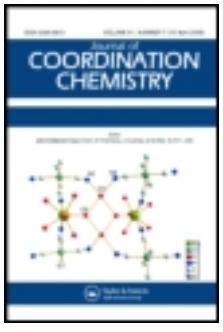

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Syntheses, structures, and host-guest interactions of 2-D grid-type cyanide-bridged compounds $[Zn(L)(H_2O)_2][M(CN)_4]\cdot 3H_2O$ (L = N,N′-bis(4-pyridylformamide)-1,4-benzene; M = Ni, Pd or Pt)

Aiyun Hu[a], Xin Chen[a], Hu Zhou[bc], Yingying Chen[a] & Aihua Yuan[a]

[a] School of Biology and Chemistry Engineering, Jiangsu University of Science and Technology, Zhenjiang, P.R. China

[b] School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, P.R. China

[c] SiYang Diesel Engine Manufacturing Co., Ltd, Zhenjiang, P.R. China

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Syntheses, structures, and host-guest interactions of 2-D grid-type cyanide-bridged compounds $[Zn(L)(H_2O)_2][M(CN)_4]\cdot 3H_2O$ (L = *N*,*N*′-bis(4-pyridylformamide)-1,4-benzene; M = Ni, Pd or Pt)

AIYUN HU†, XIN CHEN†, HU ZHOU‡§, YINGYING CHEN† and AIHUA YUAN*†

†School of Biology and Chemistry Engineering, Jiangsu University of Science and Technology, Zhenjiang, P.R. China
‡School of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, P.R. China
§SiYang Diesel Engine Manufacturing Co., Ltd, Zhenjiang, P.R. China

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Self-assembly of Zn^{2+}, the pillar ligand *N*,*N*′-bis(4-pyridylformamide)-1,4-benzene, and $[M(CN)_4]^{2-}$ (M = Ni, Pd, or Pt) formed three compounds $[Zn(L)(H_2O)_2][M(CN)_4]\cdot 3H_2O$ (**1–3**). Single-crystal X-ray diffraction (XRD) analysis reveals that **1–3** are isostructural and consist of cyanide-bridged 2-D grid-type layers built of $[Zn(L)(H_2O)_2]^{2+}$ chains cross-linked by $[M(CN)_4]^{2-}$ units. Thermogravimetric and powder XRD analyses indicate that **1** has a high thermal stability and exhibits reversibility for desorption/resorption of water guest molecules.

Keywords: Tetracyanometalates; Structures; Grid; Host-guest

1. Introduction

The design and synthesis of functional coordination compounds have grown rapidly because of their intriguing topologies and potential applications [1, 2]. Tetracyanide-bearing precursors $[M(CN)_4]^{2-}$ (M = Ni, Pd or Pt) were used to construct Hofmann-type host compounds formulated as ML_2 M'$(CN)_4$ (M = Mn, Fe, Co, Ni, Cu, Zn, or Cd; M' = Ni, Pd, or Pt; L = unidentate ligand) and the resulting materials exhibited interesting properties such as spin-crossover and gas storage [3–7]. However, there is still much to be explored in the crystal engineering of 3-D porous Hofmann-type and analogous structures.

As part of our ongoing efforts in construction of new structural types of tetracyanide-based compounds [8, 9], we employed tetracyanometalates as building blocks to react with Zn^{2+} and the linear bidentate ligand *N*,*N*′-bis(4-pyridylformamide)-1,4-benzene (L) to obtain 3-D Hofmann-type compounds, in which the metal cyanide layers are pillared by L. Unexpectedly, three isostructural 2-D grid-type compounds $[Zn(L)(H_2O)_2][M(CN)_4]\cdot 3H_2O$ (M = Ni(**1**), Pd(**2**) or Pt(**3**)) were obtained instead. Failure of the reactions may be attributed

*Corresponding author. Email: aihuayuan@163.com

to the use of the longer linear ligand L. Shorter linear diaza ligands such as pyrazine, 4,4′-bipyridine, 4,4′-dipyridylacetylene, 1,2-bis(4-pyridyl)ethylene, or 1,2-di(4-pyridyl)ethane were usually employed to construct 3-D Hofmann-type materials [6, 10]. In the present contribution, we report the syntheses, crystal structures, thermal stabilities, and host-guest interactions.

2. Experimental

2.1. *Materials and methods*

All chemicals and solvents were purchased from commercial sources and used as received. *N*,*N*′-bis(4-pyridylformamide)-1,4-benzene was synthesized according to the method described [11]. IR spectra were measured on a Nicolet FT 1703X spectrophotometer in the form of KBr pellets from 4000–400 cm^{-1}. Powder X-ray diffraction (XRD) patterns were collected with Cu-K_α radiation using a Shimadzu XRD-6000 diffractometer. Thermogravimetric (TG) analyzes were carried out at a ramp rate of 5 °C min^{-1} under N_2 using a Pyris Diamond TGA analyzer.

2.2. *Syntheses*

Single crystals of **1–3** were prepared at room temperature by slow diffusion of a CH_3CN/H_2O (1/1) solution (2 mL) containing $ZnSO_4{\cdot}7H_2O$ (0.05 mM) and L (0.05 mM) into a CH_3CN/H_2O (1/1) solution (20 mL) of $K_2M(CN)_4$ (M = Ni, Pd or Pt) (0.05 mM). Yellow block-shaped crystals were obtained after four weeks. Anal. Calcd for $C_{22}H_{24}ZnN_8NiO_7$ (**1**) (%): C, 41.51; H, 3.80; N, 17.60. Found: C, 41.39; H, 3.76; N, 17.77. IR (KBr, cm^{-1}) for compound **1**: $\nu_{C-N(amide)} = 1406$, 1417 cm^{-1}, $\nu_{C\equiv N(terminal)} = 2131$ cm^{-1}, $\nu_{C\equiv N(bridged)} = 2173$ cm^{-1}; for compound **2**: $\nu_{C-N(amide)} = 1405$, 1416 cm^{-1}, $\nu_{C\equiv N(terminal)} = 2145$ cm^{-1}, $\nu_{C\equiv N(bridged)} = 2187$ cm^{-1}; for compound **3**: $\nu_{C-N(amide)} = 1404$, 1416 cm^{-1}, $\nu_{C\equiv N(terminal)} = 2145$ cm^{-1}, $\nu_{C\equiv N(bridged)} = 2191$ cm^{-1}.

2.3. *Crystallographic data collection and structure determination*

Diffraction data for **1–3** were collected at 296(3) K on a Bruker Smart APEX II diffractometer equipped with Mo-K_α ($\lambda = 0.71073$ Å) radiation. Diffraction data analysis and reduction were performed within *SMART*, *SAINT* and *XPREP* [12]. Correction for Lorentz, polarization, and absorption effects were performed within *SADABS* [13]. Structures were solved using the Patterson method within *SHELXS-97* and refined using *SHELXL-97* [14,15]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens of L were calculated at idealized positions and included in the refinement in a riding mode with U_{iso} for H assigned as 1.2 times U_{eq} of the attached atoms. Hydrogens bound to coordinated and uncoordinated water were located from difference Fourier maps and refined as riding with $U_{iso}(H) = 1.2\ U_{eq}(O)$. The crystallographic data and experimental detail for structural analyzes are summarized in table 1. Selected bond distances and angles are listed in table 2.

Table 1. Crystallographic data and structural refinement for **1–3**.

Compounds	**1**	**2**	**3**
Formula	$C_{22}H_{24}ZnN_8NiO_7$	$C_{22}H_{24}ZnN_8PdO_7$	$C_{22}H_{24}ZnN_8PtO_7$
M_r	636.60	684.26	772.95
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*
a (Å)	8.6236(13)	8.623(3)	8.5127(9)
b (Å)	9.9335(15)	10.023(4)	9.9215(10)
c (Å)	17.025(3)	17.138(7)	17.1690(18)
α (°)	85.637(2)	85.869(5)	85.8380(10)
β (°)	82.101(2)	82.515(5)	82.2710(10)
γ (°)	65.338(2)	66.591(5)	67.5370(10)
V (Å^3)	1312.5(3)	1347.4(9)	1327.5(2)
Z	2	2	2
ρ_{Calcd} (g cm^{-3})	1.611	1.687	1.934
μ (mm^{-1})	1.689	1.614	6.224
Total, unique	11,352, 5897	11,646, 6017	9335, 4494
Observed [$I > 2\sigma(I)$]	3719	4129	4314
GOF on F^2	0.998	1.012	1.059
R_1, ωR_2 [$I > 2\sigma(I)$]	0.0321, 0.0734	0.0346, 0.0737	0.0281, 0.0748
R_1, ωR_2 (all data)	0.0684, 0.0889	0.0663, 0.0870	0.0293, 0.0767

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

1			
Ni1–C1	1.857(3)	N4–C4	1.146(3)
Ni1–C2	1.877(3)	Zn1–N1	2.053(2)
Ni1–C3	1.853(2)	Zn1–N3^{i}	2.046(2)
Ni1–C4	1.888(3)	Zn1–N5	2.231(2)
N1–C1	1.143(3)	Zn1–N8^{ii}	2.223(2)
N2–C2	1.145(3)	Zn1–O1	2.1899(19)
N3–C3	1.145(3)	Zn1–O2	2.2262(19)
N1–C1–Ni1	177.2(3)	N4–C4–Ni1	178.1(3)
N2–C2—Ni1	178.8(3)	C1–N1–Zn1	175.9(2)
N3–C3–Ni1	179.8(3)	C3–N3–Zn1^{iii}	172.0(2)
2			
Pd1–C1	1.979(3)	N4–C4	1.146(4)
Pd1–C2	2.002(3)	Zn1–N1	2.037(3)
Pd1–C3	1.976(3)	Zn1–N3^{i}	2.042(3)
Pd1–C4	2.011(3)	Zn1–N5	2.249(3)
N1–C1	1.142(4)	Zn1–N8^{ii}	2.236(3)
N2–C2	1.143(4)	Zn1–O1	2.197(2)
N3–C3	1.145(4)	Zn1–O2	2.226(2)
N1–C1–Pd1	178.0(3)	N4–C4–Pd1	178.1(3)
N2–C2–Pd1	178.5(3)	C1–N1–Zn1	174.1(2)
N3–C3–Pd1	177.8(3)	C3–N3–Zn1^{iii}	175.3(3)
3			
Pt1–C1	1.983(5)	N4–C4	1.148(7)
Pt1–C2	2.012(5)	Zn1–N1	2.033(4)
Pt1–C3	1.980(5)	Zn1–N3^{i}	2.047(4)
Pt1–C4	2.007(5)	Zn1–N5	2.248(4)
N1–C1	1.149(7)	Zn1–N8^{ii}	2.232(4)
N2–C2	1.147(6)	Zn1–O1	2.198(3)
N3–C3	1.144(7)	Zn1–O2	2.212(3)
N1–C1–Pt1	178.3(4)	N4–C4–Pt1	178.7(4)
N2–C2–Pt1	178.8(4)	C1–N1–Zn1	172.9(4)
N3–C3–Pt1	177.9(4)	C3–N3–Zn1^{iii}	174.3(4)

Symmetry codes for **1**: (i) $x-1, y+1, z$; (ii) $x-1, y, z-1$; (iii) $x+1, y-1, z$. for **2**: (i) $x+1, y-1, z$; (ii) $x-1, y, z-1$; (iii) $x-1, y+1, z$. for **3**: (i) $x-1, y+1, z$; (ii) $x+1, y, z+1$; (iii) $x+1, y-1, z$.

3. Results and discussion

Single-crystal XRD analysis revealed that **1–3** are isostructural and crystallize in the triclinic space group *P-1* (table 1). Only the structure of **1** is described in detail (figure 1). The asymmetric unit consists of one $[Zn(L)(H_2O)_2]^{2+}$, one $[Ni(CN)_4]^{2-}$, and three crystallization waters. In the $[Zn(L)(H_2O)_2]^{2+}$ fragment, the six-coordinate Zn is located in a distorted octahedral geometry, in which the average value (2.277 Å) of $Zn–N_{L\ ligand}$ bond distances is larger than 2.050 Å of $Zn–N_{cyanide}$ bonds. Zn1–O1 and Zn1–O2 lengths are 2.1899(19) and 2.2262(19) Å, respectively, while the two Zn–NC bonds are bent slightly with angles of 172.0(2) and 175.9(2)°. The $\{ZnN_4O_2\}$ coordination geometry of Zn in our case has also been observed in $Zn(DMF)_2\ M(CN)_4$ (M = Ni, Pd or Pt) [16]. As a result, $[Zn(L)(H_2O)_2]^{2+}$ units are connected alternately through *trans* L to form 2,2-chains with the intrachain Zn···Zn distance of *ca*. 20.11 Å.

$[Ni(CN)_4]$ exhibits a square planar geometry with four bridging cyanides. The average Ni–C and C–N bond distances are 1.868 and 1.145 Å, respectively, and Ni–CN bonds are nearly linear (177.2(3)–179.8(3)°). The metric parameters of $[Ni(CN)_4]$ are typical for tetracyanometalates [17–20]. As shown in figure 2, adjacent $[Zn(L)(H_2O)_2]^{2+}$ chains are further cross-linked by $[Ni(CN)_4]^{2-}$, generating a 2-D grid-like network with the two side lengths of about 10.08 and 20.11 Å (Zn···Zn distance). The *trans* coordinated waters are located on both sides of layers. Terminal cyanides, L, coordinated and uncoordinated waters are all involved in the hydrogen-bonding network of **1**. There are four types of hydrogen bonds (table 3): (1) two terminal cyanides interact with coordinated and crystallization waters through O–H···N hydrogen bonds; (2) coordinated waters interact with lattice waters and L by O–H···O hydrogen bonds; (3) lattice waters interact with coordinated/lattice waters and L by O–H···O hydrogen bonds; and (4) L interacts with coordinated and uncoordinated waters by N–H···O hydrogen bonds. As a result, neighboring layers are well separated through hydrogen bonds and π–π stacking interactions, forming a 3-D supramolecular network (figure 3). According to Cheetham [21], cyanide-based systems can be classified using I^xO^y

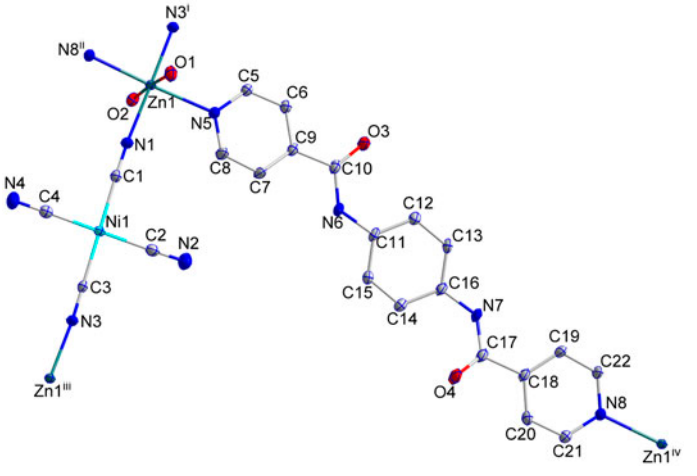

Figure 1. ORTEP of **1** with displacement ellipsoids drawn at the 30% probability level. All hydrogens and crystallization waters were omitted for clarity. Symmetry codes: (i) $x-1, y+1, z$; (ii) $x-1, y, z-1$; (iii) $x+1, y-1, z$; (iv) $x+1, y, z+1$.

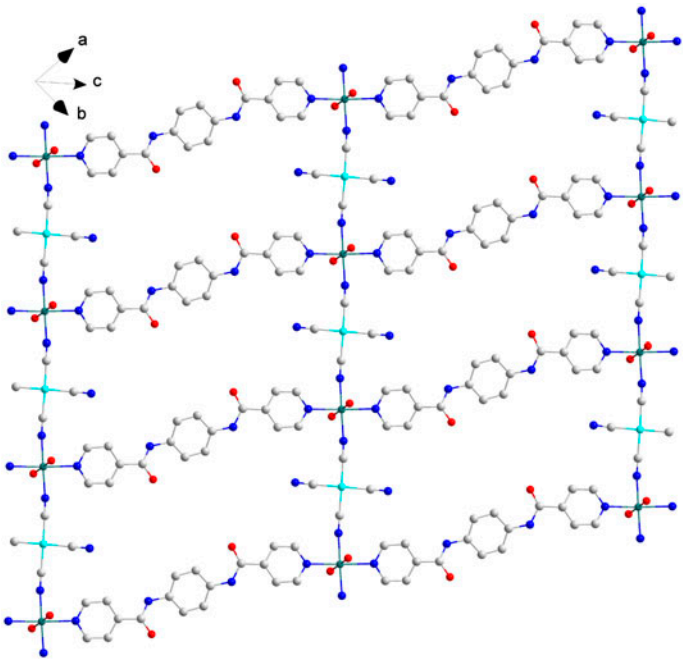

Figure 2. The 2-D grid-type structure of **1**. All hydrogens and crystallization waters were omitted for clarity.

Table 3. Hydrogen-bond geometry (Å, °) for **1**.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H1A···O4^{v}	0.85	1.94	2.739(2)	156
O1–H1B···O6^{vi}	0.85	2.01	2.855(3)	178
O2–H2A···O7	0.85	1.95	2.793(3)	169
O2–H2B···N4^{vii}	0.85	1.98	2.831(3)	176
O5–H5A···O6^{iii}	0.85	2.16	2.982(3)	162
O5–H5B···N2	0.85	2.00	2.828(3)	164
O6–H6A···O3	0.85	1.97	2.819(3)	175
O6–H6B···O5^{viii}	0.85	1.98	2.830(3)	175
O7–H7A···O1^{ix}	0.85	2.32	3.020(3)	140
O7–H7B···O4^{x}	0.85	2.55	3.137(3)	127
N7–H7C···O2^{viii}	0.86	2.37	3.205(3)	163
N6–H6C···O5	0.86	2.47	3.290(3)	161

Symmetry codes: (v) $-x+2, -y+1, -z+1$; (vi) $-x+1, -y+2, -z+1$; (vii) $-x+2, -y+1, -z$; (iii) $x+1, y-1, z$; (viii) $-x+2, -y+2, -z+1$; (ix) $x+1, y, z$; (x) $-x+3, -y+1, -z+1$.

symbols, where *x* and *y* denoted the dimensionality of the inorganic (I) and organic (O) subnetworks, respectively. In the structures of **1–3**, both the inorganic (-Zn-NC-M- linkages) and organic (-L-Zn-L- linkages) subnetworks are 1-D, so the topology can be described as I^1O^1. From the perspective of topology, the structure in our case is different obviously from those found in 2-D Hofmann-type materials $M(DMF)_2[M'(CN)_4]$ (M = Zn, Cu; M' = Ni, Pd or Pt) and $M(H_2O)_2[Ni(CN)_4]\cdot xH_2O$ (M = Mn, Fe, Co, Ni or Cd) with I^2O^0 topology, in which the layers were constructed by cyanide-bridged polymeric 2-D skeletons (inorganic subnetwork) with monodentate ligands on both sides [16, 22–25].

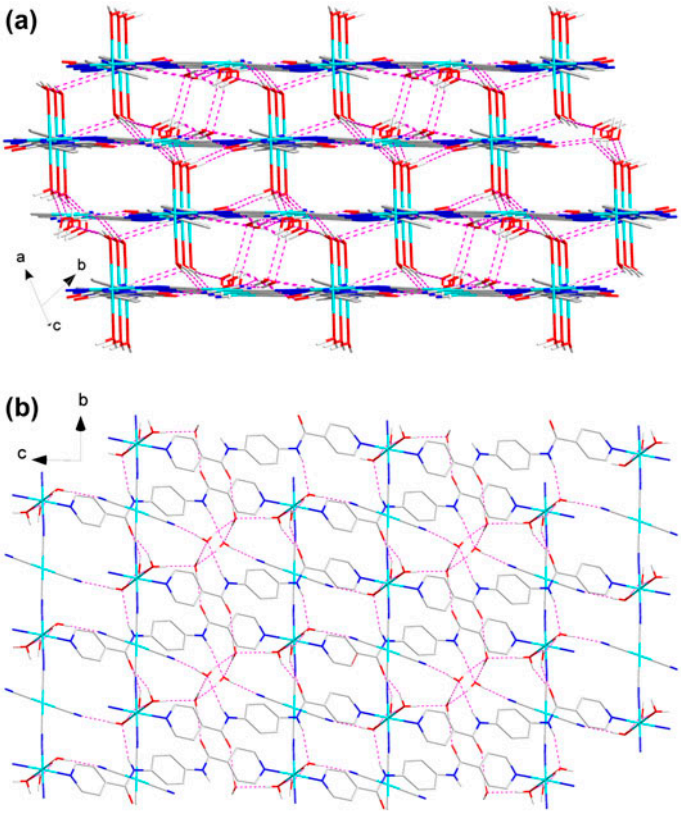

Figure 3. The 3-D supramolecular network of **1** along the (a) [1 0 1] and (b) [1 0 0] directions. All hydrogens bound to carbon were omitted for clarity and dashed lines represent hydrogen bonds.

Taking into account the high price of starting precursors $K_2Pd(CN)_4$ and $K_2Pt(CN)_4$, only the thermal stability and host-guest chemistry of **1** were investigated. TG curve (Supplementary material) showed an obvious weight loss (13.80%) between 20 and 110 °C, corresponding to loss of three uncoordinated and two coordinated waters per formula unit (Calcd 14.15%). The desolvated phase $Zn(L)M(CN)_4$ loses no further mass up to 300 °C, above which thermal decomposition occurs.

Crystal samples of **1** were heated at 150 °C under vacuum for 12 h to remove all water molecules and examine the host-guest chemistry. Powder XRD results (figure 4) showed that the compound remained highly crystalline upon removal of crystallized and coordinated water molecules, although the structure of dehydrated phase of **1** has changed, as evidenced by variable diffraction peaks. A potentially very attractive aspect of this system is that the desorption of guest molecules yielded materials with accessible, exposed coordinatively-unsaturated Zn^{2+} metal sites [26]. In fact, powder XRD patterns of the regenerated samples exhibit peak positions and intensities fully coincident to those observed for as-synthesized samples when dehydrated samples were soaked into water solution over a period of 12 h. Above results indicate that the dehydration/rehydration process of **1** is reversible and removal of water does not result in collapse of the 2-D framework.

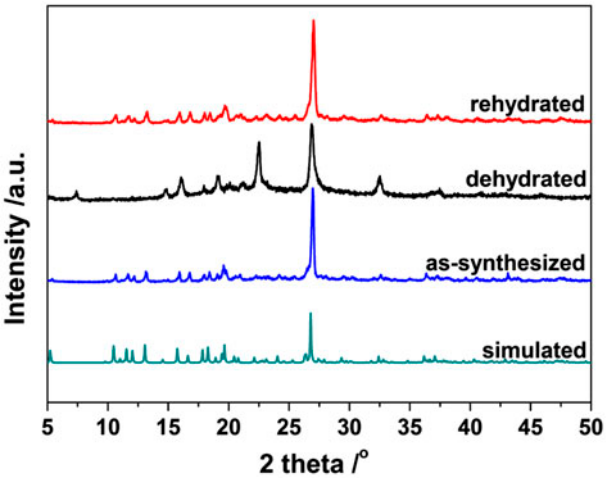

Figure 4. Powder XRD patterns of **1** with the dehydration/rehydration process.

4. Conclusion

Three 2-D grid-type tetracyanide-based compounds were synthesized and characterized structurally. The thermal decomposition and host-guest interaction results reveal that the dehydrated crystals are able to be rehydrated. Continuing work in our laboratory will focus on (1) investigating interactions between the host lattice of dehydrated compounds and other small guest molecules (ethanol, methanol, amine, DMF, etc.) and (2) employing 2-D dehydrated phases as precursors to react with pillar bidentate ligands to construct 3-D porous frameworks with gas storage properties.

Supplementary material

CCDC numbers: 925708 (**1**), 925709 (**2**) and 925710 (**3**). This data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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