Ionothermal synthesis and characterization of two cluster chalcohalides: $[Cr_7S_8Cl_2(NH_3)_{14.5}(H_2O)_{1.5}]Cl_3 \cdot H_2O$ and $[Emim]_2[Sn_2As_2S_4(S_2)_2Br_{2.43}Cl_{1.56}]$

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Supporting Information

1. Synthesis

All chemicals were commercially purchased and used without further purification. The ionic liquids [Bmmim]Cl, [Bmmim][BF_4] and [Emim]Br were purchased from Lanzhou Greenchem ILS (LICP, CAS, China). The other chemicals were purchased from the Chinese venders such as Sinopharm Chemcial Reagent Co. Ltd.

Compound **1** was obtained from an ionothermal reaction. A mixture of $CrCl_3 \cdot 6H_2O$ powder (AR, 0.136 g, 0.510 mmol), S powder (CP, 0.098 g, 3.062 mmol), [Bmmim]Cl (>99%, 1.130 g, 5.988 mmol), urea (AR, 0.121 g, 2.015 mmol) and $NH_2NH_2 \cdot H_2O$ (85%, 0.5 mL, 8.5mmol) were sealed in a stainless steel reactor with a 28 mL Teflon liner and kept at 160 ℃ for 6 days, and then was cooled to room temperature. Black sheet-like crystals were obtained by washed with ethanol and air-dried. The crystals were selected by hand (stable in the air) in 43% yield (0.035 g) based on $CrCl_3 \cdot 6H_2O$. Elemental analysis of **1**: calcd (%): H 4.49, N 18.64; found: H 4.50, N 18.91. The [Bmmim]Cl was necessary for obtaining **1**, though it did not enter the final structure of **1**. Replacing it with 4 mL $NH_2NH_2 \cdot H_2O$ (25~28%) resulted in indefinite black powders, whereas replacing it with [Bmmim][BF_4] (>99%) resulted in $(NH_4)_3CrF_6$ (Figure S1).[1]

Compound **2** was obtained from a mixture of Sn powder (>99.5%, 0.078 g, 0.65 mmol), S powder (CP, 0.064 g, 2.00 mmol), [Emim]Br (>99%, 1.32 g, 6.91 mmol),

As_2S_2 powder (CP, 0.130 g, 0.61 mmol), $AlCl_3$ powder (AR, 0.131g, 0.98 mmol), $EuCl_3·6H_2O$ powder (>99%, 0.177 g, 0.48 mmol) and thiourea powder (AR, 0.058 g, 0.76 mmol) were sealed in a stainless steel reactor with a 28 mL Teflon liner and kept at 160 ℃ for 8 days, and then was cooled to room temperature. Red block–like crystals were obtained by washed with ethanol and air–dried. The crystals were selected by hand (stable in the air) in 33% yield (0.093 g) based on As_2S_2. Elemental analysis calcd (%) of **2**: C 12.92, H 1.99, N 5.02; found: C 12.90, H 2.01, N 5.01. $EuCl_3·6H_2O$ and $AlCl_3$ might form the binary $EuCl_3$-$AlCl_3$ lewis acid,[2] and Br^- is lewis base. When the lewis acid is excessive, the ionic liquid system is acidic which is in favour of the synthesis and crystallization of cationic cluster chalcohalides.[3, 4] When the ionic liquid containing Br^- or Cl^- anion is excessive, the system is alkaline which is in favour of the synthesis and crystallization of anionic cluster chalcohalide of **2**.

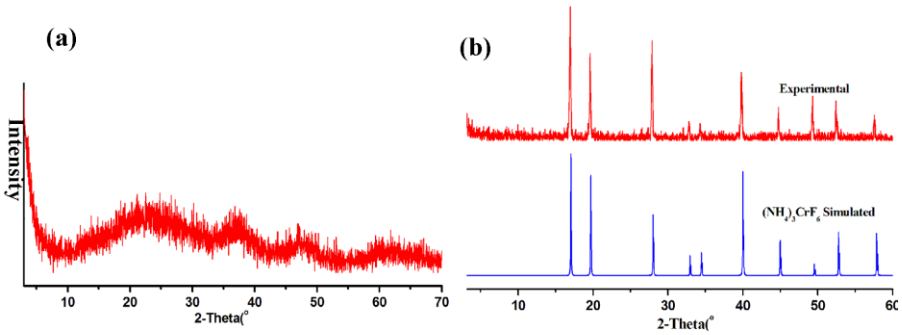


Figure S1. The PXRD patterns of the products obtained by replacing the [Bmmim]Cl with $NH_2NH_2·H_2O$ (25~28%) (a) and [Bmmim][BF_4] (b), respectively, in the synthesis of **1**.

2. Crystal Structure

The intensity data were collected on an Oxford Xcalibur Eos CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at room temperature. The data were corrected for Lorentz and Polarization effects as well as for absorption. The structure was solved by direct methods and refined by full-matrix least-squares cycles in SHELX–97.[5] The selected bond geometries and hydrogen bonds data are listed in Table S1–S4. The empirical formulae were confirmed by element analyses (EA) results and energy–dispersive X–ray spectroscopy (EDS).

In the asymmetric unit of **1** there are three and half of crystallographically independent Cr^{3+} ions, four S^{2-}, one Cl^- anions, 1.5 H_2O, 7.25 NH_3 as ligands and 1.5 Cl^- as counterions and 0.5 lattice water molecule. The $Cr(1)^{3+}$ ion are surrounded by six μ_3-S^{2-} anions, and the $Cr(3)^{3+}$ ion are surrounded by three μ_3–S^{2-} anions and three terminal NH_3 molecules. While the $Cr(2)^{3+}$ and $Cr(4)^{3+}$ ions coordinate to three μ_3–S^{2-} anions, two terminal NH_3 and one terminal Cl/H_2O (NH_3/Cl for Cr(4)).The occupancy ratios of Cl1B/O1 and Cl1/N1B were refined to be 0.25/0.75 and 0.75/0.25, respectively. There is one crystallographically independent Sn^{4+} ion, one As^{3+} ion, four S atom, 1.22 Br^-, 0.78 Cl^- and one $Emim^+$ cation in the asymmetric unit of **2**. The occupancy ratios of terminal atoms Br1/Cl1 and Br2/Cl2 were refined to be 0.556(2)/0.440 and 0.661(2)/0.340, respectively.

CCDC–923296 and 923287 contains the supplementary crystallographic data of the crystal **1** of **2**. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

Table S1. Selected bond lengths (Å) and angles (°) for compound **1**.

Cr(1)-S(1)	2.4002(8)	Cr(3)-N(4)	2.115(2)
Cr(1)-S(1)#1	2.4002(8)	Cr(3)-N(3)	2.1241(19)
Cr(1)-S(3)#1	2.4132(8)	Cr(3)-S(1)	2.3578(7)
Cr(1)-S(3)	2.4132(8)	Cr(3)-S(4)#1	2.3608(8)
Cr(1)-S(4)	2.4266(6)	Cr(3)-S(2)	2.3962(8)
Cr(1)-S(4)#1	2.4266(6)	Cr(4)-N(1B)	2.102(18)
Cr(2)-N(1)	2.123(2)	Cr(4)-N(7)	2.134(2)
Cr(2)-N(2)	2.146(2)	Cr(4)-N(6)	2.142(2)
Cr(2)-O(1)	2.155(5)	Cr(4)-S(1)	2.3518(8)
Cr(2)-S(4)#1	2.3558(8)	Cr(4)-S(3)	2.3687(8)
Cr(2)-S(3)	2.3600(7)	Cr(4)-S(2)	2.3803(7)
Cr(2)-S(2)	2.3713(8)	Cr(4)-Cl(1)	2.4708(14)
Cr(2)-Cl(1B)	2.483(5)	S(4)-Cr(2)#1	2.3558(8)
Cr(3)-N(5)	2.107(2)	S(4)-Cr(3)#1	2.3608(8)
S(1)-Cr(1)-S(1)#1	91.39(4)	N(5)-Cr(3)-S(4)#1	177.98(7)
S(1)-Cr(1)-S(3)#1	178.47(3)	N(4)-Cr(3)-S(4)#1	90.09(7)
S(1)#1-Cr(1)-S(3)#1	87.25(2)	N(3)-Cr(3)-S(4)#1	91.93(6)
S(1)-Cr(1)-S(3)	87.25(2)	S(1)-Cr(3)-S(4)#1	91.42(3)

S(1)#1-Cr(1)-S(3)	178.47(3)	N(5)-Cr(3)-S(2)	92.78(7)
S(3)#1-Cr(1)-S(3)	94.11(4)	N(4)-Cr(3)-S(2)	178.79(7)
S(1)-Cr(1)-S(4)	91.58(2)	N(3)-Cr(3)-S(2)	94.10(7)
S(1)#1-Cr(1)-S(4)	88.81(2)	S(1)-Cr(3)-S(2)	89.56(3)
S(3)#1-Cr(1)-S(4)	87.67(2)	S(4)#1-Cr(3)-S(2)	88.94(3)
S(3)-Cr(1)-S(4)	91.94(2)	N(1B)-Cr(4)-N(7)	80.3(4)
S(1)-Cr(1)-S(4)#1	88.81(2)	N(1B)-Cr(4)-N(6)	77.3(5)
S(1)#1-Cr(1)-S(4)#1	91.58(2)	N(7)-Cr(4)-N(6)	85.23(9)
S(3)#1-Cr(1)-S(4)#1	91.94(2)	N(1B)-Cr(4)-S(1)	100.5(5)
S(3)-Cr(1)-S(4)#1	87.67(2)	N(7)-Cr(4)-S(1)	90.13(7)
S(4)-Cr(1)-S(4)#1	179.44(4)	N(6)-Cr(4)-S(1)	175.15(6)
N(1)-Cr(2)-N(2)	84.88(10)	N(1B)-Cr(4)-S(3)	165.8(4)
N(1)-Cr(2)-O(1)	86.23(15)	N(7)-Cr(4)-S(3)	89.63(7)
N(2)-Cr(2)-O(1)	85.35(18)	N(6)-Cr(4)-S(3)	91.94(8)
N(1)-Cr(2)-S(4)#1	90.42(7)	S(1)-Cr(4)-S(3)	89.42(3)
N(2)-Cr(2)-S(4)#1	175.28(7)	N(1B)-Cr(4)-S(2)	101.5(4)
O(1)-Cr(2)-S(4)#1	93.94(17)	N(7)-Cr(4)-S(2)	178.07(8)
N(1)-Cr(2)-S(3)	90.79(7)	N(6)-Cr(4)-S(2)	94.59(6)
N(2)-Cr(2)-S(3)	89.88(6)	S(1)-Cr(4)-S(2)	90.09(3)
O(1)-Cr(2)-S(3)	174.58(16)	S(3)-Cr(4)-S(2)	88.45(3)
S(4)#1-Cr(2)-S(3)	90.60(3)	N(1B)-Cr(4)-Cl(1)	16.9(3)
N(1)-Cr(2)-S(2)	179.66(7)	N(7)-Cr(4)-Cl(1)	93.64(8)
N(2)-Cr(2)-S(2)	95.04(7)	N(6)-Cr(4)-Cl(1)	88.59(8)
O(1)-Cr(2)-S(2)	94.10(14)	S(1)-Cr(4)-Cl(1)	90.31(4)
S(4)#1-Cr(2)-S(2)	89.66(3)	S(3)-Cr(4)-Cl(1)	176.71(4)
S(3)-Cr(2)-S(2)	88.87(3)	S(2)-Cr(4)-Cl(1)	88.27(4)
N(1)-Cr(2)-Cl(1B)	98.67(14)	Cr(4)-S(1)-Cr(3)	90.97(3)
N(2)-Cr(2)-Cl(1B)	90.90(14)	Cr(4)-S(1)-Cr(1)	92.02(3)
O(1)-Cr(2)-Cl(1B)	13.2(2)	Cr(3)-S(1)-Cr(1)	90.20(3)
S(4)#1-Cr(2)-Cl(1B)	89.38(13)	Cr(2)-S(2)-Cr(4)	91.05(3)
S(3)-Cr(2)-Cl(1B)	170.54(13)	Cr(2)-S(2)-Cr(3)	90.07(3)
S(2)-Cr(2)-Cl(1B)	81.66(13)	Cr(4)-S(2)-Cr(3)	89.36(3)
N(5)-Cr(3)-N(4)	88.17(10)	Cr(2)-S(3)-Cr(4)	91.62(3)
N(5)-Cr(3)-N(3)	86.88(8)	Cr(2)-S(3)-Cr(1)	90.95(3)
N(4)-Cr(3)-N(3)	85.21(9)	Cr(4)-S(3)-Cr(1)	91.29(3)
N(5)-Cr(3)-S(1)	89.66(6)	Cr(2)#1-S(4)-Cr(3)#1	91.31(3)
N(4)-Cr(3)-S(1)	91.19(6)	Cr(2)#1-S(4)-Cr(1)	90.72(3)
N(3)-Cr(3)-S(1)	175.08(7)	Cr(3)#1-S(4)-Cr(1)	89.49(3)

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, *y*, -*z*+1/2

Table 2. Selected bond lengths (Å) and angles (°) for compound **2**.

Sn(1)-Cl(1)	2.394(14)	S(2)-Sn(1)#1	2.6340(10)
Sn(1)-Cl(2)	2.473(15)	S(4)-As(1)#1	2.2128(13)

Sn(1)-S(4)	2.4904(12)	N(1)-C(3)	1.287(7)
Sn(1)-S(1)	2.4944(12)	N(1)-C(1)	1.356(7)
Sn(1)-Br(2)	2.591(3)	N(1)-C(4)	1.464(6)
Sn(1)-Br(1)	2.604(4)	N(2)-C(2)	1.301(11)
Sn(1)-S(2)#1	2.6340(10)	N(2)-C(3)	1.302(9)
Sn(1)-S(2)	2.6434(10)	N(2)-C(5B)	1.524(10)
As(1)-S(1)	2.2098(13)	N(2)-C(5)	1.536(11)
As(1)-S(4)#1	2.2128(13)	C(1)-C(2)	1.328(10)
As(1)-S(3)	2.2732(13)	C(5)-C(6)	1.510(9)
S(2)-S(3)	2.0346(16)	C(5B)-C(6B)	1.501(9)
Cl(1)-Sn(1)-Cl(2)	87.0(6)	Br(1)-Sn(1)-S(2)	89.15(14)
Cl(1)-Sn(1)-S(4)	90.9(4)	S(2)#1-Sn(1)-S(2)	87.36(3)
Cl(2)-Sn(1)-S(4)	99.3(4)	S(1)-As(1)-S(4)#1	106.28(5)
Cl(1)-Sn(1)-S(1)	94.6(4)	S(1)-As(1)-S(3)	99.27(5)
Cl(2)-Sn(1)-S(1)	84.6(4)	S(4)#1-As(1)-S(3)	100.30(5)
S(4)-Sn(1)-S(1)	173.44(4)	As(1)-S(1)-Sn(1)	111.23(5)
Cl(1)-Sn(1)-Br(2)	93.3(5)	S(3)-S(2)-Sn(1)#1	107.71(5)
Cl(2)-Sn(1)-Br(2)	7.3(3)	S(3)-S(2)-Sn(1)	106.18(5)
S(4)-Sn(1)-Br(2)	95.62(7)	Sn(1)#1-S(2)-Sn(1)	92.64(3)
S(1)-Sn(1)-Br(2)	87.70(7)	S(2)-S(3)-As(1)	103.18(6)
Cl(1)-Sn(1)-Br(1)	3.4(6)	As(1)#1-S(4)-Sn(1)	110.16(5)
Cl(2)-Sn(1)-Br(1)	88.5(3)	C(3)-N(1)-C(1)	108.1(6)
S(4)-Sn(1)-Br(1)	87.69(13)	C(3)-N(1)-C(4)	126.9(6)
S(1)-Sn(1)-Br(1)	97.70(13)	C(1)-N(1)-C(4)	125.0(5)
Br(2)-Sn(1)-Br(1)	94.66(15)	C(2)-N(2)-C(3)	107.2(7)
Cl(1)-Sn(1)-S(2)#1	177.0(5)	C(2)-N(2)-C(5B)	105.0(9)
Cl(2)-Sn(1)-S(2)#1	95.1(3)	C(3)-N(2)-C(5B)	147.7(9)
S(4)-Sn(1)-S(2)#1	90.97(4)	C(2)-N(2)-C(5)	144.3(10)
S(1)-Sn(1)-S(2)#1	83.43(4)	C(3)-N(2)-C(5)	108.5(9)
Br(2)-Sn(1)-S(2)#1	88.86(6)	C(5B)-N(2)-C(5)	39.4(8)
Br(1)-Sn(1)-S(2)#1	176.34(14)	C(2)-C(1)-N(1)	104.8(7)
Cl(1)-Sn(1)-S(2)	90.4(5)	N(2)-C(2)-C(1)	109.9(8)
Cl(2)-Sn(1)-S(2)	174.1(3)	N(1)-C(3)-N(2)	109.9(7)
S(4)-Sn(1)-S(2)	86.00(4)	C(6)-C(5)-N(2)	111.4(10)
S(1)-Sn(1)-S(2)	90.33(4)	C(6B)-C(5B)-N(2)	94.6(8)
Br(2)-Sn(1)-S(2)	175.92(7)		

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1,-*y*+1,-*z*+1.

Table S3 Selected hydrogen bond data for compound **1**.

D-H---A	*d* (D-H) (Å)	*d* (H---*A*) (Å)	*d* (D---*A*) (Å)	D-H---*A* (°)
O(1)-H(1D)...Cl(2)#2	0.82	2.78	3.542(6)	154.8
N(1B)-H(1G)...O(2)#3	0.89	2.18	3.069(18)	173.1

O(2)-H(2D)...S(1)#2	0.82	3.01	3.831(11)	179.2
O(2)-H(2E)...N(2)	0.82	2.51	3.258(10)	152.8
N(1)-H(1A)...Cl(3)	0.89	2.70	3.461(4)	143.6
N(1)-H(1A)...Cl(3)#1	0.89	2.89	3.627(4)	141.2
N(1)-H(1B)...Cl(2)#2	0.89	2.81	3.667(2)	162.1
N(1)-H(1C)...Cl(1)#4	0.89	2.93	3.654(3)	140.2
N(2)-H(2A)...O(2)	0.89	2.42	3.258(10)	157.3
N(2)-H(2A)...Cl(3)	0.89	2.82	3.632(4)	152.0
N(2)-H(2B)...Cl(2)#5	0.89	2.68	3.526(3)	158.3
N(2)-H(2C)...Cl(2)#2	0.89	2.57	3.419(2)	160.8
N(4)-H(4A)...Cl(2)	0.89	2.94	3.720(2)	147.0
N(4)-H(4B)...S(1)#1	0.89	2.71	3.376(2)	132.6
N(4)-H(4B)...Cl(3)#6	0.89	2.92	3.614(4)	135.8
N(4)-H(4C)...Cl(2)#7	0.89	2.67	3.521(2)	160.1
N(5)-H(5A)...Cl(2)	0.89	2.53	3.416(2)	171.4
N(5)-H(5B)...S(2)#5	0.89	2.78	3.448(2)	133.3
N(5)-H(5B)...Cl(1B)#5	0.89	2.80	3.517(6)	138.9
N(5)-H(5B)...Cl(1)	0.89	2.96	3.358(3)	109.4
N(5)-H(5C)...O(2)#8	0.89	2.63	3.360(11)	139.9
N(5)-H(5C)...Cl(3)#8	0.89	2.92	3.624(4)	137.0
N(3)-H(6A)...Cl(2)#7	0.89	2.82	3.598(2)	147.0
N(3)-H(6B)...Cl(1)#5	0.89	2.77	3.537(2)	144.8
N(3)-H(6B)...Cl(1B)	0.89	2.80	3.353(6)	121.4
N(3)-H(6C)...Cl(2)	0.89	2.62	3.491(2)	165.0
N(7)-H(7A)...Cl(1)#9	0.89	2.77	3.643(3)	166.8
N(7)-H(7B)...S(4)	0.89	2.82	3.473(3)	131.5
N(7)-H(7C)...O(2)#3	0.89	2.52	3.305(10)	147.9
N(7)-H(7C)...Cl(3)#3	0.89	2.96	3.727(5)	145.0
N(6)-H(8A)...Cl(1)#9	0.89	2.91	3.753(3)	158.4
N(6)-H(8B)...O(2)#3	0.89	2.64	3.424(11)	148.0
N(6)-H(8B)...Cl(3)#3	0.89	2.66	3.503(4)	158.4
N(6)-H(8C)...Cl(2)#5	0.89	2.72	3.563(2)	158.6

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, *y*, -*z*+1/2; #2 *x*, *y*+1, *z*; #3 -*x*+1/2, *y*-1/2, -*z*+1/2; #4 *x*+1/2, *y*+1/2, *z*; #5 -*x*+1/2, -*y*+1/2, -*z*; #6 -*x*+1, *y*-1, -*z*+1/2; #7 -*x*+1, -*y*, -*z*; #8 *x*, *y*-1, *z*; #9 -*x*+1/2, *y*+1/2, -*z*+1/2.

Table S4. Selected hydrogen bond data for compound **2**.

D-H---A	*d* (D-H) (Å)	*d* (H---*A*) (Å)	*d* (D---*A*) (Å)	D-H---*A* (°)
C(1)-H(1A)...Cl(2)#2	0.93	2.83	3.673(16)	151.8
C(1)-H(1A)...Br(2)#2	0.93	3.08	3.906(8)	148.7
C(3)-H(3A)...Cl(1)#3	0.93	2.85	3.62(2)	140.0
C(3)-H(3A)...Br(1)#3	0.93	2.96	3.728(9)	140.9
C(2)-H(2A)...S(3)#4	0.93	2.98	3.908(8)	172.9
C(6)-H(6C)...S(3)#1	0.96	2.92	3.735(14)	142.9

C(6)-H(6B)...S(4)#5	0.96	3.01	3.844(13)	146.5
C(6B)-H(6D)...S(4)#6	0.96	2.86	3.482(11)	123.2
C(6B)-H(6E)...S(3)#1	0.96	3.02	3.882(19)	150.0

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1,-*y*+1,-*z*+1; #2 -*x*+1,*y*-1/2,-*z*+3/2; #3 *x*-1/2,*y*,-*z*+3/2; #4 *x*-1/2,-*y*+1/2,-*z*+1; #5 -*x*+1/2,*y*-1/2,*z*; #6 *x*-1/2,-*y*+3/2,-*z*+1.

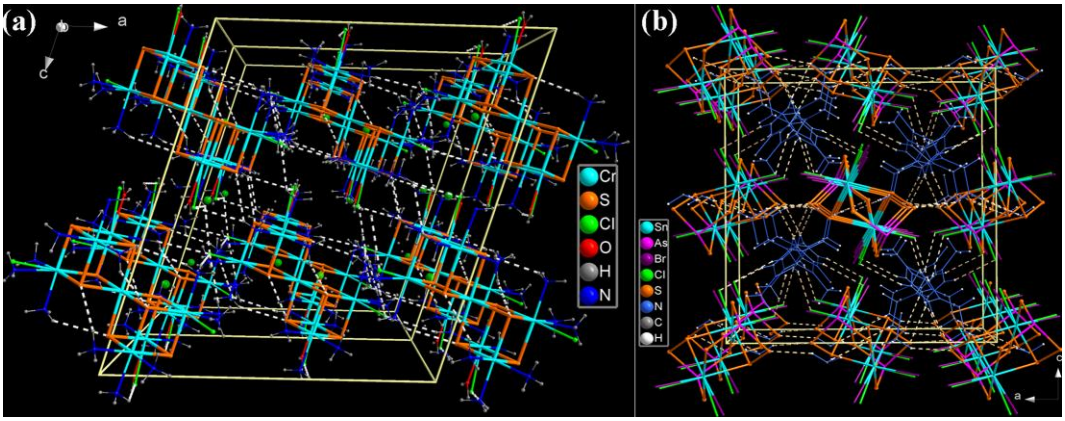


Figure S2. The H-bond networks in **1** (a) and **2** (b).

3. Physical measurements

All chemicals were used as purchased without further purification. Microprobe elemental analyses were performed by using a field–emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA), whereas element analyses of C, H and N were performed on a German Elementar Vario EL III instrument. The infrared spectrum was taken on a Magna 750 FTIR spectrometer with sample as KBr pellet in the range of 4000–450 cm^{-1}. Powder X–ray diffraction (PXRD) pattern was recorded on a Miniflex II diffractometer at 30 kV and 15 mA using Cu $K\alpha$ (1.54178 Å), with a scan speed of 0.15°/min at room temperature. The simulated PXRD pattern from single crystal data was produced using the PowderCell program. Thermoanalysis (TG) was carried out with a NETZSCH STA449F3 unit, at a heating rate of 5 ℃/min under a nitrogen atmosphere. Optical diffuse reflectance spectrum was measured at room temperature with a Perkin–Elmer Lambda 900 UV/Vis spectrophotometer by using $BaSO_4$ powder as 100% reflectance and the room–temperature optical absorption spectrum of the title compound was obtained from diffuse reflectance experiment[6, 7]. The variable–temperature magnetic susceptibilities (2~230k) were measured with a Quantum Design PPMS 6000 magnetometer under an applied field of 5000 Oe with the crystalline powder samples kept in a capsule for weighing.

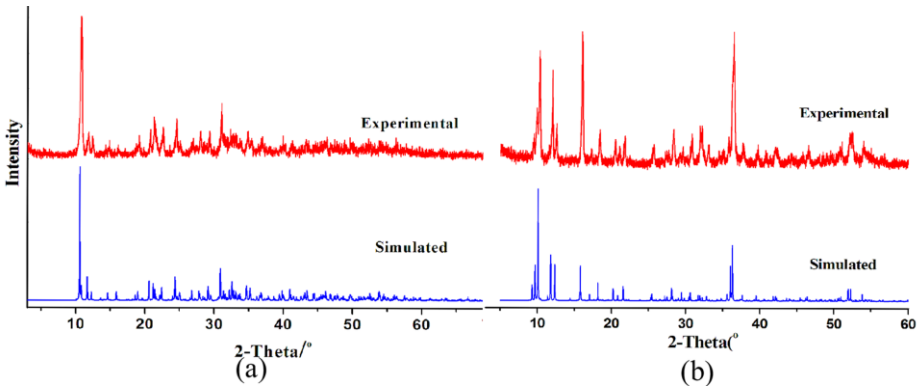


Figure S3. The PXRD patterns (red) are in good agreement with the simulated PXRD patterns (blue) for crystal structures of compounds **1** (b) and **2** (a).

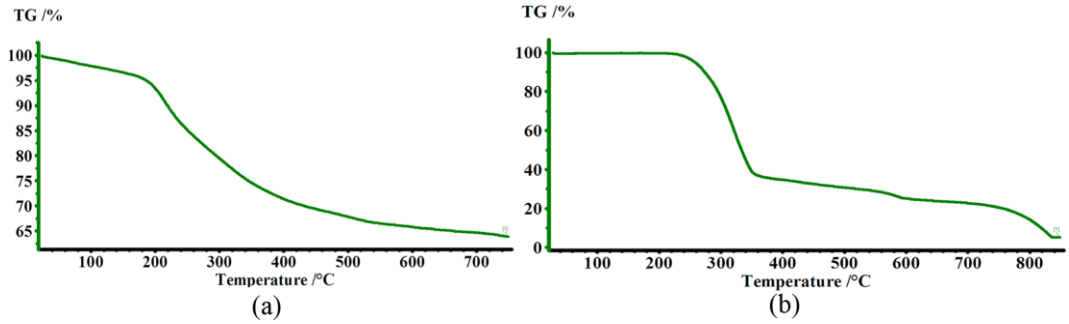


Figure S4. The TG curves for compound **1** (a) and **2** (b).

The phase purity of **1** and **2** were confirmed PXRD (Figure S3). Thermal stabilities of **1** and **2** were studied by thermogravemtric analyses (TGA) on pure crystalline samples (9.252 mg for **1** and 5.733 mg for **2**) in a NETZSCH STA449F3 unit and the TG curves are depicted in Figure S4. The TG curve of **1** indicates a weight loss of 4.14% from 25℃ to 171℃, attributed to the removal of 2.5 H_2O molecules per formula, consistent with the theoretical weight loss of 4.13%. Then **1** continues to lose a total weight of 31.57% from 171 to 730 ℃, attributed to the removal of NH_3, segmental S and Cl. Compound **2** was stable up to 200 ℃, and then it decomposed with a weight loss of 94.56% from 200 to 840℃(Figure S7).

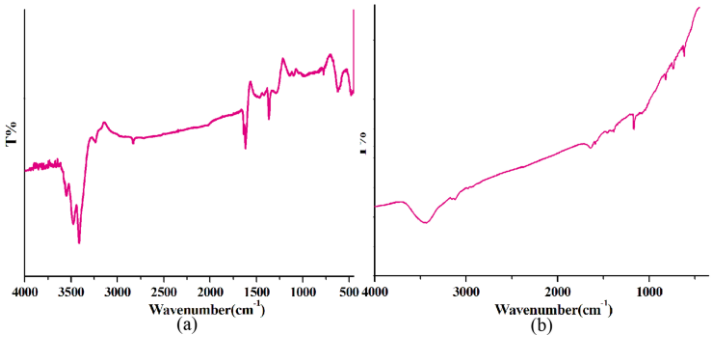
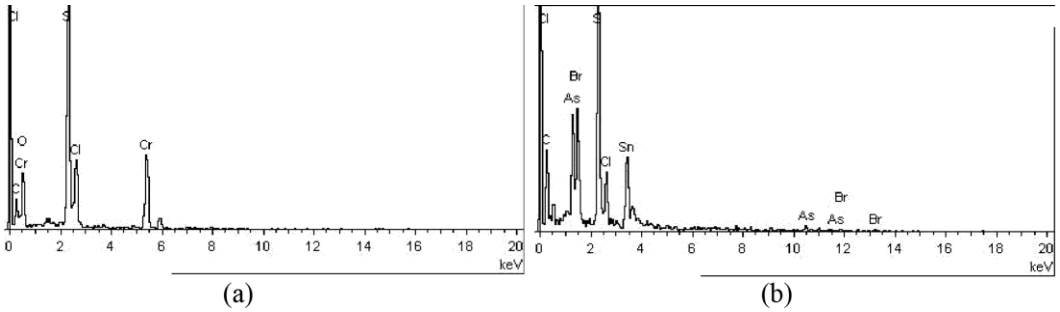
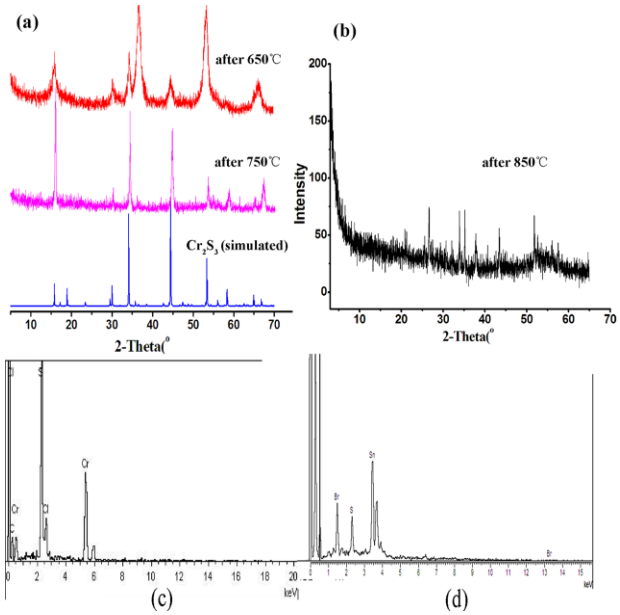


Figure S5 IR spectra of compound **1** (a) and **2** (b).



(a) (b)

Figure S6 The EDS of compounds **1** (a) and **2** (b).



(c) (d)

Figure S7 The PXRD patterns of the residues of **1** (a) and **2** (b) after TG. The residue of **1** after 750℃ is comparable with that simulated from the single crystal X–ray data of Cr_2S_3 (blue). The EDS of the residue of **1** (c) after 750℃ and **2** (d) after 850℃.

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