

A 3D Nitrate-bridging Heterometal-azido Inorganic Polymer Containing Cd₈ Cube: Synthesis, Structure, Topology and Fluorescence

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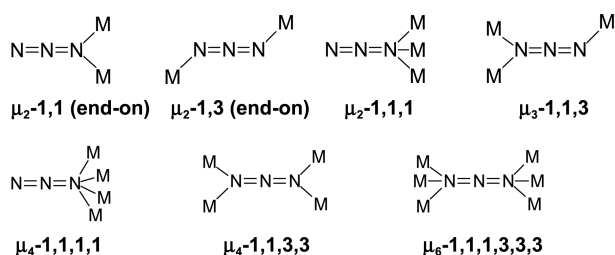
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In the past several decades, metal-azido system has been considered to be one of the most attractive systems in the design and synthesis of the magnetic materials at room temperature.¹ The bridging azide ligand is one of the most versatile ingredients for the creation of new materials. According to the valence bond theory, linear azide ligand has an important resonance structure, $N^{\ominus}=N^{\oplus}=N^{\ominus}$, which features the prominent bridging character from the outer nitrogen donors.² The possible bridging modes of the azide ligand lead its complexes to an important challenge in the field of crystal engineer (Scheme 1). The coordination modes of azide ligand have important effect on the properties. For example, the end-end (μ_2 -1,3- N_3 , EE) and end-on (μ_2 -1,1- N_3 , EO) fashions usually mediate antiferromagnetic and ferromagnetic interactions, respectively.³ Meantime, the structures and topologies of metal-azido complexes as versatile precursors attract much attention in the construction of bridged arrangements.⁴ The significance of the topological research not only realizes in the understanding of the multi-dimensional framework structures, but in the synthetic strategy of possible networks with desired properties.^{1b,5} In this work, we present the structural and topological analysis of a 3D nitrate-bridging heterometal-azido inorganic polymer, $[Cd_7Na_4(NO_3)_{12}(N_3)_6]$ (**1**), which was synthesized through solvothermal reaction and characterized with fluorescence.

Experimental

Materials and Physical Measurements. The reagents and solvents were used directly as supplied commercially without further purification except 3-amino-1,2,4-triazole (Atr, mp 158-159 °C, yield: 92.0%) synthesized as literature.⁶



Scheme 1. The reported coordination modes of azide ligand.

The IR spectrum was recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellet in the range 4000-400 cm^{-1} . Elemental analysis of **1** was carried out on a Vario EL III elemental analyzer. The solid-state fluorescent excitation and emission spectra were performed on a FluoroMax-3 spectrophotometer at room temperature with excitation and emission slits at 5.0 nm, increment 1.0 nm and integration time 0.1 s. Optical diffuse reflectance spectrum was measured at room temperature with a Lambda 900 UV-vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The sample was ground into fine powder and pressed onto a thin glass slide holder. The BaSO₄ plate was used as reference. The absorption spectrum was calculated from reflection spectra by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm , and R is the reflectance.

Synthesis of $[Cd_7Na_4(NO_3)_{12}(N_3)_6]$ (1**).** The reaction was carried out by heating $Cd(NO_3)_2 \cdot 4H_2O$ (0.0309 g, 0.1 mmol), NaN_3 (0.0131 g, 0.2 mmol), and 3-amino-1,2,4-triazole (0.0085 g, 0.1 mmol) with 5 mL DMF and 5 mL EtOH in a Teflon-lined stainless steel autoclave at 170 °C for five days, then cooled with a step of 2 °C/h to obtain suitable colorless block crystals of **1**. Elemental analysis (%) calcd. for $Cd_7N_{30}Na_4O_{36}$: N 22.41; found: N 22.53. IR (cm^{-1} , KBr): 3393.65 (m), 2975.22 (w), 2078.14 (s), 2036.56 (w), 1583.66 (s), 1432.92 (s), 1341.91 (m), 1290.18 (w), 1249.66 (w), 1201.49 (m), 1093.09 (w), 1049.13 (w), 1021.65 (w), 663.42 (m), 611.18 (w).

Structural Determination and Refinement. Data collection of **1** was performed on Rigaku Mercury CCD diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were collected by the narrow frame method at 293 K and corrected for Lorentz and polarization effects as well as for absorption by the ω scan technique and were reduced using CrystalClear program.⁷ The structure was solved by direct methods using SHELXTLTM package of crystallographic software⁸ and refined by full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of the structural determination and

Table 1. Crystal and experimental data of **1**

1	
Empirical formula	Cd ₇ N ₃₀ Na ₄ O ₃₆
Color and Habit	colorless block
Crystal Size (mm ³)	0.314 × 0.276 × 0.214
Crystal system	Cubic
Space group	<i>I</i> -43 <i>m</i>
<i>a</i> (Å)	13.807(1)
<i>V</i> (Å ³)	2631.8(4)
<i>Z</i>	2
Fw	1875.06
<i>D</i> _{calc} (Mgm ⁻³)	2.366
<i>μ</i> (mm ⁻¹)	2.924
<i>F</i> (000)	1756
<i>θ</i> (°)	2.95 to 28.15
Reflections measured	3293
Independent reflections	596 (<i>R</i> _{int} = 0.0315)
Observed Reflection [<i>I</i> > 2σ(<i>I</i>)]	477
Final <i>R</i> ₁ ^{<i>a</i>} , <i>wR</i> ₂ ^{<i>b</i>} [<i>I</i> > 2σ(<i>I</i>)]	0.0809, 0.2202
<i>R</i> ₁ ^{<i>a</i>} , <i>wR</i> ₂ ^{<i>b</i>} indices (all)	0.0921, 0.2339
<i>GOF</i> on <i>F</i> ²	1.052
(Δ/σ) _{max/min}	0.000, 0.000
Largest difference peak (e ⁻ Å ⁻³)	2.245, -1.230
<i>R</i> ₁ ^{<i>a</i>} = (Σ <i>F</i> _o - <i>F</i> _c / Σ <i>F</i> _o), <i>wR</i> ₂ ^{<i>b</i>} = [Σ(<i>w</i> (<i>F</i> _o ² - <i>F</i> _c ²) ²) / Σ(<i>w</i> <i>F</i> _o ²) ²] ^{1/2}	

refinement for the title compound is listed in Table 1 and the selected bond distances and angles are shown in Table 2.

Results and Discussion

Synthesis of [Cd₇Na₄(NO₃)₁₂(N₃)₆] (1). **1** was obtained from the solvothermal reaction of 3-amino-1,2,4-triazole, Cd(NO₃)₂ and NaN₃. However, the resulting inorganic framework didn't contain Atr. To confirm what happened, we did two contrast tests under the same conditions: one repeated the experimental process of **1**, whose resulting crystals were same as **1** with the same cell parameters; the other one without Atr ligand, which gave white powder. Therefore, the possible role of Atr ligand in the process may relate with its weak acidity (p*K*_a = 4.04).⁹ It is commonly found that Atr can be easily deprotonated with a changing p*K*_a under solvothermal reaction.¹⁰ Atr ligand as a reversed factor might decrease the reaction rate of the two inorganic components, and supply a suitable crystallization environment.

Structural Description of [Cd₇Na₄(NO₃)₁₂(N₃)₆] (1). The single crystal analysis reveals **1** is a 3D heterometal-azido inorganic polymer, in which its asymmetric unit comprises of one sixth Cd1, one eighth Cd2, one sixth Na1, a half NO₃⁻ and a quarter N₃⁻. The three-quarter positive charges on one sixth Cd1, one eighth Cd2, and one sixth Na1 were balanced by a half NO₃⁻ and a quarter N₃⁻. The coordination environments of Cd1 and Cd2 are similar, which both locate in CdN₃O₃ face octahedrons (Figure 1): three N atoms from three separated N₃⁻ ligand, and three O atoms from three NO₃⁻ anions respectively occupy the apexes of the triangular facets in the octahedron. The similar situation can be found

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

bond distances			
Cd1-O1A	2.358(4)	Cd2-Na1I	3.183(5)
Cd1-N3	2.422(1)	Na1-O1B	2.398(5)
Cd1-Na1	3.122(5)	Na1-O2D	2.346(5)
Cd1-Cd2	3.263(1)	N1-N2	1.122(9)
Cd2-N3D	2.440(1)	N2-N3	1.304(8)
Cd2-O2H	2.229(3)		
Angles			
O1A-Cd1-O1B	82.40(14)	O2H-Cd2-Cd1	133.92(2)
O1A-Cd1-N3	175.63(14)	O2A-Cd2-Cd1	78.24(8)
O1B-Cd1-N3	94.33(10)	N3D-Cd2-Cd1	47.61(3)
N3-Cd1-N3D	88.79(14)	N3G-Cd2-Cd1	107.61(10)
O1A-Cd1-Na1	49.52(9)	Na1I-Cd2-Cd1	125.70(2)
N3-Cd1-Na1	126.12(10)	O2I-Cd2-Cd1F	78.24(8)
O1A-Cd1-Cd2	75.31(9)	Cd1-Cd2-Cd1F	89.39(2)
O1B-Cd1-Cd2	133.08(2)	O2D-Na1-O2	74.61(19)
N3-Cd1-Cd2	109.05(10)	O2D-Na1-O1B	176.0(2)
N3D-Cd1-Cd2	48.07(3)	O2-Na1-O1B	102.27(9)
Na1-Cd1-Cd2	124.83(2)	O2-Na1-O1C	176.0(2)
O1A-Cd1-Cd2F	133.08(2)	O1B-Na1-O1C	80.7(2)
Cd2-Cd1-Cd2F	90.61(2)	O2-Na1-Cd1	135.59(12)
O2H-Cd2-O2A	79.29(13)	O1B-Na1-Cd1	48.41(13)
O2I-Cd2-N3D	174.15(13)	O2-Na1-Cd2A1	44.41(12)
O2A-Cd2-N3E	96.23(10)	O1A-Na1-Cd2A1	131.59(13)
N3D-Cd2-N3E	87.97(14)	Cd1-Na1-Cd2A1	180.00(9)
O2H-Cd2-Na1I	47.46(8)	Cd2A1-O2-Na1	88.13(14)
N3D-Cd2-Na1I	126.69(10)		

Symmetry code: *A* = *z*-1/2, -*x*+1/2, -*y*+3/2; *B* = *y*-1/2, *z*-1/2, *x*+1/2; *C* = -*x*+1/2, *y*-1/2, -*z*+3/2; *D* = *y*, -*z*+1, -*x*+1; *E* = -*z*+1, -*x*, *y*+1; *F* = *x*, -*y*, -*z*+2; *G* = -*x*, *y*, -*z*+2; *H* = -*y*+1/2, *z*-1/2, -*x*+3/2; *I* = -*x*+1/2, -*y*+1/2, *z*+1/2.

in the coordination geometry of Na1. With the Cd1...Cd2 (3.263(1) Å) separations (Table 2), Cd1 centers alternately connect Cd2 into a Cd₈ cube. N₃⁻ ligands adopt μ₄-1,1,1,1 mode asymmetrically binding Cd centers on each face of the Cd₈ cube with the Cd-N bond distance difference close to 0.018 Å (Cd1-N3 = 2.422(1) Å; Cd2-N3D = 2.440(1) Å). Each Cd1...Cd2 edge is bridged by a NO₃⁻ with μ₂-1,2

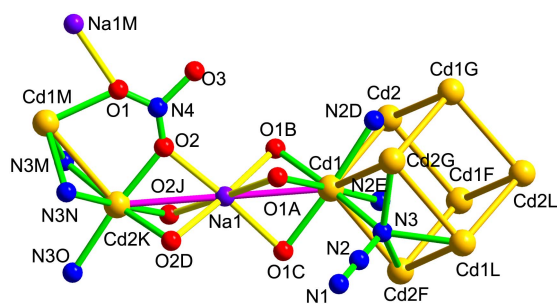


Figure 1. The coordination spheres of metal centers in **1**. Symmetry code: *A* = *z*-1/2, -*x*+1/2, -*y*+3/2; *B* = *y*-1/2, *z*-1/2, *x*+1/2; *C* = -*x*+1/2, *y*-1/2, -*z*+3/2; *D* = *y*, -*z*+1, -*x*+1; *E* = -*z*+1, -*x*, *y*+1; *F* = *x*, -*y*, -*z*; *G* = -*x*, *y*, -*z*; *J* = -*z*+1, *x*, -*y*+1; *K* = -*x*+1/2, -*y*+1/2, *z*-1/2; *L* = -*x*, -*y*, *z*; *M* = -*x*+1/2, *y*+1/2, -*z*+3/2; *N* = *z*-1/2, 1/2+*x*, 1/2+*y*; *O* = 1/2+*y*, *z*-1/2, 1/2+*x*.

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References

- (a) Mondal, K. C.; Mukherjee, P. S. *Inorg. Chem.* **2008**, *47*, 4215. (b) Abu-Youssef, M. A. M.; Escuer, A.; Mautner, F. A.; Öhrström, L. *Dalton Trans.* **2008**, 3553. (c) Stamatatos, T. C.; Christou, A. G.; Jones, C. M.; O'Callaghan, B. J.; Abboud, K. A.; O'Brien, T. A.; Christou, G. *J. Am. Chem. Soc.* **2007**, *129*, 9840. (d) Liu, C. M.; Song, Y.; Zhang, A. Q. *Inorg. Chem. Commun.* **2010**, *13*, 160. (e) Zhang, J. P.; Hu, B. W.; Yang, Q.; Zhang, X. F.; Hu, T. L.; Bu, X. H. *Dalton Trans.* **2010**, 39, 56.
- Mohamed, A. A. *Coord. Chem. Rev.* **2010**, *254*, 1918.
- (a) Zeng, Y. F.; Hu, X.; Liu, F. C.; Bu, X. H. *Chem. Soc. Rev.* **2009**, *38*, 469. (b) Wang, X. Y.; Wang, Z. M.; Gao, S. *Chem. Commun.* **2008**, 281. (c) Ribas, J.; Escuer, A.; Monfort, M.; Vicente, R.; Cortés, R.; Lezama, L.; Rojo, T. *Coord. Chem. Rev.* **1999**, 193.
- (a) Klapötke, T. M.; Krumm, B.; Scherr, M. *J. Am. Chem. Soc.* **2009**, *131*, 72. (b) Mautner, F. A.; Hanna, S.; Cortes, R.; Lezama, L.; Barandika, M. G.; Rojo, T. *Inorg. Chem.* **1999**, *38*, 4647.
- Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- Horning, E. C. *Organic Syntheses*; CV3, John Wiley & Sons: New York, 1955; p 95.
- Rigaku, CrystalClear 1.3.6, Software User's Guide for the Rigaku R-Axis, Mercury and Jupiter CCD Automated X-ray Imaging System. Rigaku Molecular Structure Corporation, 2002, Utah, USA.
- Siemens, SHELXTLTM Version 5 Reference Manual, Siemens Energy & Automation Inc. Madison, Wisconsin, 1994, USA.
- Chesnut, D. J.; Kusnetzow, A.; Birge, R.; Zubieta, J. *Inorg. Chem.* **1999**, *38*, 5484.
- Yuan, R. X.; Xiong, R. G.; Abrahams, B. F.; Lee, G. H.; Peng, S. M.; Che, C. M.; You, X. Z. *J. Chem. Soc., Dalton Trans.* **2001**, 2071.
- (a) Blatov, V. A. *Multipurpose Crystallochemical Analysis with the Program Package TOPOS*, *IUCr CompComm Newsletter*; **2006**, *7*, 4. (b) <http://www.topos.ssu.samara.ru>
- Wells, A. F. *Three-Dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977.
- For the interpretation of the three-letter net codes, please see: (a) the website of Reticular Chemistry Structure Resource (RCSR): <http://rcsr.anu.edu.au/>. (b) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *41*, 1782.
- Martin, D. P.; Staples, R. J.; LaDuca, R. L. *Inorg. Chem.* **2008**, *47*, 9754.
- Cunha-Silva, L.; Ananias, D.; Carlos, L. D.; Paz, F. A. A.; Rocha, J. *Z Kristallogr.* **2009**, *224*, 261.
- (a) Chen, S. S.; Bai, Z. S.; Fan, J.; Lv, G. C.; Su, Z.; Chen, M. S.; Sun, W. Y. *CrystEngComm.* **2010**, *12*, 3091. (b) Zeng, M. H.; Zhou, Y. L.; Wu, M. C.; Sun, H. L.; Du, M. *Inorg. Chem.* **2010**, *49*, 6336. (c) Long, D. L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2443. (d) Mahata, P.; Natarajan, S.; Panissod, P.; Drillon, M. *J. Am. Chem. Soc.* **2009**, *131*, 10140.
- (a) Wendlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966; (b) Kotuem, G. *Reflectance Spectroscopy*; Springer-Verlag: New York, 1969.
- (a) Izzet, G.; Ishow, E.; Delaire, J.; Afonso, C.; Tabet, J. C.; Proust, A. *Inorg. Chem.* **2009**, *48*, 11865. (b) Vogler, A.; Kunkely, H. *Inorg. Chim. Acta* **2006**, *359*, 4130. (c) Vogler, A.; Quett, C.; Kunkely, H. *Phys. Chem.* **1988**, *92*, 1486.