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Journal of Solid State Chemistry 180 (2007) 518–522

Journal of Solid State Chemistry

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# Structure characterization of 1:1 adducts of metal(II) halides and piperazine

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Received 22 June 2006; received in revised form 26 October 2006; accepted 29 October 2006

## Abstract

From the simple hydro/solvothermal reactions, two 1:1 adducts of $MX_2$ and piperazine (pip) $[CdI_2(pip)]$ **1** and $[CoCl_2(pip)]$ **2** were prepared. Both were characterized by elemental analyses, IR spectra, ultra-violet visible spectra, thermogravimetric analyses and X-ray single-crystal diffraction. With pip as the bridges, the 1-D linear $CdI_2$ chains are extended into a 2-D layered compound **1**, while the mononuclear $CoCl_2$ units are linked into a 1-D zigzag-type chain compound **2**. The fluorescence emission spectrum indicates that compound **1** possesses fluorescence property with the peaks at 373 nm ($\lambda_{ex} = 212$ nm) and 410 nm ($\lambda_{ex} = 293$ nm).

*Keywords:* Metal halide; Piperazine; Hydro/solvothermal prepare; Crystal structure

## 1. Introduction

In the past decade, considerable attention has been paid to the crystal engineering of metal-halo cluster compounds due to their fascinating topologies and potential functional properties [1]. At present, incorporating organic components into the resulting frameworks is the most prevalent synthetic strategy of this area. In the reported compounds, organic components exhibit multi-types of existing modes: (i) they can be protonated. The protonated organic amines template metal halides to form either open-framework halometalates or perovskites. The typical examples are the known $[HN(CH_3)_3][CuZn_5Cl_{12}]$, $[H_2N(C_2H_5)_2][CuZn_5Cl_{12}]$, $[H_2N(CH_3)_2][Cu_nZn_{6-n}Cl_{12}]$ ($n = 1, 2$) [2] and a series reported by Mercier [3] and Mitzi [1d,4]; (ii) they can act as the connectors. The bridging organic ligands extend the low-dimensional (*D*) metal-halo clusters into hybrid inorganic-organic coordination polymers. To data, the used organic linkers include 4,4′-bipyridine (bipy) [1b,5], pyrazine [6], pyridazine [7], pyrimidine [8], 1,3,5-triazine [1a], 2-mercapto-5-methyl-1,3,4-thiadiazole [9], isonicotinate [10], *bis*-2,3-(2-pyridyl)pyrazine [11], and so on; (iii) they can form metal-amine complexes. The known compounds, $[Cu(en)]_2[Cu_7Cl_{11}]$ (en = ethylenediamine) [12], $[Cu_2(OH)_2(2,2'\text{-bipy})_2][Cu_4Br_6]$ [13] and $[Cu_4(OH)_4(phen)_4][Cu_8Br_{12}]$ (phen = 1,10-phenanthroline) [14], confirm that metal-amine complexes service as not only the linkers, but also the guest species. So far, the structure characterization of 1:1 adducts of $MX_2$ and 4,4′-bipy, pyrazine as well as other bridging ligands have been reported [15]. Herein, we report the structure characterization of two 1:1 adducts: 2-D $[CdI_2(pip)]$ **1** and 1-D $[CoCl_2(pip)]$ **2**.

## 2. Experimental

### 2.1. Materials and general methods

The chemicals used to prepare the title compounds include $CdI_2$, $CoCl_2 \cdot 6H_2O$, KI, pip, succinic acid and $C_2H_5OH$ without further purification. The syntheses were carried out in 30 mL Teflon-lined stainless steel vessels under auto-genous pressure. The single crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature. Elemental analyses were performed with a Perkin-Elmer 2400LS II elemental

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doi:10.1016/j.jssc.2006.10.028

analyzer. Infrared (IR) spectra were recorded with Perkin Elmer Spectrum *1* spectrophotometer in the 4000–400 $cm^{-1}$ region using a powdered sample on a KBr plate.

### 2.2. Syntheses and characterization

The colorless needle crystals of $[CdI_2(pip)]$ **1** were obtained from a simple hydrothermal reaction of $CdI_2$ (0.37 g, 1.0 mmol), pip (0.20 g, 1.0 mmol), KI (0.50 g, 3.0 mmol) and $H_2O$ (10 mL) in a molar ratio of 1:1:3:555 at 160 °C for 3 days. Yield: ca. 35% based on Cd. IR (KBr, $v/cm^{-1}$): 3247 w, 2957 w, 2921 w, 1423 s, 1400 m, 1328 w, 1299 w, 1244 m, 1094 m, 1033 m, 991 s, 862 s, 636 m. Anal. Calc. for $Cd_{0.5}IC_2H_5N$: C, 10.62; H, 2.23; N, 6.19. Found: C, 10.58; H, 2.08; N, 6.10%.

The blue columnar crystals of $[CoCl_2(pip)]$ **2** were obtained from a simple solvothermal reaction of $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol), pip (0.20 g, 1.0 mmol), succinic acid (0.12 g, 1.0 mmol) and $C_2H_5OH$ (16 ml) in a molar ratio of 1:1:1:350 at 160 °C for 3 days. Yield: ca. 55% based on Co. IR (KBr, $v/cm^{-1}$): 3191 s, 2969 w, 2929 w, 1456 m, 1409 s, 1382 w, 1349 m, 1336 w, 1259 w, 1130 s, 1119 s, 1083 s, 1025 s, 996 s, 874 s, 662 w. Anal. Calc. for $CoCl_2C_4H_{10}N_2$: C, 22.24; H, 4.67; N, 12.97. Found: C, 22.34; H, 3.82; N, 12.68%.

### 2.3. Crystal structure determination

All data were collected with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Rigaku R-AXIS RAPID IP diffractometer. With SHELXTL program, compound **1** was solved using heavy atom methods, and compound **2** was solved using direct methods. Both are refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement and the hydrogen atoms were treated using a riding model. The structures were then refined on $F^2$ using SHELXL-97. Cd atom in **1** is in disorder (occupancy ratio: Cd1, 0.25; Cd1′, 0.25). CCDC numbers of compounds **1–2** are 609469 and 609470, respectively. Basic information pertaining to the crystal parameters and structure refinement of the title compounds is summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

## 3. Results and discussion

### 3.1. Structure descriptions

So far, lots of 1:1 adducts of $MX_2$ and 4,4′-bipy have been reported. In them, most exhibit 2-D sheet structures with the identical topology, whose formation can be described as a linkage of 1-D linear-type $MX_2$ chains by 4,4′-bipy bridges. Using pip in place of 4,4′-bipy, the 1-D $CdX_2$ ($X$ = Cl [16], Br [15a]) chains take on zigzag type, and are further bridged by pip molecules into 3-D network structures (see Fig. 1(a)). Obviously, the ligand's kind has an effect on the dimension of the adduct. With the different ligands, the $ML_2^{2+}$ units may adopt the different geometric configuration. For the $ML_2^{2+}$ unit, the *cis*-type arrangement corresponds to the 3-D network, while the *trans*-mode configuration leads to the 2-D sheet.

Table 1
Crystal data and structure refinement for the title compounds

| Empirical formula | $Cd_{0.5}IC_2H_5N$ **1** | $CoCl_2C_4H_{10}N_2$ **2** |
|---|---|---|
| Formula weight | 226.18 | 215.97 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | *P*2/c | *P*2$_1$/n |
| *a* (Å) | 7.5728(15) | 6.3719(13) |
| *b* (Å) | 4.5026(9) | 10.238(2) |
| *c* (Å) | 15.042(4) | 12.142(2) |
| $\alpha$ (°) | | |
| $\beta$ (°) | 119.75(3) | 103.55(3) |
| $\gamma$ (°) | | |
| *U* (Å$^3$) | 445.29(17) | 770.0(3) |
| *Z* | 4 | 4 |
| $\mu$ ($mm^{-1}$) | 3.374 | 1.863 |
| *D* ($g\,cm^{-3}$) | 9.311 | 2.835 |
| Reflections collected | 3458 | 7422 |
| Independent reflections | 869 | 1754 |
| $R_{int}$ | 0.0385 | 0.0329 |
| *S* | 1.073 | 1.081 |
| Final $R_1$, w$R_2$ [$I > 2\sigma(I)$] | 0.0264, 0.0445 | 0.0288, 0.0724 |
| [all data] | 0.0370, 0.0478 | 0.0335, 0.0754 |

Table 2
Selected bond lengths (Å) and angles [°] for the title compounds

| | | | |
|---|---|---|---|
| **1** | | | |
| I(1)–Cd(1) | 3.171(2) | Cd(1)–N(1) | 2.299(4) |
| I(1)–Cd(1)#1 | 2.949(2) | | |
| N(1)–Cd(1)–I(1) | 89.97(14) | I(1)#3–Cd(1)–I(1)#4 | 89.15(8) |
| Cd(1)#1–I(1)–Cd(1) | 94.68(2) | I(1)#4–Cd(1)–I(1) | 176.17(8) |
| N(1)#2–Cd(1)–N(1) | 179.9(3) | I(1)#2–Cd(1)–I(1) | 81.49(7) |
| N(1)–Cd(1)–I(1)#3 | 90.03(13) | | |
| **2** | | | |
| Co(1)–N(1) | 2.070(2) | Co(1)–N(2) | 2.051(2) |
| Co(1)–Cl(1) | 2.2487(8) | Co(1)–Cl(2) | 2.2513(9) |
| N(1)–Co(1)–Cl(1) | 112.11(6) | N(1)–Co(1)–Cl(2) | 111.66(7) |
| N(2)–Co(1)–Cl(1) | 107.38(6) | N(2)–Co(1)–Cl(2) | 111.45(6) |
| N(2)–Co(1)–N(1) | 108.99(8) | Cl(1)–Co(1)–Cl(2) | 105.14(3) |

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

The title compound **1** is the 1:1 adduct of $CdI_2$ and pip. It is interesting that it shows a 2-D layered structure with the same topology as the reported 2-D $[MX_2(4,4'\text{-bpy})]$. In compound **1**, the crystallographically unique Cd(1) center with a octahedral geometry is coordinated by four I atoms and two N atoms from two pip molecules. Through two $\mu_2$-I bridges, the Cd centers are linked into a 1-D infinite chain of edge-sharing octahedra. The $Cd(pip)_2^{2+}$ unit is in a *trans*-position, which makes the $CdI_2$ chain linear. On the other hand, the *trans*-configuration for $Cd(pip)_2^{2+}$ unit helps to extend the 1-D $CdI_2$ into a 2-D layered structure. As shown in Fig. 1(b), the pip molecules bridge the linear $CdI_2$ chain to form a 2-D sheet with rectangular micro-porous rings characterized by the size of 7.5 × 4.5 Å in [1 0 0] direction. Compound **1** give an example that the $X$ ion also influences the dimension of the adduct.

In the known 1:1 adducts of $MX_2$ and 4,4′-bipy, only several examples such as [Zn$X_2$(4,4′-bpy)] ($X$ = Cl, Br) [17] and [$HgI_2$(4,4′-bpy)] [15b] exhibit 1-D zigzag chain structures. This phenomenon is derived from the metals' tetrahedral coordination. Another aspect, it is well known that in the ethanol solvent the tetrahedral geometry for the Co(II) ion is stable and the corresponding complex is blue. X-ray data reveal that the structure of blue crystal **2** is in agreement with the expected result. It really possesses 1-D chain structure, comprising the tetrahedral Co atoms linked by pip bridges. The crystallographically independent Co(1) atom in a tetrahedral site bonds to two terminal Cl atoms and two N atom from two pip molecules. The Co–Cl bond lengths and Co–N bond lengths, 2.2487(8)–2.2513(9) and 2.070(2)–2.051(2) Å, are basically comparable with those observed in reported compounds [$CoCl_2$L] (L = α,α′-*bis*(pyrazolyl)-*m*-xylene) [18]. The angles around Co atom, 105.14(3)–112.11(6)° slight deviate from the normal value (109.5°), suggesting that the Co tetrahedron is somewhat distorted. As shown in Fig. 2, the bridging pip ligands link the Co centers into a zigzag-type chain. The chain's camber is characterized by N(2)–Co–N(1) angle of 108.99(8)°. In a word, it is not difficult to find that the geometry of the metal center also determines the dimension of the adduct.

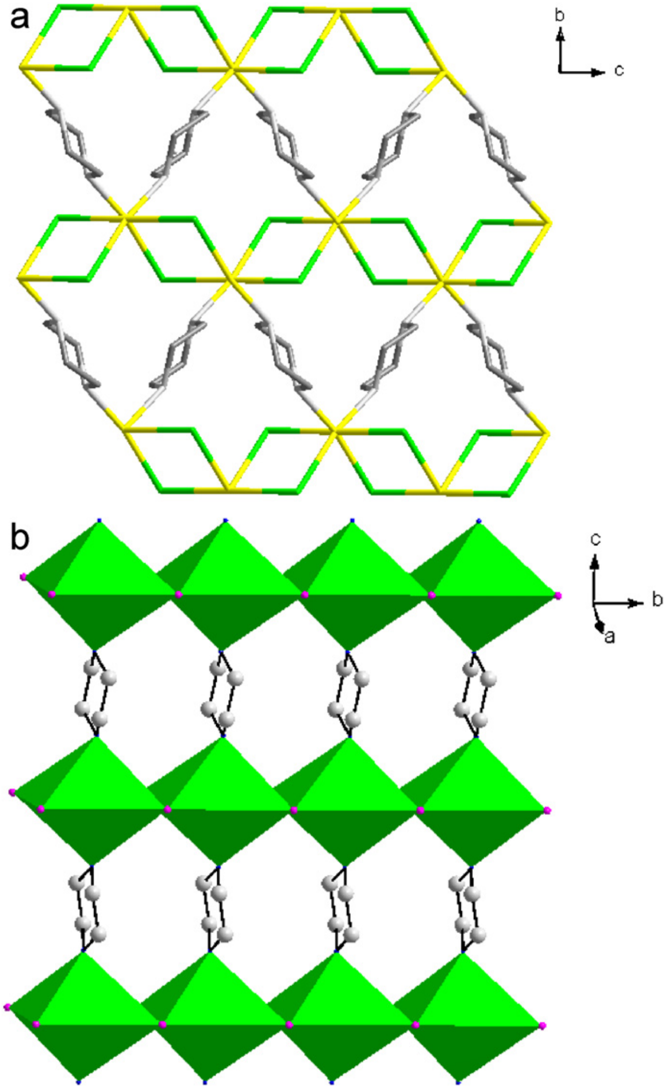

Fig. 1. 3-D network of [Cd$X_2$(pip)] ($X$ = Cl, Br) (a) and 2-D sheet of [$CdI_2$(pip)] **1** (b).

As shown in Fig. 3, via the interchain C–H · Cl hydrogen bonds (C1–H · $Cl_2$ = 140.4°, C1 · $Cl_2$ = 3.683 Å; C3–H · $Cl_1$ = 137.2°, C3 · $Cl_1$ = 3.619 Å), the adjacent 1-D zigzag chains are self-assembled into a 3-D supramolecular network with 1-D irregular channels in [1 0 0] direction. The alternate linkage of three pip molecules and three $CoCl_2N$ tetrahedra encloses the channel.

### 3.2. TG analyses

Thermogravimetric (TG) behaviors were investigated on a Perkin-Elmer TGA-7 instrument with a heating rate of 20 °C min$^{-1}$ in air. The TG curves show that both underwent two-stage mass losses (see Fig. 4). For **1**, although the platform between two stages is not obvious, it is sure that the organic pip molecule first lost (calc.: 19.0%). For **2**, the first weight loss is ca. 30.0%, corresponding to the loss of inorganic terminal Cl (calc.: 32.8%). The second stage occurred between 500 and 650 °C was attributed to the loss of organic pip molecule. The final residue is proved to be CoO (calc.: 34.7%; found: ca. 35.0%).

### 3.3. Fluorescence properties

Ultra-violet visible (Uv-vis) spectra in solid state were obtained on a Rigaku-UV-3100 spectrophotometer on a

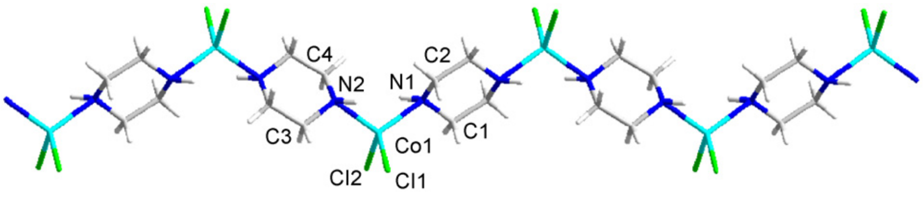

Fig. 2. 1-D zigzag chain of **2**.

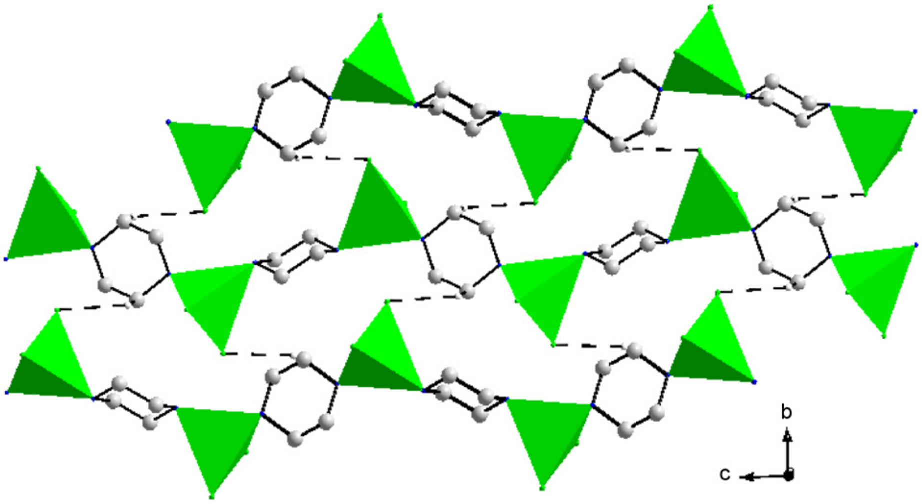

Fig. 3. 3-D supramolecular network of **2** in [1 0 0] direction.

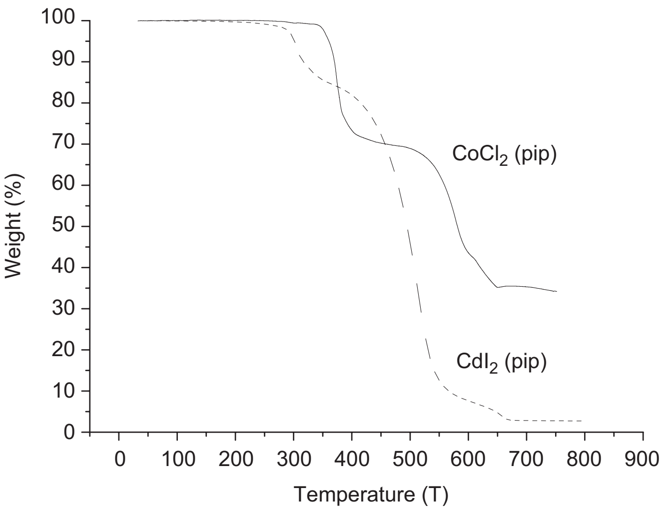

Fig. 4. TGA curves of the title compounds.

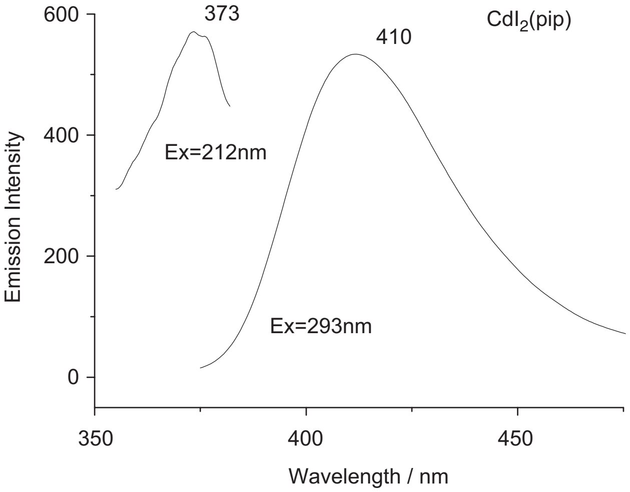

Fig. 5. Fluorescence emission spectrum of **1**.

$BaSO_4$ plate. The peaks in the ultra-violet region are related to the organic ligand such as 215, 310 nm for **1** and 225, 245 nm for **2**. In the visible region, no absorbance peak for a $d^{10}$ Cd(II) ion for **1** is found, while for a $d^7$ Co(II) for **2**, the peak at 610 nm is attributed to electronic transfer from $e_g$ to $t_{2g}$.

Fluorescence spectra in solid state were obtained on a LS 55 florescence/phosphorescence spectrophotometer at room temperature. Based on Uv-vis spectra of **1**, using $\lambda = 215$ and 310 nm as the excitation wavelengths, two maximum emission signals at 373 and 410 nm were got from its emission spectra, respectively (see Fig. 5). Next, with $\lambda = 373$ and 410 nm as the excitation wavelengths, the peaks at 212 and 293 nm in its fluorescence absorbance spectra confirm that the fluorescence signals mentioned above are effective and compound **1** possesses the fluorescence property. Tentatively, the former is attributed to the intra-ligand fluorescence, whereas the latter is assigned to the charge transfer between the metal and the ligand [19].

## 4. Conclusion

Based on the literature and two adducts of 2-D [$CdI_2$(pip)] and 1-D [$CoCl_2$(pip)] reported in this article, a conclusion can be drawn that the structure of 1:1 adduct of $MX_2$ and organic ligand will be determined by a compositive factor including the geometric configuration of the metal center, the nature of the organic ligand and the size of the $X$ ion.

## Acknowledgments

This research was supported by grants from the National Natural Science Foundation of China (Nos. 20333070 and 20571032).

## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.10.028.

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