Series of Two-Dimensional Hofmann-DMF-Type Compounds $M(DMF)_2M'(CN)_4$ (M = Cd, Fe; M' = Ni, Pd, Pt): Syntheses, Structures, and Thermal Stabilities

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Abstract. Five two-dimensional Hofmann-DMF-type compounds $M(DMF)_2M'(CN)_4$ [M = Cd, M' = Ni (**1**), Pd (**2**), Pt (**3**); M = Fe, M' = Ni (**4**), Pt (**5**)] were synthesized by solution diffusion method. X-ray diffraction analysis revealed that compounds **1–5** are isomorphous and crystallize in the monoclinic $C2/m$ space group. The structure consists of corrugated cyanide-bridged polymeric networks, in which the DMF-ligated octahedral M and square-planar M' atoms occupy special positions of the 2/m site symmetry. In addition, the non-hydrogen atoms of DMF molecules locate on a crystallographic mirror plane and coordinate to the axial sites of M atoms from both sides of the sheets. Thermal stabilities of such system are associated with the metal ions involved in structures and the host framework begins to collapse with the loss of coordinated DMF molecules.

Introduction

The design and elaboration of functional coordination compounds have grown rapidly in recent years.[1] In particular, cyanide-bearing precursors have been employed extensively to construct bimetallic assemblies with flexible architectures and fascinating potential applications.[2–4] Among them, Hofmann clathrates with general formula $ML_2M'(CN)_4$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd; M' = Ni, Pd, Pt; L = multidentate ligand), especially three-dimensional (3D) Hofmann-type materials have attracted increasing attention due to their ability to trap organic guest molecules and intrinsic properties such as spin-crossover and gas storage.[5–8] The design strategy for preparations of 3D Hofmann-type materials usually involves the pillared-layer motif wherein an extended 2D layer is built into a 3D open framework through the incorporation of pillar ligands. These ligands can be varied in both length and functionalization to give a wide range of Hofmann-type materials derived from the same structural motif.[9] However, considerable efforts should be devoted to construct 3D Hofmann-type and analogous because of limited examples established on the basis of single-crystal structures to date.

In our previous work, Hofmann-DMF-type layered compounds $Zn(DMF)_2M'(CN)_4$ (M' = Ni, Pd, Pt) were obtained by the self-assembly between Zn^{2+} ions and $[M'(CN)_4]^{2-}$ units in a DMF/H_2O solution, where the planar $Zn[M'(CN)_4]_n$ net-

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works are well-suited for the pillared-layer design strategy.[10] As one part of our ongoing efforts to explore $[M'(CN)_4]$-based functional materials,[11–13] we extend above studies to further construct 3D Hofmann-type materials through the incorporation of the linear N-donor ligand into the 2D system. Unfortunately, series of 2D Hofmann-DMF-type compounds without pillared ligands was obtained instead by the reaction of M^{2+} (M = Zn, Fe, Cd), N,N'-bis(4-pyridylformamide)-1,4-benzene, and $[M'(CN)_4]^{2-}$ (M' = Ni, Pd, Pt), among which the Zn-DMF-$M'(CN)_4$ system has been documented as described above.[10] In this paper, we presented the syntheses, crystal structures, and thermal stabilities of 2D Hofmann-DMF-type compounds $M(DMF)_2M'(CN)_4$ [M = Cd, M' = Ni (**1**), Pd (**2**), Pt (**3**); M = Fe, M' = Ni (**4**), Pt (**5**)]

Results and Discussion

Single-crystal X-ray crystallographic analysis revealed that compounds **1–5** are isostructural and crystallize in the monoclinic $C2/m$ space group (Table 1). Selected bond lengths and angles for compounds **1–5** are listed in Table S1 (Supporting Information). The structure of compound **1** was described in detail, which consists of an octahedral site occupied by the central Cd^{II} atom and a square-planar site defined by the $[Ni(CN)_4]$ unit (Figure 1). In the $[Ni(CN)_4]$ moiety, the Ni1–C1 and C1–N1 bond lengths are 1.956(3) and 1.149(4) Å, respectively, whereas the Ni1–CN bond exhibit almost linear with the deviation from linearity of 3.5°. The metric parameter of the Ni^{II} atom is typical for tetracyanometallates.[14–16]

The equatorial positions of the $[CdN_4O_2]$ octahedron are occupied by four nitrogen atoms of $[Ni(CN)_4]^{2-}$ groups, whereas the axial sites are accomplished by two oxygen atoms from

Table 1. Crystallographic data and structural refinement for compounds **1–5**.

	1	**2**	**3**	**4**	**5**
Formula	$C_{10}H_{14}N_6O_2CdNi$	$C_{10}H_{14}N_6O_2CdPd$	$C_{10}H_{14}N_6O_2CdPt$	$C_{10}H_{14}N_6O_2FeNi$	$C_{10}H_{14}N_6O_2FePt$
M_r	421.38	471.09	557.76	364.83	501.21
Temperature /K	291(2)	296(2)	173(2)	296(2)	173(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/m$	$C2/m$	$C2/m$	$C2/m$	$C2/m$
a /Å	16.9010(10)	16.097(3)	16.057(7)	15.657(3)	15.715(2)
b /Å	7.968(3)	7.8111(13)	7.793(3)	7.4822(15)	7.6600(11)
c /Å	7.3930(10)	7.2523(13)	7.268(3)	6.8273(14)	7.0346(11)
α /°	90.00	90.00	90.00	90.00	90.00
β /°	111.714(11)	111.886(2)	111.540(4)	110.632(2)	109.938(2
γ /°	90.00	90.00	90.00	90.00	90.00
V /Å^3	924.9(4)	846.1(3)	845.9(6)	748.5(3)	796.0(2)
Z	2	2	2	2	2
$\rho_{calcd.}$ /g·cm^{-3}	1.513	1.849	2.190	1.619	2.091
μ /mm^{-1}	2.174	2.328	9.525	2.235	9.697
Total, unique	4416, 974	3665, 1045	3254, 887	3315, 931	3092, 846
Observed [$I > 2\sigma(I)$]	852	910	887	678	845
GOF on F^2	1.096	1.181	1.083	1.083	1.046
R_1, wR_2 [$I > 2\sigma(I)$]	0.0314, 0.0589	0.0215, 0.0586	0.0171, 0.0405	0.0300, 0.0554	0.0144, 0.0313
R_1, wR_2 (all data)	0.0382, 0.0600	0.0238, 0.0613	0.0171, 0.0405	0.0569, 0.0676	0.0144, 0.0313
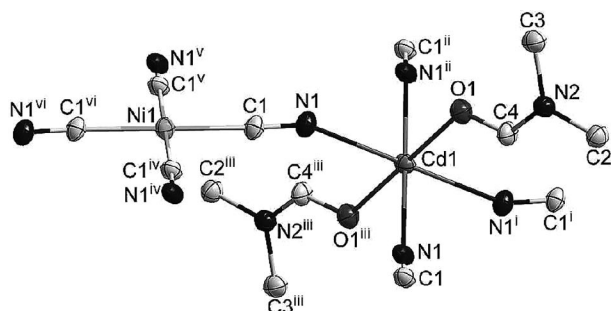
Figure 1. ORTEP diagram of compound **1** with thermal ellipsoids at the 30% probability level. All hydrogen atoms were omitted for clarity. Symmetry code: (i) –x + 1, –y + 2, –z + 2; (ii) x, –y + 2, z; (iii) –x + 1, y, –z + 2; (iv) x, –y + 1, z; (v) –x + 1, y, –z + 3; (vi) –x + 1, –y + 1, –z + 3.

two DMF ligands. The Cd1–N1 and Cd1–O1 bond lengths of 2.475(3) and 2.369(3) Å, respectively, whereas the Cd1–NC unit is bent obviously with the angle of 152.6(2)°. The geometrical data of the central Cd^{II} atoms are practically identical to those observed in the tetracyanometallate-based Cd^{II} compounds.[17–19] It should be noted here that the average distance (2.115 Å) of Fe1–O1 bonds in compounds **4** and **5** are shorter than those (2.333 Å) of the Cd1–O1 bonds in compounds **1**–**3**, which may be induced by the types of metal ions involved in structures.

In particular, the central Cd^{II} and Ni^{II} atoms at (1/2 0 0) and (1/2 1/2 1/2), respectively, lie on sites with 2/m symmetry. Additionally, the [Cd(DMF)$_2$]$^{2+}$ and [Ni(CN)$_4$]$^{2-}$ units are linked alternatively through cyanide bridges to form grid-type layers with the side length of ca. 5.435 Å (Cd···Ni distance) (Figure 2). Similarly, the side distances are ca. 5.329 Å for **2**, 5.328 Å for **3**, 5.064 Å for **4**, and 5.200 Å for **5**. The cyanide layers are not planar but puckered significantly with the dihedral angle of 36.27° between [CdN$_4$] and [NiC$_4$] planes. This distortion can be attributed to [Ni(CN)$_4$]$^{2-}$ units alternate along

the *a* axis above and below the plane defined by cadmium ions, and thereby the sheet doubles the unit cell in the *a* direction and different Cd···Cd distances along the *b* (ca. 7.968 Å) and *c* (ca. 7.393 Å) axes.
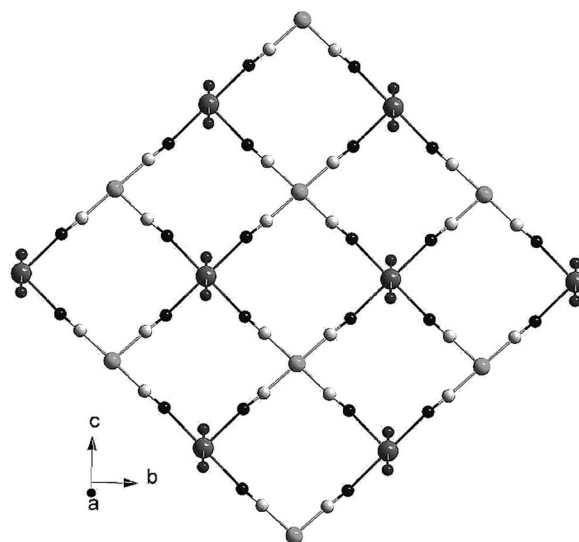
Figure 2. The 2D grid-type structure of compound **1**. Carbon and nitrogen atoms of coordinated DMF molecules and all hydrogen atoms are omitted for clarity.

The parallel and corrugated metal cyanide sheets in compounds **1**–**5** are shifted by the symmetry operation of $C2/m$, and stack together in an ABAB mode along the *a* axis (Figure 3). The offset distances between adjacent sheets are *b*/2 [ca. 3.984 (**1**), 3.906 (**2**), 3.897 (**3**), 3.741 (**4**), 3.830 (**5**) Å] or *c*/2 [ca. 3.697 (**1**), 3.626 (**2**), 3.634 (**3**), 3.414 (**4**), 3.517 (**5**) Å] in the *bc* plane, together the interplanar spacing of *a*/2 [ca. 8.451 (**1**), 8.049 (**2**), 8.029 (**3**), 7.829 (**4**), 7.858 (**5**) Å] (Figure 4). Obviously, both the offset distance and interplanar spacing in compounds **1**–**3** are larger than those found in com-

pounds **4** and **5**. Notably, all non-hydrogen atoms of DMF molecules lie on a mirror plane parallel to the *bc* plane. This shift can be attributed to the large size of DMF ligands because an eclipse layer stacking pattern would make large void space. Similar corrugated polymeric layers are also observed in Hofmann-H_2O/DMF-type materials.[10,20–22] Unlike other cyanide layers reported previously,[23,24] no hydrogen bonds or other weak interactions were found in compounds **1**–**5**.
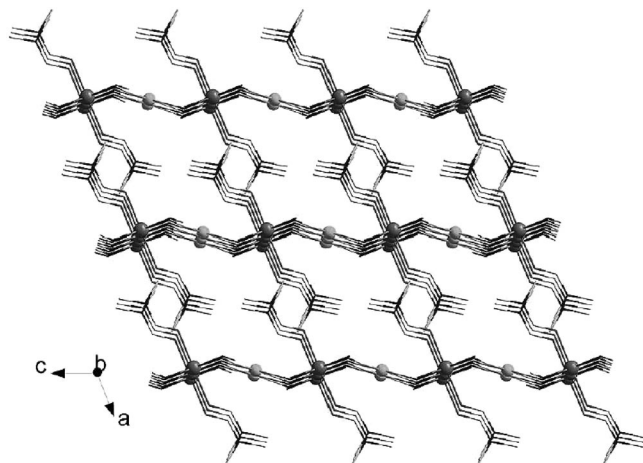

Figure 3. The 2D corrugated sheets of compound **1** stacking along the *b* axis.
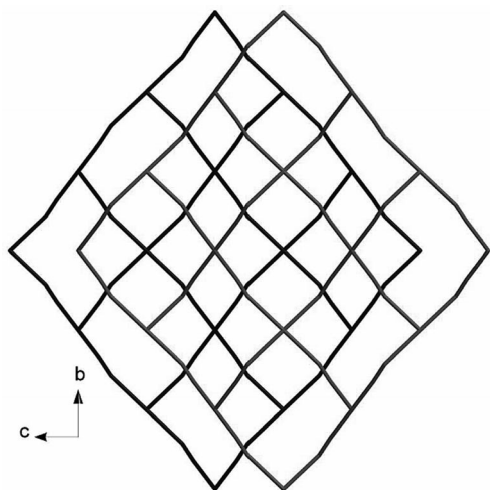

Figure 4. The 2D corrugated sheets of compound **1** stacking along the *a* axis in a ABAB mode.

As shown in Figure 5, powder X-ray diffraction patterns of as-synthesized compounds **4** are in accordance with those simulated from single-crystal XRD data. However, several diffraction peaks are shifted and in some cases differ in relative intensity for compound **1**. This may be attributed to the fact the samples used to powder XRD experiments are single crystals, which were not be ground into powders. Thermogravimetric curves of compounds **1** and **4** are shown in Figure 6. Two curves showed no further mass up to 140 (**1**) and 170 (**4**) °C because of the anhydrous nature. For compound **1**, the weight loss of 34.0 % at 140–203 °C corresponded to the calculated
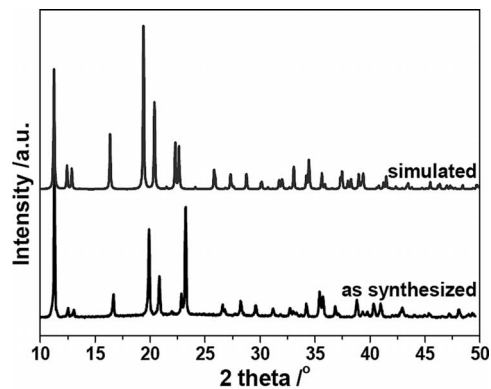
(*a*)
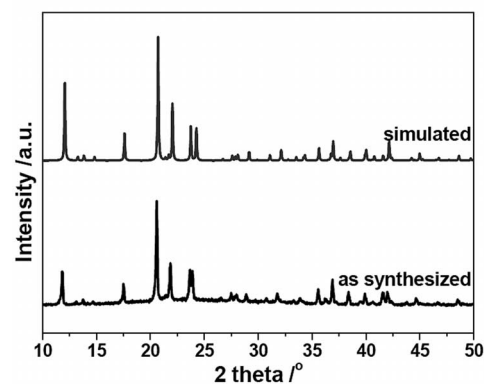
(*b*)

Figure 5. Powder XRD patterns of as synthesized products (a) **1** and (b) **4**, and simulated from single crystal diffraction data.
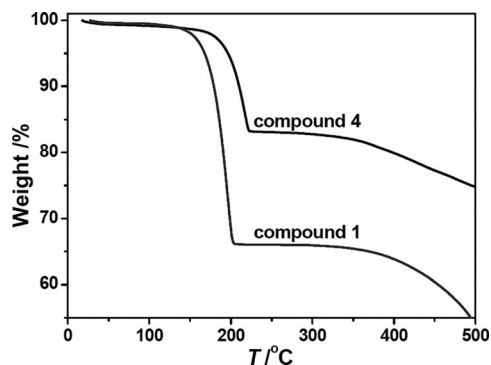

Figure 6. TG curves of compounds **1** and **4**.

value of 1.7 coordinated DMF ligand. In contrast to compound **1**, the weight loss of 16.8 % at 170–222 °C for compound **4** is slightly lower than the theoretical value (17.4 %) of one DMF molecule. In fact, compounds **1** and **4** are also isostructural to the $Zn(DMF)_2M'(CN)_4$ (M' = Ni, Pd, Pt) materials reported previously by our group.[10] Studies revealed that the latter frameworks began to collapse with the loss of coordinated DMF ligands from 110 °C. In our case, the thermal decomposition of Hofmann frameworks also occurred upon the removal of coordinated DMF molecules. So the stable phases are not

present after DMF loss for both compounds. The different thermal stabilities between $Zn(DMF)_2M'(CN)_4$ and our materials arise from the variation in metal ions involved in structures. Based on above analysis, it is not suitable to introduce different ligand/guest into the networks of both compounds.

Conclusions

Series of Hofmann-DMF-type compounds were synthesized in the presence of the bidentate N-donor ligand and the structure consists of 2D corrugated polymeric networks. In fact, the ligand was found not to work well as pillars in the synthesis of expected 3D Hofmann-type materials, which may be attributed to the larger steric hindrance of the ligand. Our work is currently in progress to vary in both length and functionalization of pillared ligands to obtain more systematic information about structures of such system.

Experimental Section

Materials and General Methods: All chemicals and solvents were purchased from commercial sources and used without further purification. The ligand N,N'-bis(4-pyridylformamide)-1,4-benzene (**L**) was synthesized according to the method described in the literature.[25] Elemental analyses for C, H, and N were performed with a Perkin-Elmer 240C elemental analyzer. IR Spectra were measured were measured with a Nicolet FT 1703X spectrophotometer in the form of KBr pellets in the 4000–400 cm^{-1} region. Thermogravimetry (TG) analysis was carried out at a ramp rate of 10 K·min^{-1} in a nitrogen atmosphere with a Perkin-Elmer Pyris Diamond TGA analyzer. Powder X-ray diffraction (XRD) patterns were collected at 4°·min^{-1} with Cu-K_α radiation using a Shimadzu XRD-6000 diffractometer.

Syntheses: Single crystals of compounds **1–5** were prepared at room temperature by slow diffusion of a DMF/H$_2$O (V/V = 1:1) solution (2 mL) containing $MSO_4 \cdot nH_2O$ (M = Cd, Fe) (0.05 mmol) and **L** (0.05 mmol) into a DMF/H$_2$O (V/V = 1:1) solution (20 mL) of $K_2M'(CN)_4$ (M' = Ni, Pd, Pt) (0.05 mmol). Colorless (**1–3**) or pale yellow (**4**, **5**) block-shaped crystals were obtained after about two weeks. Yield for compound **1**: 31% based on the Cd salt. The other compounds have similar mass yields. Taking into account the higher price of the precursors K$_2$Pd(CN)$_4$ and K$_2$Pt(CN)$_4$, the elemental analysis, IR spectra, powder XRD, and TG experiments of only compound **1** and **4** were investigated. C$_{10}$H$_{14}$N$_6$O$_2$CdNi (**1**): calcd. C 28.50; H 3.35; N 19.95%; found: C 28.39; H 3.36; N 19.83%. C$_{10}$H$_{14}$N$_6$O$_2$FeNi (**4**): calcd. C 32.92; H 3.87; N 23.04%; found: C 32.84; H 3.74; N 23.09%. **IR (KBr)** for compound **1**: $\nu(C \equiv N)$ = 2156 cm^{-1}; for compound **4**: $\nu(C \equiv N)$ = 2153 cm^{-1}. Further experiments revealed that the absence of **L** ligand has also lead to the isolation of above compounds.

X-ray Crystallographic Analysis: Diffraction data for **1–5** were collected with a Bruker Apex II diffractometer equipped with Mo-K_α (λ = 0.71073 Å) radiation. Diffraction data analysis and reduction were performed within SMART and SAINT.[26] Correction for Lorentz, polarization, and absorption effects were performed within SADABS.[27] Structures were solved using Patterson method within SHELXS-97 and refined using SHELXL-97.[28–30] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of coordinated DMF ligands were calculated at idealized position and include in the refinement in a riding mode. It is worth noting that the displacement param-

eters of C2 and C3 atoms from DMF molecules for compounds **2–5** are larger obviously than other atoms in the structure, characteristic of disorder. As generally observed for guest molecules in the 2D Hofmann-type system,[17,31] the disorder may be attributed to the symmetry operation of the space group, thermal motion and/or rearrangement of guest molecules in the cavities. The location disorder of corresponding coordination polymer Fe-DMF-Pd was probably associated with the difficulty in obtaining high-quality single crystals suitable for X-ray diffraction experiment.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-949023 (**1**), CCDC-949024 (**2**), CCDC-949025 (**3**), CCDC-949026 (**4**), and CCDC-949027 (**5**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles for compounds **1–5**.

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