



A 'kagome dual' (**k_{gd}**) sheet based on triangular rigid ligand: Synthesis, structure, photoluminescence and anion exchange properties



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ABSTRACT

A cadmium coordination polymer with 'Kagomé dual' (**k_{gd}**) sheet structure, $\{[\text{Cd}(\text{tipa})_2] \cdot 2\text{NO}_3 \cdot 5\text{DMF}\}_n$ (**1**), has been synthesized by employing an elongated triangular rigid N-containing ligand tris(4-(1H-imidazol-yl)phenyl)amine (tipa) and structurally characterized by X-ray single-crystal diffraction. The Cd(II) ion is six coordinated with N atoms from tipa ligands, forming a CdN_6 octahedron geometry. The tridentate tipa ligand connects the Cd(II) ions into a 2D sheet. Topologically, if the triangular tipa ligand and the Cd(II) ions are regarded as 3- and 6-connected nodes respectively, the overall 2D sheet can be simplified to a (3,6)-connected **k_{gd}** net with a Schläfli symbol of $(4^3)2(4^6 \cdot 6^6 \cdot 8^3)$. Moreover, the photoluminescence at 298 and 77 K and anion exchange properties of **1** were also discussed.

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1. Introduction

The construction of metal–organic frameworks (MOFs) has attracted considerable interest in the past decade, due to their intriguing architectures and topologies as well as their potential applications in gas adsorption, catalysis, magnetism and luminescence [1–10]. It is well-known that applications rely intensively on the structures, so the synthesis of desirable structural and functional MOFs remains a vigorous research area. Generally, the architectures of the MOFs can be controlled by the deliberate design of the organic ligands and coordination geometries of the metals and influenced by many other factors such as the nature of the counterions, the molar ratio of the reagents, and the composition of the solvent media [11–15]. In these aspects, the structural features of the organic ligands, such as geometry, functional group, flexibility, and length, can influence structure types of the MOFs directly [16–18]. Among various organic ligands, the N-donor ligand as a good candidate for the construction of diverse MOFs has aroused a good deal of interests [19–27]. To date, many imidazole-based ligands such as 2,4,6-tri(1H-imidazol-1-yl)-1,3,5-triazine and 1,3,5-tris(1-imidazolyl)-benzene, have been widely used [28–32]. However, the MOFs constructed by tipa (tris(4-(1H-imidazol-yl)phenyl)amine), Scheme 1 are still in its infancy, although some intriguing examples have been reported [32–37]. An impressive example is a 54-fold interpenetrating 10^3 -**srs** Ag(I) network

constructed by tipa, it is a record in the interpenetrated MOFs reported to date [38]. On the other hand, various 2-periodic coordination networks, such as uninodal square lattice (**sql**) and hexagonal lattice (**hcb**) have been widely studied, but 2-periodic binodal 'kagome dual' (**k_{gd}**) sheet is less encountered in MOFs [39–43]. Recently, Blatov and co-workers performed comprehensive summary on the topological analysis of 2-periodic coordination networks in 10371 MOFs. Among them, **sql** and **hcb** nets are most common and second most common, respectively, as they are realized in two-thirds cases, however, **k_{gd}** net only occur 3.5% [44]. Based on above considerations, we herein report synthesis, structure, temperature-dependent photoluminescence and anion exchange properties of a **k_{gd}** net named $\{[\text{Cd}(\text{tipa})_2] \cdot 2\text{NO}_3 \cdot 5\text{DMF}\}_n$.

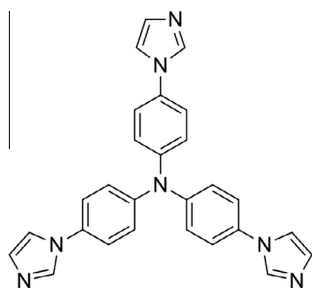
2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were measured on a Nicolet 330 FTIR Spectrometer at the range of $4000\text{--}400\text{ cm}^{-1}$. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu $K\alpha$ radiation. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer equipped with dewar flask with a Suprasil quartz cold finger.

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Scheme 1. Structure of tipa ligand.

2.2. Synthesis of $\{[Cd(tipa)_2] \cdot 2NO_3 \cdot 5DMF\}_n$ (**1**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (31 mg, 0.1 mmol) and tipa (44 mg, 0.1 mmol) was stirred in methanol–DMF mixed solvent (5 mL, v/v: 1/1). Then aqueous NH_3 solution (25%, 2 mL) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was allowed to evaporate slowly in darkness at room temperature for 4 days to give colorless crystals of **1** (Yield, 56%). The product was washed with a small volume of cold EtOH and diethyl ether. *Anal. Calc.* for $C_{69}H_{77}N_{21}CdO_{11}$: C, 55.66; H, 5.21; N, 19.76. Found: C, 55.52; H, 5.03; N, 19.69%. Selected IR peaks (cm^{-1}): 3417 (m), 3040 (w), 2915 (w), 2835 (w), 1598 (s), 1555 (m), 1445 (w), 1380 (s), 1302 (s), 1227 (m), 1072 (w), 991 (w), 815 (m), 627 (w).

3. X-ray crystallography

Single crystal of the complex **1** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** was collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation source ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Cell parameters were retrieved using smart software and refined with SAINT on all observed reflections [45]. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS [45]. In all cases, the highest possible space group was chosen. The structure was solved by direct methods using SHELXS-97 [46] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97 [47]. Atoms were located from iterative examination of difference F -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. The structure was examined using the Addsym subroutine of PLATON [48] to assure that no additional symmetry could be applied to the models. The crystallographic details of **1** are summarized in Table 1. Selected bond lengths and angles for **1** are collected in Table 2. There are large solvent accessible void volumes in the crystals of **1** which are occupied by highly disordered DMF molecules and NO_3^- . No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities. The SQUEEZE function of the program PLATON reveals a residual electron density of 781 electrons/cell in cell-remaining voids where the residual electron density was tentatively assigned to 164 molecules of the DMF solvent [$781/3 \approx 260$ for per formula of **1**; $262 = 40 (\text{DMF}) \times 5 + 32 (NO_3^-) \times 2$]. The number of DMF and NO_3^- was also proved by the elemental analysis and consideration of the electrical neutrality of whole molecule. A refinement using reflections modified by the SQUEEZE procedure behaved well, and the R_1 were significantly reduced from 0.18 to 0.068.

Table 1
Crystallographic data for **1**.

Complex 1	After SQUEEZE	Before SQUEEZE
Empirical formula	$C_{69}H_{77}CdN_{21}O_{11}$	$C_{69}H_{77}CdN_{21}O_{11}$
Formula weight	1488.92	1488.92
T (K)	173(2)	173(2)
Crystal system	trigonal	trigonal
Space group	R-3	R-3
a (\AA)	16.4460(12)	16.4460(12)
b (\AA)	16.4460(12)	16.4460(12)
c (\AA)	22.776(4)	22.776(4)
α ($^\circ$)	90.00	90.00
β ($^\circ$)	90.00	90.00
γ ($^\circ$)	120.00	120.00
V (\AA^3)	5334.9(11)	5334.9(11)
Z	3	3
ρ_{calc} (mg/mm^3)	1.390	1.028
μ (mm^{-1})	0.382	0.349
F(000)	2322.0	1626.0
Crystal size (mm)	$0.21 \times 0.15 \times 0.1$	$0.21 \times 0.15 \times 0.1$
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$)	Mo $K\alpha$ ($\lambda = 0.71073$)
2θ range for data collection	$3.38\text{--}49.98^\circ$	$3.38\text{--}49.98^\circ$
Index ranges	$-19 \leq h \leq 19$, $-19 \leq k \leq 12$, $-25 \leq l \leq 27$	$-19 \leq h \leq 19$, $-19 \leq k \leq 12$, $-25 \leq l \leq 27$
Reflections collected	8717	8717
Independent reflections	2090 ($R_{int} = 0.0357$, $R_{sigma} = 0.0345$)	2090 ($R_{int} = 0.0358$, $R_{sigma} = 0.0328$)
Data/restraints/parameters	2090/114/129	2090/108/129
Goodness-of-fit (GOF) on F^2	1.097	11.456
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0684$, $wR_2 = 0.2026$	$R_1 = 0.1802$, $wR_2 = 0.4196$
Final R indexes (all data)	$R_1 = 0.0850$, $wR_2 = 0.2164$	$R_1 = 0.2109$, $wR_2 = 0.4270$
Largest difference in peak/hole ($e \text{ \AA}^{-3}$)	0.69/−0.54	3.18/−1.11

Table 2
Selected bond distance (\AA) and angles ($^\circ$) for **1**.

Cd1–N1	2.355 (4)
N1 ⁱ –Cd1–N1 ⁱⁱ	93.24 (16)
N1 ⁱⁱ –Cd1–N1	180.0
N1 ⁱⁱ –Cd1–N1 ⁱⁱⁱ	86.76 (16)

Symmetry codes: (i) $y, -x + y, -z$; (ii) $-x, -y, -z$; (iii) $-x + y, -x, z$.

4. Results and discussion

4.1. Crystal structure of $\{[Cd(tipa)_2] \cdot 2NO_3 \cdot 5DMF\}_n$ (**1**)

The molecular structure of **1** determined from single crystal X-ray diffraction data is illustrated in Fig. 1a. X-ray single crystal diffraction analysis indicates that complex **1** crystallized in hexagonal crystal system with space group of R-3. The asymmetric unit contains one third tipa ligands and one Cd(II) ion as well as the disordered NO_3^- and free DMF solvent molecules. The Cd(II) ion not only sits on the inversion center but also is passed by one 3-fold axis, giving it a site occupancy factor (SOF) of 1/6. The 3-fold axis passes through the central N atom from tipa, showing a highly symmetrical geometry. As shown in Fig 1a, each Cd is coordinated by six N atoms from six different tipa ligands forming an octahedral geometry. The Cd–N bond length is uniformly 2.355(4) \AA , which is in the normal range observed in related Cd(II) MOFs. The dihedral angles between the N and the phenyl planes and phenyl and imidazolyl are 60.1° and 33.1° , respectively. The tipa ligands adopt μ^3 -coordinated fashion to joint the Cd(II) ions into a 2D sheet (Fig 1b). The

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