound $[Zn_2(S_2CN(CH_2)_4)_4]$ (**2**) is built up of centro-symmeric dimeric entities. The coordination sphere of the Zn(II) ion is best described as a distorted tetrahedral geometry. The two dithiocarbamate ligands each bridge two zinc atoms to form an eight-membered $Zn_2S_4C_2$ ring.

In compound **1**, the bond lengths of S(1)—Cu(1) and

Table 4 Bond lengths (nm) and angles (°) for **1**[a]

Cu(1)—S(3)	0.22852(2)	Cu(1)—S(1)	0.23192(2)
S(1)—C(1)	0.1735(6)	S(3)—C(1)	0.1709(6)
N(1)—C(1)	0.1321(7)	N(1)—C(5)	0.1455(7)
N(1)—C(2)	0.1462(8)	C(2)—C(3)	0.1525(8)
S(3)-Cu(1)-S(1) # 1	102.25(5)	S(3) # 1-Cu(1)-S(1) # 1	177.75(5)
S(3)-Cu(1)-S(1)	77.75(5)	S(3) # 1-Cu(1)-S(1)	102.25(5)
C(1)-S(1)-Cu(1)	83.30(2)	C(1)-S(3)-Cu(1)	84.9(2)
C(1)-N(1)-C(5)	125.5(5)	C(1)-N(1)-C(2)	123.2(5)
C(5)-N(1)-C(2)	111.3(5)	N(1)-C(1)-S(3)	123.1(5)
N(1)-C(1)-S(1)	122.9(4)	S(3)-C(1)-S(1)	114.1(3)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y, -z+1$.

Table 5 Bond lengths (nm) and angles (°) for **2**[a]

Zn(1)—S(4)	0.2320(2)	Zn(1)—S(1)	0.2348(2)
Zn(1)—S(3)	0.2385(2)	Zn(1)—S(2)	0.2492(2)
S(1)—C(1)	0.1737(8)	S(2)—C(1)	0.1744(9)
S(3)—C(6)	0.1774(8)	S(4)—C(6) # 1	0.1716(7)
N(1)—C(1)	0.1293(1)	N(1)—C(2)	0.1480(1)
N(1)—C(5)	0.1488(1)	N(2)—C(6)	0.1307(1)
N(2)—C(7)	0.1479(1)	N(2)—C(10)	0.1500(1)
S(4)-Zn(1)-S(1)	134.54(9)	S(4)-Zn(1)-S(3)	106.77(9)
S(1)-Zn(1)-S(3)	114.05(8)	S(4)-Zn(1)-S(2)	107.10(8)
S(1)-Zn(1)-S(2)	75.89(8)	S(3)-Zn(1)-S(2)	111.71(8)
C(1)-S(1)-Zn(1)	85.2(3)	C(1)-S(2)-Zn(1)	80.7(3)
C(6)-S(3)-Zn(1)	98.3(3)	C(6) # 1-S(4)-Zn(1)	96.0(3)
C(1)-N(1)-C(2)	124.6(7)	C(1)-N(1)-C(5)	124.4(7)
C(2)-N(1)-C(5)	110.9(6)	C(6)-N(2)-C(7)	124.3(7)
C(6)-N(2)-C(10)	122.7(6)	C(7)-N(2)-C(10)	112.6(6)
N(1)-C(1)-S(1)	121.8(7)	N(1)-C(1)-S(2)	120.5(6)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x, -y+1, -z+1$.

S(3)—Cu(1) are 0.2319(1) and 0.2285(1) nm, respectively; and the bond angles of S(1)-Cu(1)-S(3) and S(1)#1-Cu(1)-S(3) are 77.75(5)° and 102.25(5)°, respectively. The carbon-sulfur bonds have an average distance of 0.1722(6) nm. These data are consistent with those in $Cu(S_2CNiPr_2)_2$,[13] which has a similar monomeric structure. In compound **2**, the Zn—S(4) [0.2320(2) nm] and Zn—S(1) [0.2348(2) nm] distances are shorter than Zn—S(2) [0.2492(2) nm] and Zn—S(3) [0.2385(2) nm] ones. The reason is that S(4) and S(1) have anion charge, which form ion bond and coordinational bond with Zn atom. The longest bond length is Zn—S(2), which is related to four-membered chelate ring. In both structures, the N(1)—C(1) bond distance [0.1316(3) nm in **1** and 0.1300(1) nm in **2**] is shorter than the other N—C bond distances, which are indicative of considerable double-bond character. The S—C bond distance of 0.1709—0.1735(6) nm for **1** and 0.1716—0.1774 nm for **2** agree with those in related dtc metal compounds,[13-15] being intermediate between 0.182 nm for a C—S single bond and 0.156 nm for a C = S double-bond.[14] All these parameters are in agreement with those reported before.[16] It is worth noting that, in all the M(II) metal complexes formed with the monovalent anionic bidentate ligands such as dithiocarbamate and xanthate, the two sulfur atoms from each ligand are chelated to only one metal atom to form nearly planar structure.[16] It is therefore surprising that the pyrrolidinedithiocarbamato ligand in **2** maintains the μ-bridging mode and coordinates to two metal atoms form a dimeric structure. It is also noteworthy that the dimeric structure of **2** is quite different from those of $[MeZnS_2CNEt_2]_2$[17] and $[Zn(S_2CNEt_2)_2]_2$[18] in which each dithiocarbamate chelates one zinc atom and bridges the next. The structure of **2** is reminiscent of $Ni[S_2P(OEt)_2]_4$, which also exhibits a dimeric structure containing an eight-membered ring.[19]

From the discussion above, it can be seen that among those 1:1 dithiochelate complexes of divalent metals, those of Cu(II) and Zn(II) complexes with the pyrrolidyldithiocarbamate ligand are unusual. The complexes are isomorphous, and the M···S interactions result in different structures for the two metal complexes of the same ligand.

IR *spectra*

IR spectra of the compounds **1** and **2** exhibit the characteristic absorption. The strong band between 1330 and 1500 cm^{-1} (1498, 1444 and 1335 cm^{-1} in **1**; 1498, 1446 and 1334 cm^{-1} in **2**) is attributed to the stretching vibration of ν_{C-N}, and the band at 946 cm^{-1} to the ν_{C-S} stretching vibration.[20] The band at 913 and 1004 cm^{-1} in those two metal complexes is assigned to asymmetric stretching modes of the CSS group. This band must be highly coupled with other modes and is very sensitive to environmental change. Accordingly, this band has been used to distinguish between disulfur and unisulfur chelation. With disulfur chelation a single band is usually found, whereas when unisulfur chelation occurs, this band is split. The asymmetric band in our case is unsplit, indicating the bidentate modes of the dithio-ligands.[21] Nevertheless, it is necessary to note that the spectra of the Cu and Zn complexes, of which the structures have been determined here using X-ray diffraction and to a bidentate chelate, do not show any complexity in the range of ν_{C-N} or ν_{C-S}. For this reason it does not seem easy to decide from such IR data whether chelate bridging dithiocarbamates are present.

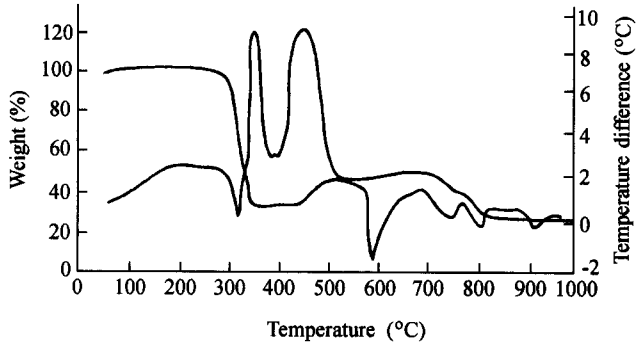

Fig. 4 TG-DTA diagram of compound **1**.

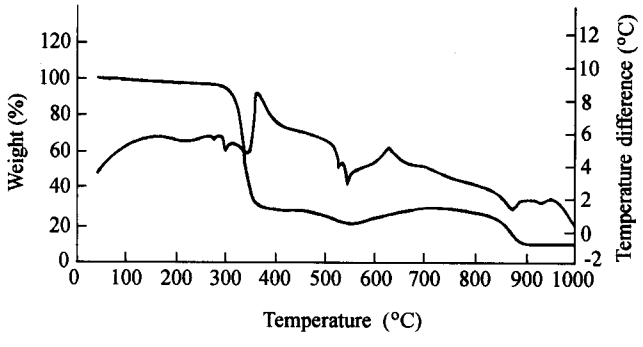

Fig. 5 TG-DTA diagram of compound **2**.

Thermal analysis

Thermal analysis curves of the title compounds **1** and **2** are shown in Figs. 4 and 5, respectively. From Fig. 4, it can be seen that there are two steps of weight loss and one step of weight addition. There is one endothermic peak in the DTA curve at 290 ℃, and about 65.55 wt% weight loss in the TG curve between 270—310 ℃, which is attributed to the decomposition of compound **1** and formation of CuS_2 (calcd 64.14 wt%). Between 324 and 700 ℃, there is about 11.91 wt% weight addition and several exothermic peaks and endothermic peaks, which are ascribed to the adsorption of CuS_2. In this process, CuS_2 will adsorb gas and the weight will increase.[22] With the temperature increasing, the adsorption of CuS_2 decreases and the weight loses. When the temperature is over 700 ℃, CuS_2 decomposes. The weight loss of 74.6 wt% suggests that the residue may be CuS (calcd 73.14 wt%). Thermal analysis curve of the compound **2** is similar to that of compound **1**. It shows no decomposition before 294 ℃, but at 294 ℃, decomposition occurs. At 348 ℃, the weight loss of 61.3 wt% suggests that the residue may be Zn_2S_5 (calcd 59.48 wt%). Between 538 and 870 ℃, there is about 13.91 wt% weight addition, which is ascribed to the adsorption of Zn_2S_5. In this process, Zn_2S_5 will adsorb gas and the weight will increase.[22] With the temperature increasing, the adsorption of Zn_2S_5 decreases and the weight loses. When the temperature is over 870 ℃, Zn_2S_5 decomposes. The weight loss of 84.34 wt% suggests that the residue may be Zn atom (calcd 81.73 wt%). Meanwhile, no structural transitions were found in these two compounds, which implies a high thermal stability in them.

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(E0201283 LU, Y. J.; DONG, L. J.)