Syntheses, crystal structures, and thermal stabilities of the first Hofmann-DMF-type complexes Zn(DMF)$_2$M(CN)$_4$ (M = Ni, Pd, Pt)

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The first Hofmann-DMF-type complexes Zn(DMF)$_2$M(CN)$_4$ (M = Ni (**1**), Pd (**2**), Pt (**3**)) have been synthesized by solution diffusion and characterized structurally by single-crystal X-ray diffraction. The structure consists of 2-D corrugated sheets stacking along the *a*-axis in an ABAB packing mode without interpenetration. The octahedral Zn ions and square-planar M ions occupy special positions of $\bar{2}/m$ site symmetry. The DMF, except for six methyl H atoms, lies on a crystallographic mirror plane; the DMF molecules coordinate to axial sites of Zn on both sides of the sheet. The framework of **1** begins to collapse with loss of coordinated DMF.

Keywords: Hofmann; Cyano-bridged; Tetracyanometalate; Crystal structure

1. Introduction

The synthesis and characterization of multidimensional coordination networks has been an area of rapid growth. Cyanometalate chemistry has experienced a renaissance owing to remarkable magnetic [1, 2], electrical [3], optical [4], catalytic [5], gas-storage [6, 7], and negative thermal expansion properties [8, 9]. Several types of cyanide-containing materials based on different building blocks, such as SCN^- [10], NCO^- [11], $[Fe(bipy)(CN)_4]^-$ [12], $[Ni(CN)_4]^{2-}$ [13], $[M(CN)_6]^{3-}$ (M = Fe, Co, Cr) [14–17] and $[M(CN)_8]^{3-/4-}$ (M = Mo, W) [18, 19], have been synthesized and characterized. Hofmann-type host complexes, $ML_2M(CN)_4$ (M = Mn, Fe, Co, Ni, Cu, Zn or Cd; M = Ni, Pd or Pt; L = unidentate ligand), play an important role owing to their ability to trap organic molecules and intriguing spin-crossover [20–23], and hydrogen storage properties [24, 25].

There is still much to be explored in the crystal engineering of Hofmann-type and analogous structures, although a number of the isostructural series have been established on the basis of the single-crystal structures. Herein, we present the

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2. Experimental

2.1. *General considerations*

All chemicals purchased were of reagent grade or better and used without purification. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C analyzer. Fourier-transform IR (FT-IR) spectra were recorded (400–4000 cm^{-1}) in KBr pellets on a Nicolet FT-IR 17SX. Thermogravimetry (TG) was performed using a Perkin-Elmer Diamond TG/DTA instrument under nitrogen at a heating rate of 10°C min^{-1}. Variable temperature powder X-ray diffraction (XRD) patterns were collected with Cu-Kα radiation using a D8-Advance X-ray diffractometer (Bruker-AXS) under vacuum. All patterns were collected from 5 to 50° per 2θ with a rate of 2° min^{-1}. Temperature-dependent Raman spectra were recorded in back-scattering geometry using a JY-T6400 monochromator. The 488 nm light from an Ar$^+$ laser was focused onto the sample surface under nitrogen. The temperature stability of the sample was controlled within 0.1 K (THMS600/HFS91). The scattered signal from the sample was detected by a charge-coupled device detection system.

2.2. *Preparations of Zn(DMF)$_2$M(CN)$_4$ (M = Ni, Pd, Pt)*

2.2.1. Zn(DMF)$_2$Ni(CN)$_4$ (1). Colorless block-shaped crystals of Zn(DMF)$_2$Ni(CN)$_4$ suitable for single-crystal X-ray structure determination were grown at room temperature by slow diffusion of a DMF solution (15 mL) of ZnSO$_4$·7H$_2$O (29 mg, 0.10 mmol) and a DMF solution (15 mL) of K$_2$[Ni(CN)$_4$]·H$_2$O (26 mg, 0.10 mmol). The resulting crystals were collected, washed with H$_2$O and dried in air. Yield: 30%. Anal. Calcd for C$_{10}$H$_{14}$N$_6$NiO$_2$Zn: C 32.08, H 3.77, N 22.45%; Found: C 31.99, H 3.79, N 22.72%. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ = 2162.

2.2.2. Zn(DMF)$_2$Pd(CN)$_4$ (2). Colorless block-shaped crystals of Zn(DMF)$_2$Pd(CN)$_4$ suitable for single-crystal X-ray structure determination were grown at room temperature by slow diffusion of a DMF solution (15 mL) of ZnSO$_4$·7H$_2$O (29 mg, 0.10 mmol) and a DMF solution (15 mL) of K$_2$[Pd(CN)$_4$]·3H$_2$O (34 mg, 0.10 mmol). The resulting crystals were collected, washed with H$_2$O, and dried in air. Yield: 28%. Anal. Calcd for C$_{10}$H$_{14}$N$_6$PdO$_2$Zn: C 28.46, H 3.34, N 19.91%; Found: C 28.64, H 3.31, N 19.78%. IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ = 2203.

2.2.3. Zn(DMF)$_2$Pt(CN)$_4$ (3). Colorless block-shaped crystals of Zn(DMF)$_2$Pt(CN)$_4$ suitable for single-crystal X-ray structure determination were grown at room temperature by slow diffusion of a DMF solution (15 mL) of ZnSO$_4$·7H$_2$O (29 mg, 0.10 mmol) and a DMF solution (15 mL) of K$_2$[Pt(CN)$_4$]·3H$_2$O (43 mg, 0.10 mmol). The resulting crystals were collected, washed with H$_2$O, and dried in air. Yield: 31%. Anal. Calcd for

$C_{10}H_{14}N_6PtO_2Zn$: C 23.52, H 2.76, N 16.45%; Found: C 23.64, H 2.75, N 16.52%. IR (KBr, cm^{-1}): $\nu_{C\equiv N} = 2173, 2199$.

2.3. *X-ray crystallography*

Diffraction data for **1**–**3** were collected on a Bruker Apex II diffractometer equipped with Mo-Kα ($\lambda = 0.71073$ Å) radiation. Diffraction data analysis and reduction were performed with *SMART* and *SAINT* [26]. Correction for Lorentz, polarization, and absorption effects were performed with *SADABS* [27]. Structures were solved using the Patterson method with *SHELXS-97* and refined using *SHELXL-97* [28]. All non-H atoms were refined anisotropically. The C(H) of DMF were placed in calculated position (C–H = 0.96 Å) and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$. The crystallographic data and experimental details for structural analyses are summarized in table 1. Selected bond lengths and angles for **1**–**3** are listed in table 2.

3. Results and discussion

3.1. *Crystal structures of* **1**–**3**

Single-crystal X-ray crystallographic analysis confirms that the three complexes are isostructural and the asymmetric unit of **1** is shown in figure 1. In the structure of **1**–**3**, the [M(CN)$_4$] has a square-planar geometry with four bridging cyano ligands and the M

Table 1. Crystallographic data and structure refinement of X-ray data collection for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{10}H_{14}N_6NiO_2Zn$	$C_{10}H_{14}N_6NiO_2Pd$	$C_{10}H_{14}N_6NiO_2Pt$
Formula weight	374.34	422.04	510.73
Temperature (K)	173(2)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*m*	*C*2/*m*	*C*2/*m*
Unit cell dimensions (Å, °)			
a	15.750(3)	15.832(5)	15.802(7)
b	7.4355(1)	7.618(2)	7.599(3)
c	6.8302(1)	7.015(2)	7.031(3)
α	90	90	90
β	110.196(2)	109.923(3)	109.542(4)
γ	90	90	90
Volume (Å^3), *Z*	750.7(2), 2	795.4(4), 2	795.6(6), 2
Calculated density (g cm^{-3})	1.656	1.762	2.132
F(000)	380	416	480
Reflections collected	3256	3442	3341
Independent reflections	926	984	970
Data/restraints/parameters	926/0/62	984/0/63	970/0/63
Goodness-of-fit on F^2	1.10	1.22	1.17
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0194$, $\omega R_2 = 0.0527$	$R_1 = 0.0209$, $\omega R_2 = 0.0571$	$R_1 = 0.0310$, $\omega R_2 = 0.0900$
R indices (all data)	$R_1 = 0.0227$, $\omega R_2 = 0/0552$	$R_1 = 0.0227$, $\omega R_2 = 0.0766$	$R_1 = 0.0319$, $\omega R_2 = 0.0906$

sits on the center of inversion. The C–N and M–C bond distances of the square-planar M coordination environment are comparable with those in the related Hofmann-dma-type complex $Cd(dma)_2Ni(CN)_4 \cdot xG$ [29] and the M–C–N bonds are nearly linear. Zinc is six-coordinate by four cyano-nitrogens and two oxygens from two DMF, {MN4O2}, in a slightly distorted octahedral geometry. Equatorial coordination sites are occupied by four nitrogens of bridging cyano, whereas the *trans* axial sites are occupied by DMF. The average M–N and M–O bond distances (2.128 Å

Table 2. Selected bond distances (Å) and angles (°) for **1–3**.

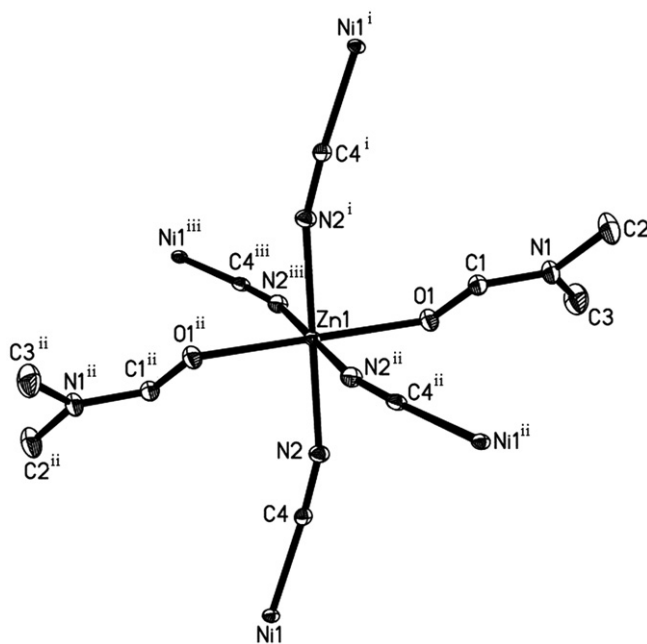| **1**			
Zn1–O1	2.1269(1)	N2–C4	1.1520(2)
Zn1–N2	2.1336(1)	N2–C4–Ni1	176.11(1)
Ni1–C4	1.8634(2)		
2			
Zn1–O1	2.136(3)	N2–C4	1.145(4)
Zn1–N2	2.140(2)	N2–C4–Pd1	175.6(2)
Pd1–C4	1.995(3)		
3			
Zn1–O1	2.142(7)	N2–C4	1.161(9)
Zn1–N2	2.138(6)	N2–C4–Pt1	176.8(6)
Pt1–C4	1.977(6)		

Figure 1. ORTEP diagrams of $Zn(DMF)_2Ni(CN)_4$ (**1**). Displacement ellipsoids are drawn at 30% probability and H atoms are omitted for clarity. Symmetry codes for **1**: [i] $-x + 1, -y, -z$; [ii] $-x + 1, y, -z$; and [iii] $x, -y, z$.

and 2.152 Å, respectively) are both slightly higher than those found in the Hofmann-H_2O-type $Co(H_2O)_2Ni(CN)_4 \cdot 4H_2O$ (2.098 Å and 2.128 Å, respectively) [30].

The Zn and M atoms both lie on sites with $2/m$ symmetry. As a result, the Zn and M centers are linked by cyanides, resulting in 2-D corrugated metal cyanide sheets without interpenetration stacking along the *a*-axis with an ABAB packing pattern (figures 2 and 3). DMF molecules are located on both sides of the sheets, and DMF, except for six hydrogens, lie on a crystallographic mirror plane parallel to the *ac*-plane. The offset distance between the adjacent sheets is *ca* 2.5 Å (about half the distance of $Zn \cdots M$) along the [0 1 1] or [0 1 −1] in the *bc*-plane. The distance between two adjacent sheets is $a/2$ (*ca* 7.8 Å). Similar corrugated polymeric sheets are also reported in some related Hofmann-H_2O-type complexes [30–33].

3.2. *Thermal analysis of* 1

Thermogravimetric experiments of **1**–**3** were performed under nitrogen from room temperature to 730°C for **1**, and 800°C for **2** and **3** (Supplementary material). The absence of weight loss below 100°C confirms their anhydrous nature. From about 110°C for **1**, and 160°C for **2** and **3**, a well-pronounced weight loss is detected which ends above 165°C for **1**, and close to 220°C for **2** and **3**.

Owing to the higher price of $K_2[Pd(CN)_4]$ and $K_2[Pt(CN)_4]$, the temperature-dependent powder XRD and Raman spectra for only **1** were performed to identify the mechanism of weight loss. The powder X-ray patterns of **1** indicated decomposition of the original structures when heated to 100°C (Supplementary
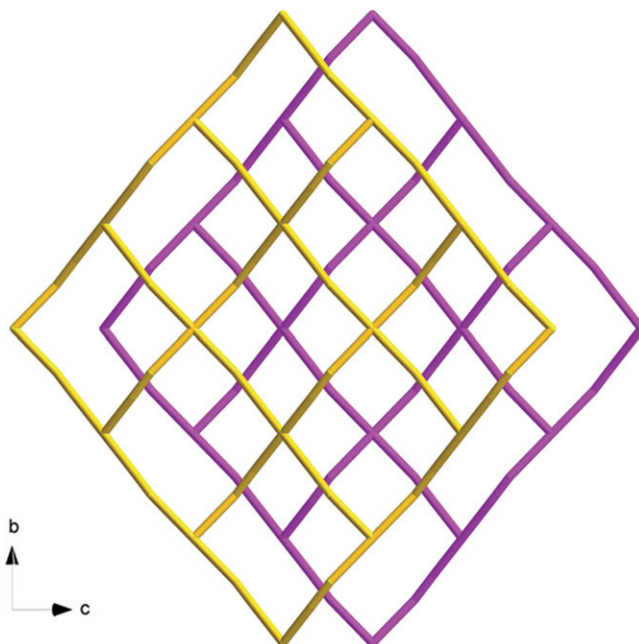

Figure 2.   Stacking without interpenetration of sheets along the *a*-axis of **1**–**3**.
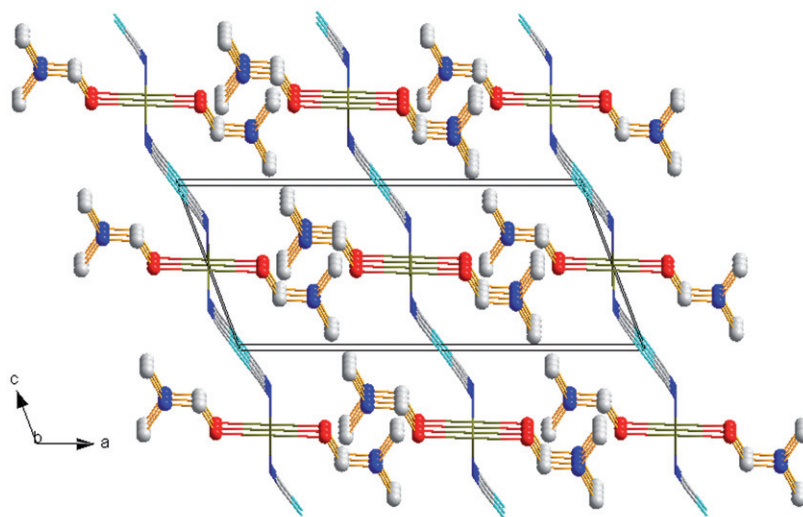
Figure 3.   The 2-D corrugated sheets of **1**–**3** stacking along the *a*-axis.

material), attributed to framework collapse with loss of coordinated DMF at about 110°C. The lower decomposition temperature (100°C) observed from the variable temperature powder XRD patterns than that (110°C) from TG analysis result can be due to the former performed under vacuum, while the latter was done under nitrogen. Strong CN peaks were still observed from Raman spectra up to 200°C (Supplementary material), which indicated CN groups in the framework during the process of the pronounced weight loss. Thereafter, the remainder obtained at about 165°C lost no further mass up to 400°C, above which thermal decomposition continued.

4. Conclusions

We have synthesized and characterized structurally the first Hofmann-DMF-type complexes $Zn(DMF)_2M(CN)_4$ (M = Ni(**1**), Pd(**2**), Pt(**3**)). Single-crystal XRD reveals that the structure consisted of 2-D corrugated sheets stacking along the *a*-axis. The framework of **1** begins to collapse with loss of coordinated DMF. Further work will concentrate on self-assembly reaction between $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) and other metal ions to obtain new Hofmann-type complexes with interesting structures and properties.

Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 737776–737778 for **1**–**3** in the article, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic

Data Center, 12 Union Road, Cambridge CB21EZ, UK, Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

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