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New organically templated thiocyanatocadmates and chlorocuprate(II): synthesis and structural characterization

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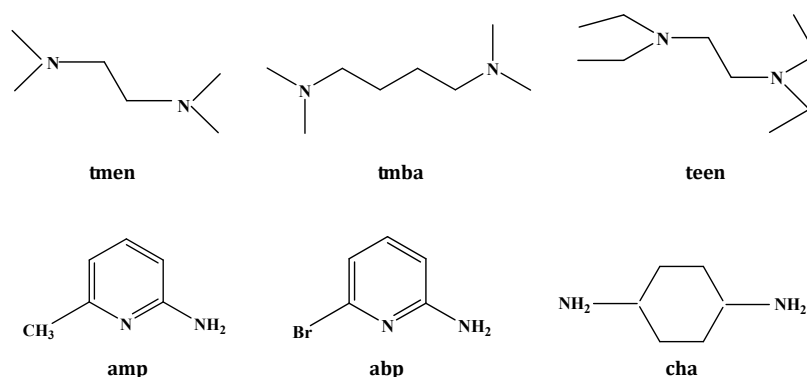
With various organic base molecules as the counteranions, five new thiocyanatocadmates [H₂(tmen)][Cd(SCN)₄] (tmen = *N,N,N',N'*-tetramethylethylenediamine) **1**, [H₂(tmba)][Cd₂(SCN)₆] (tmba = *N,N,N',N'*-tetramethyl-1,4-butanediamine) **2**, [H₂(teen)][Cd₂(SCN)₆] (teen = *N,N,N',N'*-tetra-ethylethylenediamine) **3**, [H(amp)][Cd(SCN)₂(CH₃COO)] (amp = 2-amino-6-methylpyridine) **4** and [H(abp)]₄[Cd(SCN)₄]SO₄·H₂O (abp = 2-amino-6-bromopyridine) **5**, and one new chlorocuprate(II) [H₂(cha)][CuCl₄] (cha = 1,4-cyclohexanediamine) **6** were obtained from a series of simple room-temperature self-assemblies at pH = 2 or 6.5. X-ray single-crystal diffraction analysis reveals that (i) templated by [(CH₃)₂NH(CH₂)₂NH(CH₃)₂]²⁺ (H₂(tmen)²⁺), the anion [Cd(SCN)₄]²⁻ in **1** shows a 1-D linear single-chain structure, whereas templated by [(CH₃)₂NH(CH₂)₄NH(CH₃)₂]²⁺ (H₂(tmba)²⁺), the anion [Cd₂(SCN)₆]²⁻ in **2** shows a 1-D linear double-chain structure. The number of the C atom between two N atoms in the templating agent controls the width of the anionic chain through the N_{amino}-H...N_{SCN} interactions; (ii) templated by [(C₂H₅)₂NH(CH₂)₂NH(C₂H₅)₂]²⁺ (H₂(teen)²⁺), the anion [Cd₂(SCN)₆]²⁻ in **3** exhibits a 3-D open-framework structure, which is based on the zigzag anionic chains. A direct change of the substituent group from -CH₃ to -C₂H₅ alter indirectly the shape of the anionic chain from a linear shape to a zigzag shape; (iii) **4** shows a 3-D supramolecular network structure, which is constructed up from the 1-D zigzag anionic structures by the H(amp)⁺ molecules via the N-H...O interactions. The formation of the zigzag chain derives from the chelation of the CH₃COO⁻ groups to the Cd²⁺ centers; (iv) **5** is indeed a double salt of [H(abp)]₂[Cd(SCN)₄] and [H(abp)]₂SO₄. SO₄²⁻ and H(abp)⁺ form a supramolecular aggregation. Surrounded by the aggregations, the anion [Cd(SCN)₄]²⁻ only shows a dinuclear structure; and (v) templated by H₂(cha)²⁺, the anion [CuCl₄]²⁻ in **6** displays a 2-D perovskite layer structure. The photoluminescence analysis indicates that upon excitation (λ_{ex} = 335 nm for **4**, λ_{ex} = 395 nm for **5**), **4** and **5** emit light (λ_{em} = 365 nm for **4**, λ_{em} = 470 nm for **5**), which can be seen clearly under the UV lamp.

Introduction

As an important branch of hybrid inorganic-organic materials, a certain attention has been paid to the design and synthesis of novel organically templated halometallates and pseudohalometallates.¹ Over the last thirty years, a number of related hybrid compounds have been obtained by using various organic base molecules as the counteranions.² For example, (i) compound [H(py)]₂[Cu₃I₅] (py = pyridine) is a discrete iodocuprate(I) with the highest core number (Cu₃I₅4²⁰⁻);³ (ii) compound [Cu(en)]₂[Cu₇I₁₁] (en = ethylenediamine) is the first example of 3-D chlorocuprate(I) with the occluded [Cu(en)]₂²⁺ cations;⁴ (iii) compound [H₂(edamp)]₂[Pb₇I₁₈]·4H₂O (edamp = Et₂NC₆H₄CH₂C₆H₄NEt₂) is the unique example of 3-D iodoplumbate

with the occluded $\text{H}_2(\text{edamp})^{2+}$ cations.⁵ The continuous investigation of this field for the researchers is generally based on two aims: revealing how the organic cation controls the structure of the inorganic anion, based on the structural information of these hybrid compounds;⁶ obtaining some new materials with the special properties, which derive from a hybrid formation of two moieties.⁷ For instance, (i) the hybrid formation changes the $\text{Cu(I)}\cdots\text{Cu(I)}$ distance in the halocuprate(I). Those with the short $\text{Cu(I)}\cdots\text{Cu(I)}$ distances emit green, yellow or red light, while those with the long $\text{Cu(I)}\cdots\text{Cu(I)}$ distances emit blue light;⁸ (ii) the hybrid formation alter the $\text{Cu(II)}\cdots\text{Cu(II)}$ interaction in the halocuprate(II). Those with the short $\text{Cu(II)}\cdots\text{Cu(II)}$ interactions may exhibit a ferromagnetic property;⁹ (iii) the hybrid formation makes the viologen-templated chlorobismuthates(III) possess the different anionic structures. The anionic size directly influences its photochromic behavior.¹⁰

Our current investigation is focused on the structural characterization of organically templated thiocyanatocadmates.¹¹ The employed templating agents are the multidentate N-containing organic base molecules. Now, some interesting structures have been obtained, such as the 2-D $[\text{H}(2,2'\text{-dtdpy})][\text{Cd}(\text{SCN})_3]$ (dtdpy = dithiodipyridine)¹² and $[\text{H}_2(\text{pdma})][\text{Cd}_2(\text{SCN})_4(\text{SO}_4)]$ (pdma = 1,4-phenylenedimethanamine),¹³ and the 3-D $[(\text{Hdabco})_2\text{Cd}_3(\text{SCN})_8]$ (dabco = 1,4-diazabicyclo[2,2,2]octane)¹⁴ and $[\text{H}_2(\text{tmen})][\text{Cd}_3\text{Cl}_6(\text{SCN})_2]$ (tmen = *N,N,N',N'*-tetramethylethylenediamine).¹⁵ Moreover, some interesting phenomena have also been observed. For instance, the anion of the Cd^{2+} precursor sometimes can appear in the final anionic framework.¹⁶ In our latest report, based on the structural information of compound $[\text{H}(\text{ba})]_2[\text{CdCl}_2(\text{SCN})_2]$ (ba = tert-butylamine) and $[\text{H}_2(\text{tmen})][\text{Cd}_3\text{Cl}_6(\text{SCN})_2]$, we give two possible reasons. One is the special arrangement between $-\text{NH}_3^+$ and Cl^- , making the supramolecular packing more stable. The other is due to the formation of the Cd-Cl oligomer. The SCN^- groups only displace the Cl^- ions on the outside of the Cd-Cl oligomer, so the Cl^- ions on the inside are retained.¹⁵ In this article, five new organic base molecules (*N,N,N',N'*-tetramethylethylenediamine (tmen), *N,N,N',N'*-tetramethyl-1,4-butanediamine (tmba), *N,N,N',N'*-tetra-ethylethylenediamine (teen), 2-amino-6-methylpyridine (amp), and 2-amino-6-bromopyridine (abp)) were selected to continue preparing the organically templated thiocyanatocadmates. Considering that the organically templated halocuprate(II) possess the diverse structures and the nice magnetic properties,^{9,17} we also employ the multidentate N-containing organic base molecules to construct the novel halocuprate(II). Fortunately, from a series of simple room-temperature reactions at pH = 2 or 6.5, six new hybrid Cd^{2+} and Cu^{2+} compounds were obtained, including five thiocyanatocadmates $[\text{H}_2(\text{tmen})][\text{Cd}(\text{SCN})_4]$ **1**, $[\text{H}_2(\text{tmba})][\text{Cd}_2(\text{SCN})_6]$ **2**, $[\text{H}_2(\text{teen})][\text{Cd}_2(\text{SCN})_6]$ **3**, $[\text{H}(\text{amp})][\text{Cd}(\text{SCN})_2(\text{CH}_3\text{COO})]$ **4**, and $[\text{H}(\text{abp})]_4[\text{Cd}(\text{SCN})_4]\text{SO}_4\cdot\text{H}_2\text{O}$ **5**, as well as one chlorocuprate(II) $[\text{H}_2(\text{cha})][\text{CuCl}_4]$ (cha = 1,4-cyclohexanediamine) **6**. Scheme 1 illustrates the molecular structures of organic bases in the title compounds.



Scheme 1 Structures of amine cations in 1-6.

Experimental

Materials and physical measurement

All chemicals are of reagent grade quality, obtained from commercial sources without further purification. Elemental analysis (C, H and N) was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in 4000-400 cm^{-1} region using a powdered sample on a KBr plate. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). TG behavior was investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. Fluorescence spectrum was obtained on a LS 55 fluorescence/phosphorescence spectrophotometer at room temperature. Ultraviolet-visible (UV-vis) spectrum was obtained on a Rigaku-UV-3100 spectrophotometer.

Synthesis of title compounds

[H₂(tmen)][Cd(SCN)₄] 1. A solution of tmen (0.1 ml) in C₂H₅OH (3 ml) was carefully layered over an aqueous solution (5 ml) of a mixture of 3CdSO₄·8H₂O (257 mg, 1 mmol) and NH₄SCN (152 mg, 2 mmol). A few drops of dilute H₂SO₄ were added to acidify the solution to pH = 2. The colorless needle crystals of **1** were obtained after *ca.* 50 days of slow evaporation. Yield: *ca.* 30% based on Cd(II). Anal. Calcd for C₁₀H₁₈N₆S₄Cd **1**: C 25.94, H 3.92, N 18.15. Found: C 25.83, H 3.93, N 17.67%. IR (cm^{-1}): 2100 s, 1465 m, 1398 m, 1332 w, 1152 m, 1056 m, 928 m, 923 w, 773 w, 514 w.

[H₂(tmba)][Cd₂(SCN)₆] 2. A solution of tmba (0.1 ml) in C₂H₅OH (3 ml) was carefully layered over an aqueous solution (5 ml) of a mixture of 3CdSO₄·8H₂O (257 mg, 1 mmol) and NH₄SCN (152 mg, 2 mmol). A few drops of dilute HCl were added to acidify the solution to pH = 2. The colorless needle crystals of **2** were obtained after *ca.* 6 days of slow evaporation. Yield: *ca.* 25% based on Cd(II). Anal. Calcd for C₁₄H₂₂N₈S₆Cd₂ **2**: C 23.37, H 3.08, N 15.57. Found: C 23.55, H 3.04, N 15.25%. IR (cm^{-1}): 2131 s, 2108 s, 1477 m, 1375 m, 1158 w, 1044 w, 1002 w, 953 w, 833 w, 743 w.

[H₂(teen)][Cd₂(SCN)₆] 3. A solution of teen (0.1 ml) in C₂H₅OH (3 ml) was carefully layered over an aqueous solution (5 ml) of a mixture of CdBr₂·4H₂O (344 mg, 1 mmol) and NH₄SCN (152 mg, 2 mmol). A few drops of dilute H₂SO₄ were added to acidify the solution to pH = 2. The colorless needle crystals of **3** were obtained after *ca.* 7 days of slow evaporation. Yield: *ca.* 20% based on Cd(II). Anal. Calcd for C₁₃H₂₆N₅S₃Cd **3**: C 25.70, H 3.51, N 14.99. Found: C 25.29, H 3.59, N 14.28%. IR (cm^{-1}): 2131 w, 2116 s, 2050 s, 1471 m, 1447 m, 1393 w, 1351 w, 1278 w, 1098 w, 1037 w.

[H(amp)][Cd(SCN)₂(CH₃COO)] 4. A solution of amp (108 mg, 1 mmol) in CH₃OH (3 mL) was added slowly to an aqueous solution (5 mL) of a mixture of Cd(CH₃COO)₂·2H₂O (267 mg, 1 mmol) and NH₄SCN (152 mg, 2 mmol). A few drops of dilute NH₃·H₂O were added to neutralize the solution to pH = 6.5. The mixture was stirred for *ca.* 2 days, and then filtered. The light-yellow needle crystals of **4** were obtained after *ca.* 7 days of slow evaporation from the filtrate. Yield: *ca.* 30% based on Cd(II). Anal. Calcd for C₁₀H₁₂N₄O₂S₂Cd **4**: C 30.27, H 3.05, N 14.12. Found: C 30.45, H 3.17, N 14.22%. IR (cm^{-1}): 2129 w, 2108 s, 1669 s, 1530 s, 1416 m, 1308 w, 1176 w, 1002 w, 785 m, 713 m.

[H(abp)]₄[Cd(SCN)₄]SO₄·H₂O 5. A solution of abp (173 mg, 1 mmol) in CH₃OH (3 mL) was added slowly to

an aqueous solution (5 mL) of a mixture of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (267 mg, 1 mmol) and NH_4SCN (152 mg, 2 mmol). A few drops of dilute H_2SO_4 were added to acidify the solution to pH = 2. The mixture was stirred for *ca.* 2 days, and then filtered. The light-yellow needle crystals of **5** were obtained after *ca.* 30 days slow evaporation from the filtrate. Yield: *ca.* 25% based on Cd(II). Anal Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_{12}\text{O}_5\text{S}_5\text{Br}_4\text{Cd}$ **5**: C 24.96, H 2.27, N 14.55. Found: C 25.14, H 2.50, N 14.89%. IR (cm^{-1}): 2123 w, 2096 m, 2033 s, 1657 s, 1596 m, 1466 w, 1375w, 1306 w, 1094 m, 1078 s, 982 m, 797 w, 710 w.

[H₂(cha)][CuCl₄] 6. A solution of cha (114 mg, 1 mmol) in $\text{C}_2\text{H}_5\text{OH}$ (3 ml) was carefully layered over an aqueous solution (5 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (341 mg, 2 mmol). A few drops of dilute H_2SO_4 were added to acidify the solution to pH = 2. The green needle crystals of **6** were obtained after *ca.* six months of slow evaporation. Yield: *ca.* 15% based on Cu(II). Anal Calcd for $\text{C}_6\text{H}_{16}\text{N}_2\text{CuCl}_4$ **6**: C 22.41, H 5.02, N 8.71. Found: C 22.43, H 4.94, N 8.67%. IR (cm^{-1}): 1603 s, 1559 w, 1438 s, 1435 w, 1398 m, 1284 w, 1128 m, 1086 w.

X-ray crystallography

The data were collected with Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Rigaku R-Axis RAPID IP diffractometer for compounds **1** and **2**, and on a Siemens SMART CCD diffractometer for compounds **3-6**. With SHELXTL program, the structures of compounds **1-6** were all solved using direct methods.¹⁸ The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement, and the other hydrogen atoms were treated using a riding model. The hydrogen atoms on N4 in compound **2**, N4 in compound **3**, and on N1 in compound **6** were obtained from the difference Fourier map. The hydrogen atoms on N3 in compound **1**, and on Ow1 in compound **5** were not located. Abp IV in compound **5** suffered from the severely disorder, so the AFIX 66 instruction was employed to fix the pyridine ring, and the anisotropy was not carried out for the disordered atoms. As a result, a larger Q peak around the disordered atoms appeared. The structures were then refined on F^2 using SHELXL-97.¹⁸ CCDC numbers are 1058262-1058267 for compounds **1-6**, respectively. The crystallographic data for the title compounds are summarized in Table 1.

Table 1 Crystal data of **1-6**.

	1	2	3	4	5	6
Formula	$\text{C}_{10}\text{H}_{18}\text{N}_6\text{S}_4\text{Cd}$	$\text{C}_{14}\text{H}_{22}\text{N}_8\text{S}_6\text{Cd}_2$	$\text{C}_{16}\text{H}_{26}\text{N}_8\text{S}_6\text{Cd}_2$	$\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2\text{S}_2\text{Cd}$	$\text{C}_{24}\text{H}_{26}\text{N}_{12}\text{O}_5\text{S}_5\text{Br}_4\text{Cd}$	$\text{C}_6\text{H}_{16}\text{N}_2\text{CuCl}_4$
<i>M</i>	462.99	719.64	747.63	396.76	1154.93	321.56
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	5.9229(12)	5.9186(12)	10.5331(6)	11.1025(7)	9.9159 (4)	9.3655(6)
<i>b</i> (Å)	8.1307(16)	10.709(2)	11.2159(6)	10.9745(5)	12.9791(8)	7.2877(5)
<i>c</i> (Å)	10.051(2)	10.863(2)	15.0643(7)	12.9968(6)	16.8359(8)	8.6164(7)
α (°)	107.23(3)	73.96(3)			68.545(3)	
β (°)	97.19(3)	76.92(3)	128.416(3)	103.624(4)	88.854(3)	92.869
γ (°)	93.76(3)	81.30(3)			79.115(4)	
<i>V</i> (Å ³)	455.97(16)	641.6(2)	1394.41(13)	1539.03(14)	1977.49(17)	587.36(7)
<i>Z</i>	1	1	2	4	2	2
<i>D_c</i> (g cm ⁻³)	1.686	1.862	1.781	1.712	1.940	1.818
μ (mm ⁻¹)	1.656	2.164	1.995	1.692	4.908	2.728
Reflections collected	4145	6297	7690	8461	1124	3235

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Unique reflections	2039	2912	2457	2713	11231	1056
R_{int}	0.0217	0.0270	0.0583	0.0212	0.0317	0.0326
Gof	1.070	1.147	1.198	1.050	1.084	1.129
$R_1, I > 2\sigma(I)$	0.0550	0.0339	0.0329	0.0221	0.0603	0.0453
wR_2 , all data	0.2145	0.1123	0.0859	0.0547	0.1893	0.1175

Results and discussion

Synthetic analysis

All of the reactions were carried out at the ambient conditions. All of the title hybrid compounds were obtained at the acidic environments. On the one hand, the H^+ ion can aid the reactive precursors to dissolve quickly in the solvents to form a clear solution. The single crystals grow easily from a clear solution. On the other hand, the acidic environment can ensure the organic base to be completely protonated. It is noteworthy that the amino-substituted pyridine molecules show an exceptional situation. The pyridyl N atom is found to be easily protonated. For example, the pyridyl N is found to have been protonated at pH = 6.5, based on the preparation of compound **4**. But the amino group is generally not protonated, even when pH = 2, based on the preparation of compounds **4**, **5** and $[H(\text{apy})][Cd(\text{SCN})_3]$ (apy = 4-aminopyridine) reported previously.¹⁵ H_2SO_4 can act as the H^+ resource. But sometimes the SO_4^{2-} group can be mixed into the final framework, as observed in compound **5**. This situation has also been encountered in the past investigation, producing the hybrid compounds $[H_2(\text{pip})]_4[Cd_3Br_8(\text{SCN})_2(\text{SO}_4)_2(\text{H}_2\text{O})] \cdot 4H_2O$ (pip = piperazine), $[H_2(\text{bim})][Cd(\text{SCN})_2(\text{H}_2\text{O})_2]SO_4$ (bim = 2,2'-biimidazole), $[H_2(\text{pympip})]_2[Cd_2(\text{SCN})_4(\text{SO}_4)_2(\text{H}_2\text{O})_4] \cdot 2H_2O$ (pympip = 1-(2-pyrimidyl)piperazine), $[H_2(\text{pdma})][Cd_2(\text{SCN})_4(\text{SO}_4)]$, and $[H_2(4,4'\text{-dtdpy})]_2[CdBr_4]SO_4 \cdot 2.5H_2O$ (dtdpy = dithioidipyrindine). Only when preparing compound **4**, the anion (CH_3COO^-) for the Cd^{2+} salt appears in the resulting framework. In fact, only in the limited example, the CH_3COO^- group is mixed in the final Cd-SCN backbone.¹⁵ As the anion of the Cd^{2+} salt, the X^- ion ($X^- = Cl^-, Br^-$) appears frequently in the resulting Cd-SCN framework, creating some new thiocyanatocadmades with the interesting structures. The typical examples have $[H_2(\text{dabco})]_2[Cd_3Cl_8(\text{SCN})_2] \cdot H_2O$, $[H_2(\text{pip})][CdCl_3(\text{SCN})] \cdot 2H_2O$ ^{16d} and $[CdI(\text{SCN})L]$ ($L = SC(-OC_2H_5)=NH_2$).^{16c} Moreover, with the different acids as the H^+ resource, maybe the distinct products are obtained. For instance, acidified by H_2SO_4 , compound **3** is obtained, while acidified by HBr, compound $[H_2(\text{teen})][CdBr_4]$, a mononuclear compound, is obtained.¹⁹ In the past five years, we employed various organic base molecules to serve as the countercations, self-assembling a series of thiocyanatocadmades. In this article, we attempt to use these organic bases to construct the new halocuprates(II) for the first time. Now, a chlorocuprate(II) **6** has been obtained.

Structural description

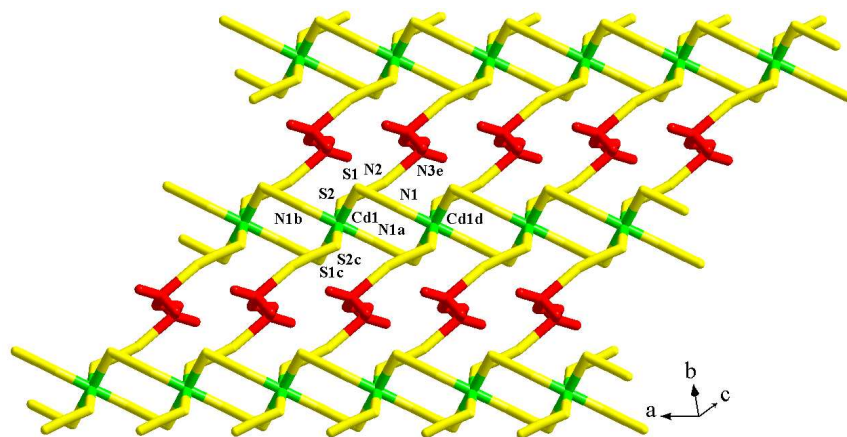


Fig. 1 2-D supramolecular layer network of **1** (a: $-x+2, -y+2, -z$; b: $x-1, y, z$; c: $-x+1, -y+2, -z$; d: $x+1, y, z$; e: $x, y+1, z$).

[H₂(tmen)][Cd(SCN)₄] **1**. X-ray single-crystal diffraction analysis reveals that compound **1** is a chained thiocyanatocadmuate with H₂(tmen)²⁺ as the counteranion. The asymmetric unit of compound **1** is found to be composed of a half Cd²⁺ ion (Cd1), two types of SCN⁻ groups (SCN I labeled as S₍₁₎C₍₁₎N₍₁₎, SCN II labeled as S₍₂₎C₍₂₎N₍₂₎), and a half H₂(tmen)²⁺ cation. Fig. 1 plots the 2-D supramolecular layer network of compound **1**. Templated by H₂(tmen)²⁺, the SCN I groups double bridge the Cd²⁺ centers into a 1-D endless single chain (see Fig. S1 for better understanding). Since two terminal SCN II groups around each Cd²⁺ center adopt a *trans*-configuration arrangement, the chain shows a linear shape ($\angle \text{Cd} \cdots \text{Cd} \cdots \text{Cd} = 180^\circ$). The chain can also be described as a linear arrangement of the 8-membered Cd₂(SCN)₂ loops along the *a*-axial direction. The Cd₂(SCN)₂ loop adopts a chair-shape arrangement (mean deviation: 0.1570 Å), making the chain more stable. The Cd1...Cd1d distance is 5.923 Å. The H₂(tmen)²⁺ cations occupy the space between the chains. Via the N_{tmen}-H...N_{SCN} interactions (N2...N3e = 2.807 Å), the H₂(tmen)²⁺ cations extend the 1-D Cd(SCN)₄²⁻ chains into a 2-D supramolecular network. Cd1 is in an octahedral site, surrounded by four SCN⁻ S atoms (S1, S1c, S2, S2c; Cd1-S = 2.711(2)-2.763(2) Å) and two SCN⁻ N atoms (N1a, N1b; Cd1-N = 2.296(7) Å).

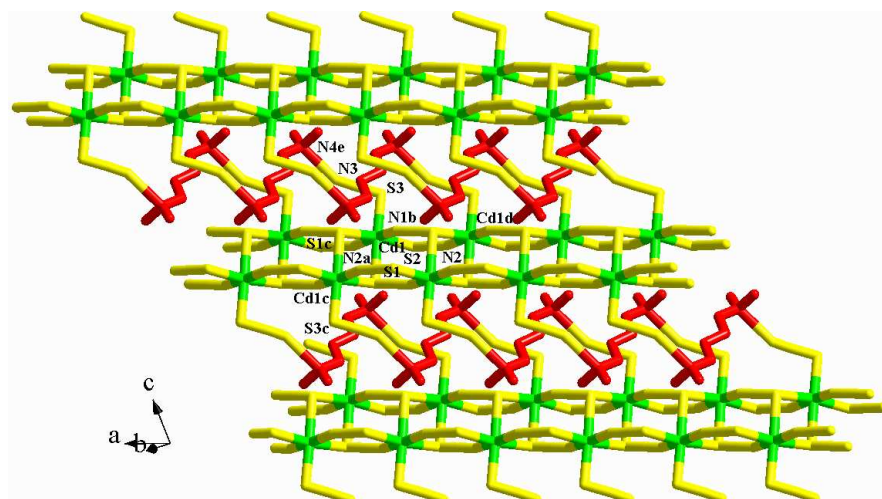


Fig. 2 2-D supramolecular layer network of **2** (a: $x+1, y, z$; b: $-x+1, -y+1, -z$; c: $-x+2, -y+1, -z$; d: $x-1, y, z$; e: $x+1, y, z$).

[H₂(tmba)][Cd₂(SCN)₆] 2. Compound **2** is a ribboned thiocyanatocadmte with H₂(tmba)²⁺ as the counteranions. The asymmetric unit of compound **2** is found to be composed of one Cd²⁺ ion (Cd1), three types of SCN⁻ groups (SCN I labeled as S₍₁₎C₍₁₎N₍₁₎, SCN II labeled as S₍₂₎C₍₂₎N₍₂₎, SCN III labeled as S₍₃₎C₍₃₎N₍₃₎) and a half H₂(tmba)²⁺ cation. As shown in Fig. 2, compound **2** possesses a similar supramolecular network structure to that of compound **1**. The different is that the inorganic anion for compound **2** exhibits a 1-D ribbon structure, templated by H₂(tmba)²⁺ (see Fig. S2 for better understanding). This ribbon indeed can be regarded as a stacking of two single chains. The terminal SCN⁻ groups on one side of each single chain are displaced by a set of double-bridged SCN⁻ S atoms of another single chain, producing finally this ribbon. Synchronously, a kind of triple-bridged SCN⁻ group forms, namely SCN I. The octahedral Cd1 is still completed by two N atoms (N1b, N2a; Cd1-N = 2.273(3)-2.300(3) Å) and four S atoms (S1, S2, S3, S1c; Cd1-S = 2.6292(13)-2.8739(13) Å), but two S atoms (S1, S1c) are from the triple-bridged SCN⁻ groups. The shortest Cd...Cd distance is Cd1...Cd1c = 4.194 Å. The organic amine cations still serve as the bridge in compound **2**, propagating the 1-D infinite ribbons into a 2-D supramolecular layer network via the N_{tmba}-H...N_{SCN} interactions (N3...N4e = 2.841 Å).

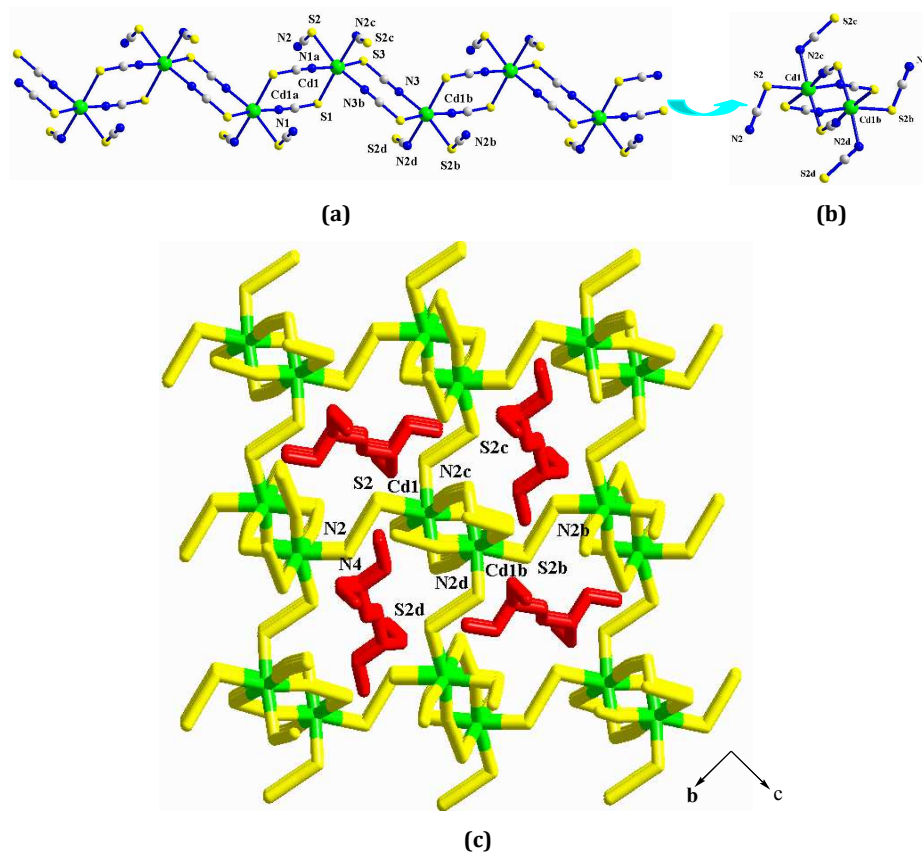


Fig. 3 3-D network structure of **3** with occluded H₂(teen)²⁺ cations (a: -x+1, -y, -z-1; b: -x, -y, -z-1; c: -x+1, y+1/2, -z-1/2).

[H₂(teen)][Cd₂(SCN)₆] 3. Compound **3** is a 3-D thiocyanatocadmte with the occluded H₂(teen)²⁺ cations. The asymmetric unit of compound **3** is found to be composed of one Cd²⁺ ion (Cd1), three types of SCN⁻ groups (SCN I labeled as S₍₁₎C₍₁₎N₍₁₎, SCN II labeled as S₍₂₎C₍₂₎N₍₂₎, SCN III labeled as S₍₃₎C₍₃₎N₍₃₎) and a half

$\text{H}_2(\text{teen})^{2+}$ cation. As shown in Fig. 3c, templated by $\text{H}_2(\text{teen})^{2+}$, the inorganic anion exhibits a 3-D network structure, which is based on the 1-D single chains. The SCN I and SCN III groups double bridge the octahedral Cd1 centers to form this 1-D single chain. Different from the situation observed in compound **1**, this 1-D single chain shows a zigzag shape, since two symmetry-related SCN II groups around each Cd1 center adopt a *cis*-configuration (see Fig. 3a). The zigzag shape is characterized by two structural factors: (i) the Cd...Cd...Cd angle of 124° , and (ii) the dihedral angle (89.1°) between two adjacent $\text{Cd}_2(\text{SCN})_2$ loop planes. Since the *cis*-mode $\text{Cd}(\text{SCN})_2$ units are alternately distributed on both sides of the zigzag chain, each single zigzag chain has a chance to interact with the neighboring four single zigzag chains (N2, N2b, S2c, S2d acting as the donors), forming finally a 3-D network of compound **3** with the 1-D channels (see Fig. 3b). The $\text{H}_2(\text{teen})^{2+}$ cations occlude the channels. The octahedral Cd1 center is surrounded by three SCN $\cdot$ S atoms (S1, S2, S3; Cd1-S = 2.6898(9)-2.7181(8) Å), and three SCN $\cdot$ N atoms (N1a, N2c, N3b; Cd1-N = 2.286(3)-2.466(3) Å). Three types of SCN $\cdot$ groups all adopt a double-bridged coordination mode. Two types of $\text{Cd}_2(\text{SCN})_2$ loops are nearly planar with the smaller mean deviations (0.0554 Å for $\text{Cd}_2(\text{SCN}_{\text{I}})_2$, 0.0674 Å for $\text{Cd}_2(\text{SCN}_{\text{III}})_2$). The Cd1...Cd1a separation is 5.953 Å.

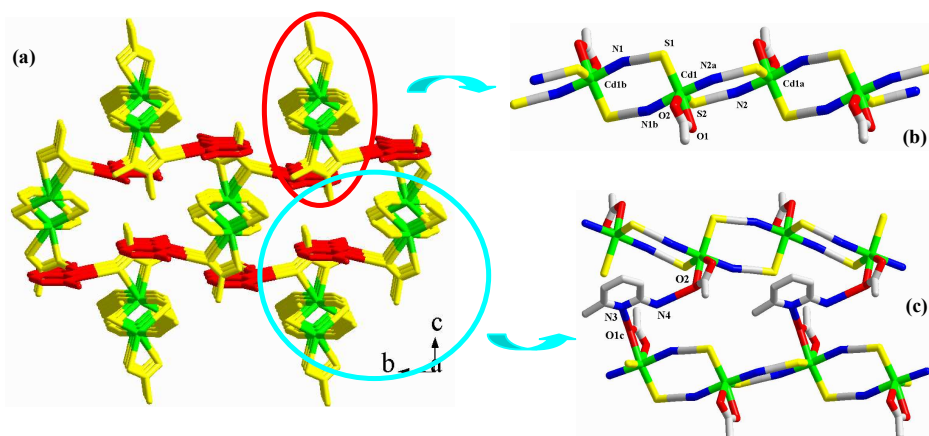
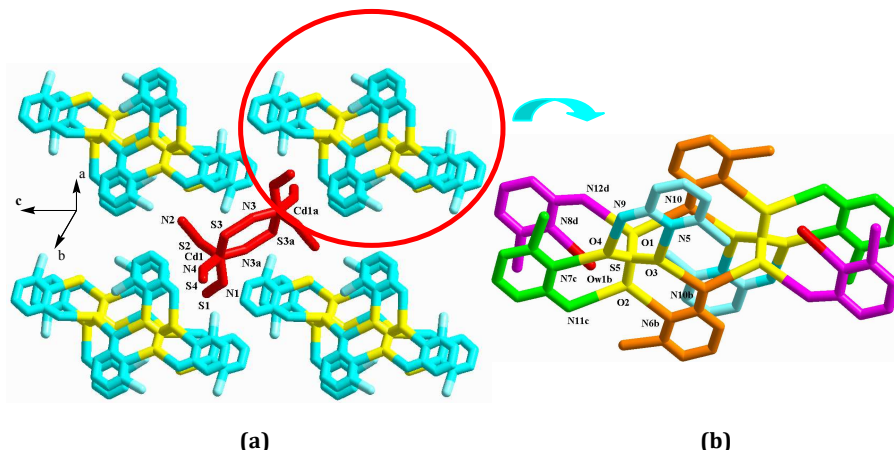


Fig. 4 3-D supramolecular network (a), 1-D zigzag chain (b), and hydrogen-bonded interactions (c) in **4** (a: $-x+2, -y-1, -z+1$; b: $-x+1, -y-1, -z+1$; c: $-x+1, y+1/2, -z+1/2$).

[H(amp)][Cd(SCN) $_2$ (CH $_3$ COO)] 4. Compound **4** is a chained thiocyanatocadmte with $\text{H}(\text{amp})^+$ as the counteranion. CH_3COO^- appears in the final framework of compound **4**. The asymmetric unit of compound **4** is found to be composed of one Cd^{2+} ion (Cd1), two types of SCN $\cdot$ groups (SCN I labeled as $\text{S}_{(1)}\text{C}_{(1)}\text{N}_{(1)}$, SCN II labeled as $\text{S}_{(2)}\text{C}_{(2)}\text{N}_{(2)}$), one CH_3COO^- group, and one amp molecule. Amp should be monoprotonated in order to balance the anionic charge, although it has a potential to be diprotonated. Two structural factors determine that the pyridyl N atom is protonated, while the amine N atom is non-protonated. (i) The N3...O1c distance of 2.811 Å implies that there exists the hydrogen-bonded interaction between the pyridyl N atom and one CH_3COO^- O atom (see Fig. 4c). (ii) Based on the difference Fourier map, two Q atoms around the amine N atom (N4) for amp are found. The QN4Q angle of *ca.* 120° indicates that N4 is in a planar trigonal site. The zigzag single chain is also observed in compound **4** ($\angle \text{Cd}\cdots\text{Cd}\cdots\text{Cd} = 142^\circ$), but here its formation is due to the chelation of the CH_3COO^- group (see Fig. 4b and Fig. S3). The octahedral Cd1 is coordinated by two SCN $\cdot$ N atoms (N1b, N2a; Cd1-N1 = 2.307(2)-2.351(2) Å), two SCN $\cdot$ S atoms (S1, S2; Cd1-S = 2.6043(8)-2.6300(8) Å) and two CH_3COO^- O atoms (O1, O2; Cd1-O = 2.346(2)-2.432(2) Å). The $\text{Cd}_2(\text{SCN})_2$ ring is nearly planar (mean deviation: 0.0840 Å), and the Cd1...Cd1a separation is 5.837 Å. As shown in Fig. 4a, via two types of

hydrogen-bonded interactions ($N3\cdots O1c = 2.811 \text{ \AA}$, $N4\cdots O2 = 2.837 \text{ \AA}$), the amp cations act as the bridges, linking the neighboring zigzag chains into a 3-D supramolecular network. Similar to the situation observed in compound **3**, the formation of the 3-D supramolecular network of compound **4** is due to two structural factors: (i) a zigzag shape for 1-D single chain; (ii) an alternate arrangement on both sides of the chain for CH_3COO^- .



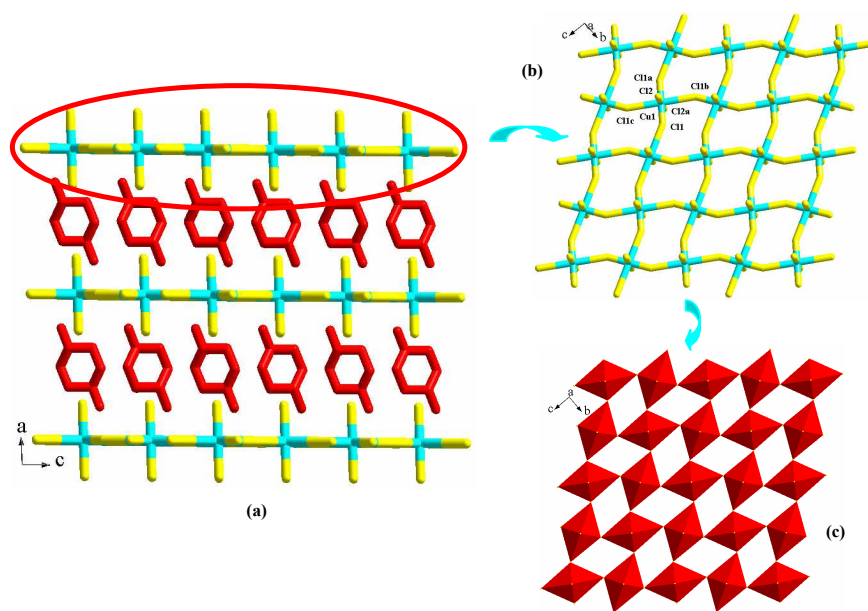


Fig. 6 Projection plot in (010) direction (a), and 2-D perovskite single-layer network (b, c) in **6** (a: $-x+1, -y-1, -z+1$; b: $-x+1, y-1/2, -z+1/2$; c: $x, -y-1/2, z+1/2$)

[H₂(cha)][CuCl₄] **6**. Compound **6** is a layered chlorocuprate(II) with H₂(cha)²⁺ as the counteranion. The asymmetric unit of compound **6** is found to be composed of a half Cu²⁺ ion (Cu1), two types of Cl⁻ ions (Cl1, Cl2) and a half H₂(cha)²⁺ cation. As shown in Fig. 6b, Cu1 is involved in a planar square site, surrounded by four Cl⁻ ions (Cl1, Cl2, Cl1a, Cl2a). The Cu1-Cl range is 2.2726(7)-2.2983(8) Å. In fact, the divalent Cu ion with a square geometry is rather rare. On the axial position(s), there should be one or two donor atom(s). The different is that the distance between Cu²⁺ and the donor atom is longer than the normal, due to the Jahn-Teller effect for a *d*⁹ Cu²⁺ ion. The Cu1-Cl1b/Cl1c distance of 3.496 Å is within the accepted range,¹⁷ⁱ indicating that Cl1b and Cl1c occupy the axial positions of Cu1. So Cu1 is actually in a 4+2 site (see Fig. S5 for better understanding). By the way, in some Cu²⁺ compounds reported previously, the longer Cu-Cl distances have been observed.¹⁷ⁱ Via the longer Cu1-Cl interactions, the planar CuCl₄²⁻ units are linked into a 2-D single-layer network. Fig. 6c is the polyhedral plot of this 2-D single-layer network. All symmetry-related Cu1 centers adopt a distorted octahedral configuration. Via sharing the corners, the Cu²⁺ octahedra are linked into a 2-D single-layer network. So this 2-D layer network possesses a classical perovskite single-layer network. The H₂(cha)²⁺ cations occupy the space between the inorganic anion layers (see Fig. 6a).

Structural discussion

With various organic base molecules as the counteranions, five new hybrid Cd(II) compounds and one new chlorocuprate(II) were obtained. The anionic Cd-SCN frameworks in compounds **1-5** exhibit the different structures: the 1-D linear chain in compound **1**, the 1-D ribbon in compound **2**, the 3-D open framework in compound **3**, the 1-D zigzag chain in compound **4**, and the discrete dimer in compound **5** (see Scheme S1a). The concept of dimensional reduction and recombination should be employed to understand the formation of these anionic structures.^{1c,6c,i,j,17b} In this concept, the Cd-SCN frameworks are thought to derive from the 2-D Cd(SCN)₂ layer, in which all of the Cd²⁺ ions are in an octahedral site, and all of the SCN⁻ groups adopt a triple-bridged coordination mode. The organic base molecule is visualized as the so-called molecular scissors. With the role of organic base molecules, the 2-D Cd(SCN)₂ layer is cut into the different structures. For

example, cut by $\text{H}_2(\text{tmen})^{2+}$, a 1-D single chain forms (as observed in **1**), while cut by $\text{H}_2(\text{tmba})^{2+}$, a 1-D ribbon forms (as observed in **2**). But the zigzag chains observed in compounds **3** and **5** are not a slice of the 2-D $\text{Cd}(\text{SCN})_2$ layer. This means that the recombination occurs. As shown in Scheme S1b, the 1-D zigzag chain should originate from the recombination of the 1-D linear chain, in order to form a more stable network. Two structural factors determine that the zigzag chain has a potential to form a 3-D stable network through further interactions, as observed in compounds **3** and **5**: (i) the appearance of the *cis*-configuration $\text{Cd}(\text{SCN})_2$ unit; (ii) the alternate distribution of the *cis*- $\text{Cd}(\text{SCN})_2$ units on both sides of the zigzag chain. So far, the organically templated thiocyanatocadmite with the 3-D structure are rather rare. Only two examples $[(\text{Hdabco})_2\text{Cd}_3(\text{SCN})_8]$ and $[\text{H}_2(\text{tmen})][\text{Cd}_3\text{Cl}_6(\text{SCN})_2]$ have been reported.^{14,15} Besides the role of $\text{H}(\text{abp})^+$, the formation of the dimer in compound **5** should derive from the incorporation of $[\text{H}(\text{abp})]_2\text{SO}_4$. This situation has also encountered in the past investigation. For example, compound $[\text{H}_2(4,4'\text{-dtdpy})][\text{Cd}_2\text{Br}_6]$ possesses a 1-D ribbon structure,¹⁴ while compound $[\text{H}_2(4,4'\text{-dtdpy})]_2[\text{CdBr}_4]\text{SO}_4 \cdot 2.5\text{H}_2\text{O}$, a double salt of $[\text{H}_2(4,4'\text{-dtdpy})][\text{CdBr}_4] \cdot [\text{H}_2(4,4'\text{-dtdpy})]_2\text{SO}_4$, only exhibits a mononuclear structure.^{16a} Moreover, based on the supramolecular structures of compounds **1** and **2** (see Fig. S6), we can find that the number of the C atom between two N atoms in the templating agent controls the width of the 1-D linear chain. With the increasing of the number of the C atom from 2 (tmen) to 4 (tmba), the width of the chain increases from 1 (single chain) to 2 (double chain).

Characterization

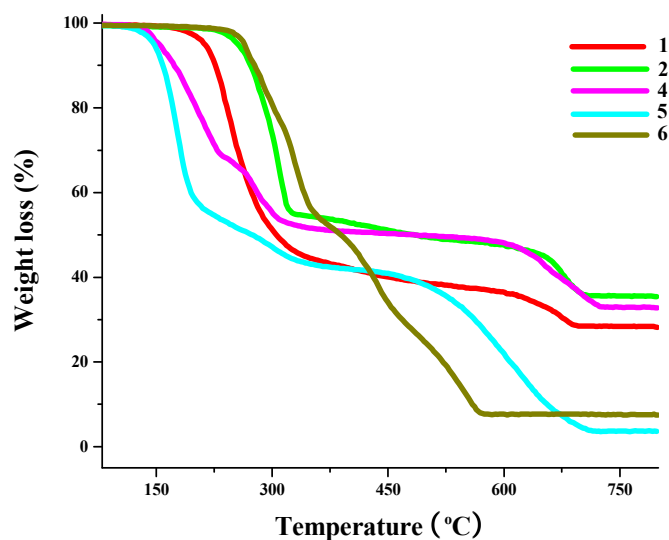


Fig. 7 TG curves of title compounds.

The TG behaviors of the title compounds were investigated. Fig. 7 plots the temperature vs. weight-loss curves. Compounds **1** and **2** underwent two steps of similar weight loss. In the first step, the counteranion lost in the form of ammonium thiocyanate. The observed weight loss (44% for **1**, 55% for **2**) is lower than that calculated (50.1% for **1**, 64.3% for **2**), indicating that the part intermediates $\text{Cd}(\text{SCN})_2$ has transformed into CdO . So the actual intermediates is a double compound $x\text{Cd}(\text{SCN})_2 \cdot y\text{CdO}$. The final residues for both are proved to be CdO (Calcd: 27.7%, Found: 28.4% for **1**; Calcd: 35.7%, Found: 35.6% for **2**), suggesting that $\text{Cd}(\text{SCN})_2$ thoroughly transformed into CdO in the second step of weight loss. Compound **4** underwent three

steps of weight loss. The initial two steps of weight loss are assigned to the sequential sublimation of amp and CH_3COOH . Synchronously, a little $\text{Cd}(\text{SCN})_2$ intermediates transformed into CdO . So the intermediates is a double compound of $\text{Cd}(\text{SCN})_2$ and CdO after two steps of weight loss. The remaining is still CdO , and the calculated value of 32.4% is comparable with that observed (33.0%). Compound **5** also underwent three-steps of weight loss. *Ca.* 41.0% weight loss for the first step is attributed to the removal of $[\text{H}(\text{abp})]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Calcd: 40.0%). At this time, the intermediates is $[\text{H}(\text{abp})]_2[\text{Cd}(\text{SCN})_4]$. The residue content of 4.11% implies that during the weight-loss process, some Cd evaporated. Based on the previous related investigation, $\text{Cd}(\text{SCN})_2$ does not evaporate generally at the high temperature, but CdBr_2 is frequently found to evaporate upon heating.¹²⁻¹⁶ So we speculate that during the weight-loss process, the intermediates $\text{CdBr}_2 \cdot \text{Cd}(\text{SCN})_2$ should form. The Br^- ion came from abp. Upon further heating, CdBr_2 evaporated completely, and $\text{Cd}(\text{SCN})_2$ transformed to CdO . The residue content is calculated to be 5.56%, basically comparable with that observed. Different from the situation of CdX_2 , the part CuCl_2 transformed into CuO along with the evaporation of CuCl_2 . So the residue content for compound **6** is 7.5%, rather than the zero. In the title compounds, compounds **2** and **6** have the better thermal stability, and can be thermally stable up to *ca.* 240 °C.

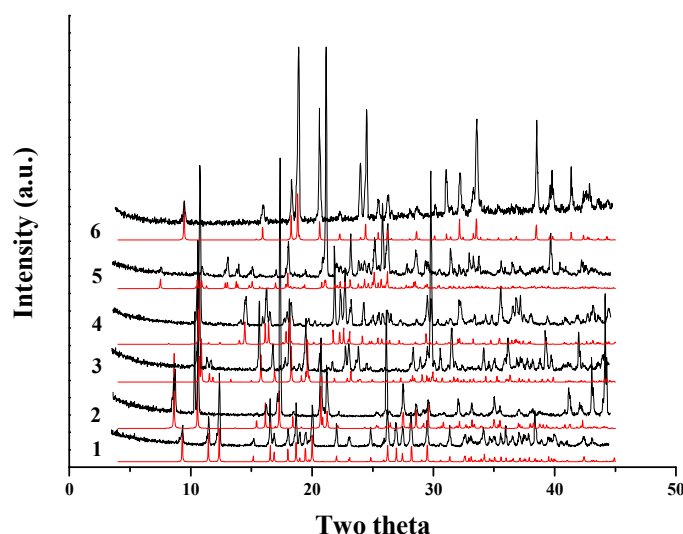


Fig. 8 Powder XRD patterns of title compounds.

Fig. 8 plots the experimental and simulated powder XRD patterns of the title compounds. The experimental powder XRD pattern for each compound is in accord with the simulated one generated on the basis of structural data, confirming that the as-synthesized product is pure phase. Based on the IR spectra of the title compounds (see Fig. S7), we can know that (i) there are exist bridged- SCN^- groups in compounds **1-5**, since the peaks larger than 2100 cm^{-1} are observed (2100 cm^{-1} for **1**, 2131 and 2108 cm^{-1} for **2**, 2131 and 2116 cm^{-1} for **3**, 2129 and 2108 cm^{-1} for **4**, 2123 cm^{-1} for **5**);²⁰ (ii) the appearance of the peaks at 1094 , 1078 (ν_3 and ν_4 vibration modes for SO_4^{2-}) and 982 cm^{-1} (ν_1 mode for SO_4^{2-}) suggests that SO_4^{2-} is mixed into the final framework of compound **5**; (iii) the appearance of the peaks at 1669 ($\nu_{\text{as}}(\text{COO}^-)$) and 1416 cm^{-1} ($\nu_{\text{s}}(\text{COO}^-)$) indicates that CH_3COO^- is incorporated in the resulting backbone of compound **4**.²² These results are in agreement with those obtained from X-ray single-crystal diffraction analysis.

Property

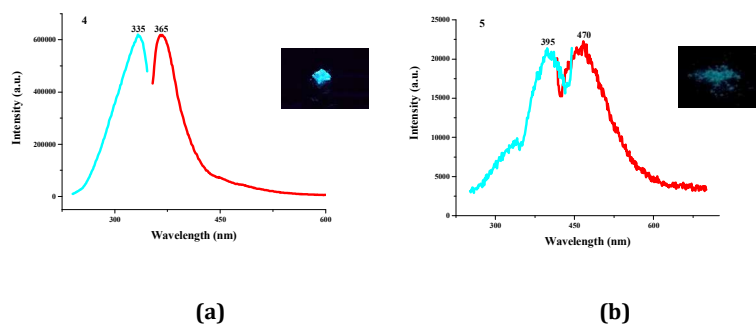


Fig. 9 Photoluminescence spectra of **4** (a) and **5** (b) (inserted images are corresponding emissions under UV lamp).

The photoluminescence properties of five Cd^{2+} hybrids were investigated. In order to compare the emission intensities of the compounds, the same slit widths were used when all were measured. Fig. 9 plots the photoluminescence spectra of compounds **4** and **5**. Obviously, compounds **4** and **5** possess the photoluminescence properties. Upon excitation at 335 nm, compound **4** exhibits a violet-light emission centered at 365 nm (Fig. 9a), while upon excitation at 395 nm, compound **5** emits the different blue-green light, and the maximum appears at 470 nm (Fig. 9b). The emissions for compounds **4** and **5** are strong, and can be seen clearly under the UV lamp (see the inserted images). Based on the images, we can find that the emission intensity of compound **4** is apparently stronger than that of compound **5**, which is in agreement with the conclusion drawn from their emission spectra. In order to reveal the emission mechanism of two hybrids, the photoluminescence behaviors of the amp and abp molecules were also studied. As shown in Fig. S8, the amp molecule emits green light ($\lambda_{\text{em}} = 495 \text{ nm}$) when excited at 410 nm, whereas the abp molecule emits violet light ($\lambda_{\text{em}} = 390 \text{ nm}$) when excited at 360 nm. Only the 6-position substituent group is different ($-\text{CH}_3$ for amp, $-\text{Br}$ for abp), two organic molecules show the distinct emission behaviors. Compared with the emission of the corresponding organic molecule, the emission of compound **4** shows a larger blue shift (130 nm), whereas the emission of compound **5** shows a larger red shift (80 nm). Although a larger shift is observed, the emission of compounds **4** and **5** should be tentatively attributed to the ligand-centered electronic excitation ($\pi^* \rightarrow \pi$). In the past related reports, the larger shift has also been observed.¹⁵ Since the emission of the amp molecule is lower in the energy (495 nm), this is not original emission from the amp molecule. The green light emission light should originate from the trap sites in the crystal.

In order to reveal the effect of the hybrid formation on the photoluminescence behavior of the compound, the diagrams of the energy levels of the abp molecule and compound **5** are drawn in Fig. 10, based on their photoluminescence spectra.²³ As shown in Fig. 10a, when excited at 360 nm, the electron transfers from the ground-state E0 to the excited-state E2. Then it decays nonradiatively to E1 energy level (HOMO, the highest occupied molecular orbital). From E1 energy level, the electron returns to the ground-state E0 energy level with the light energy emission (390 nm), so the abp molecule emits violet light. After a hybrid formation, the energy level value of HOMO decreases from 390 nm to 470 nm, so the red shift occurs and compound **5** emits blue-green light (see Fig. 10b). The emission of the amp molecule is too small to be discussed, so only the energy level diagram of compound **4** is drawn (see Fig. S9). Compounds **1**, **2**, and **3** do not emit light. Based on their solid-state UV-vis spectra (see Fig. S10), we can find that the electron can be excited to the excited-state energy level E2. However, due to the lack of the π -conjugated structure in the organic molecule,

the electron on HOMO returns to the ground-state energy level E_0 in a nonradiative form. Hence, compounds **1**, **2** and **3** do not emit light. Moreover, the composition of HOMO also has a possibility to be changed after a hybrid formation. Once this situation occurs, the emission for the hybrid compound will be assigned to a new attribution.²⁴

The emission intensity can also be changed after a hybrid formation. The emission intensity of compound **4** is apparently stronger than that of the amp molecule, while the emission intensity of compound **5** is slightly weaker than that of the abp molecule. On the one hand, due to a hybrid formation, some hydrogen-bonded interactions appear in the packing structure of the compound. This provides a possible path for the excited-state proton to transfer. While the occurrence of the intra(inter)molecular excited-state proton transfer (IEXPT) can significantly enhance or quench the emission of the compound.²⁵ On the other hand, the hybrid formation can alter the molecular packing of the compound. The molecular packing is another important impact of influencing the emission behavior of the compound.²⁶ The close packing of the molecules even quenches completely the emission of the compound. In nature, the hybrid formation changes the quantum yield, so the emission intensity for the hybrid compound is different from the corresponding organic molecule.

Based on the photoluminescence behaviors of the title compounds and the previous related reports,¹²⁻¹⁶ we can know that: (i) some aromatic base-templated thiocyanatocadmates emit light, while due to the lack of the π -conjugated structure in the organic molecule, the aliphatic amine-templated thiocyanatocadmates do not emit light; (ii) since the emission originates from the ligand-centered electronic excitations, they generally emit the high-energy blue or violet light; (iii) the hybrid formation influences the photoluminescence behavior of the hybrid compound. The hybrid formation can alter the energy level value of HOMO, as a result that the hybrid compound may emit the different light. The hybrid formation can lead to the appearance of the excited-state proton transfer path as well as the change of the molecular packing, indirectly altering the emission behavior of the hybrid compound. The decay curve for compound **4** fit into a double exponential function, and the lifetimes were calculated to be $\tau_1 = 2.26$ ns and $\tau_2 = 12.21$ ns, respectively. The luminescence lifetime for compound **5** was calculated to be $\tau_1 = 1.16$ ns and $\tau_2 = 3.22$ ns, respectively (see Fig. S11).

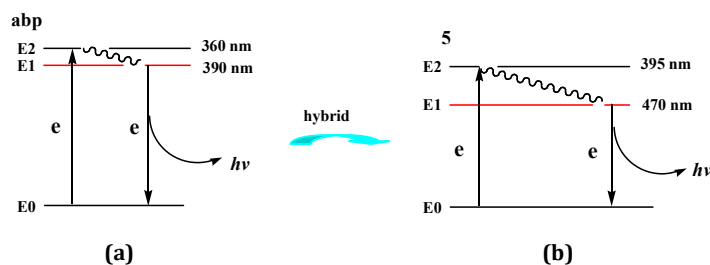


Fig. 10 Diagrams of energy levels of abp (a) and corresponding hybrid **5** (b).

Conclusion

In summary, we reported the synthesis and structural characterization of five new thiocyanatocadmates and one new chlorocuprate(II). Based on the structural information of compounds **1-5**, we can know that with different organic base molecules as the countercations, the inorganic anions can form various structures. The concept of the dimensional reduction and recombination can be employed to better understand the formation of these structures. The organic base molecule serves as the so-called molecular scissors, cutting the 2-D $\text{Cd}(\text{SCN})_2$ layer into the 1-D ribbon (in **2**) or the 1-D linear chain (in **1**). With the limitation of ammonium sulfate, the Cd-SCN oligomer can be further cut into the discrete structure (dimer in **5**). The 1-D zigzag chain

derives from the recombination of the 1-D linear chain, in order to form a more stable network as a 3-D open framework (in **3**) or a 3-D supramolecular network (in **4**). The number of the C atom between two N atoms in the templating agent maybe controls the width of the inorganic anion chain. The photoluminescence analysis reveals that the aromatic base-templated thiocyanatocadmte may emit light, which is generally assigned to the ligand-centered electronic excitation ($\pi^* \rightarrow \pi$). After a hybrid formation, (i) the energy level of HOMO maybe changes; (ii) the transferring path for the excited-state proton maybe appears; and (ii) the molecular packing maybe changes. So an organic-inorganic hybrid may show a different emission, compared with the emission of the corresponding organic base molecule. In addition, compound **3** possesses a 3-D open-framework structure. So far, the 3-D thiocyanatocadmte is rather rare. While compound **6** shows a 2-D perovskite single-layer structure.

Acknowledgements

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