# **Electronic Supplementary Information**

for

# Insight into the molecular dynamics of guest cation confined in deformable azido

## coordination frameworks

Zi-Yi Du,\* Yu-Zhi Sun, Shao-Li Chen, Bo Huang, Yu-Jun Su, Ting-Ting Xu, Wei-Xiong Zhang,\* and Xiao-Ming Chen

### Index

I. Experimental details

II. Crystal structures of compound 2

III. Thermal analysis for compound 3

Table S1 Summary of crystal data and structural refinements for 3 at two different temperatures

Table S2 Selected bond lengths (Å) for 3 at two different temperatures

**Table S3** The geometry (Å,  $^{\circ}$ ) of hydrogen-bonds in **3** at two different temperatures

- **Fig. S1** Crystal structures of  $2\alpha$  at 298 K (a),  $2\beta$  at 350 K (b), and  $2\gamma$  at 360 K (c). The  $[(CH_3)_3NH]^+$  cation is disordered at  $2\beta$  and  $2\gamma$  phases, and the  $N_3^-$  anions is disordered at  $2\gamma$  phase. The figures are drawn based on the supplementary crystallographic data of reference 24.
- **Fig. S2** Symmetry changing in **2** during heating and cooling processes. The space-group diagrams are copied from *International Tables for Crystallography, Volume A* (5th Edition, T. Hahn *Ed.*, Dordrecht, Netherlands: Springer, 2002).
- Fig. S3 Variable-temperature PXRD patterns of 3
- Fig. S4 Heat capacity measurement for 2. The insets show the  $\Delta C_P$  and  $\Delta S$  related to the phase transition.

Fig. S5 TGA curve for 3

- **Fig. S6** MDSC measurement for **3** (8.9 mg) at a heating/cooling rate of 3 K min<sup>-1</sup>. The reversing and non-reversing part of total heat flow are translated along vertical ordinate for clarity.
- Fig. S7 Heat capacity measurement for **3**. The insets show the  $\Delta C_P$  and  $\Delta S$  related to the phase transition
- **Fig. S8** The Cd…Cd distances (Å) and Cd…Cd…Cd angles (°) within a  $[Cd(N_3)_3]^-$  cage unit of of  $3\alpha$  at 283 K (a) and  $3\beta$  at 348 K (b).

#### References

#### I. Experimental details

**Materials and methods.** All chemicals were obtained from commercial sources and used without further purification. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets from 4000 to 400 cm<sup>-1</sup>. Powder X-ray diffraction (PXRD) patterns (Cu-K $\alpha$ ) were collected on a Bruker Advance D8  $\theta$ –2 $\theta$  diffractometer. Thermogravimetric analysis (TGA) was carried out on a TA Q50 system at a heating rate of 5 °C/min under a nitrogen atmosphere. Modulated differential scanning calorimeter (MDSC) measurement was performed on a TA Q2000 instrument at a heating/cooling rate of 3 K/min with modulation period of 40 s and amplitude of 1 K. The measurements were carried out under a nitrogen atmosphere in aluminum crucibles. Heat capacity ( $C_p$ ) measurement was carried out on the Physical Property Measurement System (PPMS). The complex permittivities were measured under a nitrogen atmosphere, using a Tonghui TH2828A LCR meter in a Mercury iTC cryogenic environment controller of Oxford Instrument, and the sample was ground and pressed into tablet under a pressure of *ca*. 9 MPa.

**Syntheses of compound 3.** Cadmium nitrate tetrahydrate (0.5 mmol) was added into a hot aqueous solution (70  $^{\circ}$ C, 8 mL) of sodium azide (5.0 mmol) and trimethylammonium bromide (4.0 mmol), and the resultant clear solution was allowed to stand at room temperature. After one day later, colorless block-shaped crystals of **3** were deposited from the filtrates, in a ca. 81% yield based on Cd. The PXRD on bulky crystals indicated that the experiment pattern matches well with the simulated one (Fig. S3). IR data (KBr, cm<sup>-1</sup>): 3375(m), 3145(m), 3031(m), 2956(m), 2086(s), 2042(s), 1468(s), 1364(s), 1226(m), 1041(m), 973(s), 811(m), 643(m), 611(m).

Caution! Although our sample never exploded during handing, azide metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

**Single-crystal X-ray crystallography for compound 3.** The in-situ variable-temperature single-crystal X-ray diffraction intensities for **1** were collected on a Rigaku R-AXIS SPIDER IP diffractometer, with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The measurement temperatures were controlled by a dry nitrogen open flow using a Rigaku Gas Flow GN2 apparatus, and corrected by a thermal couple at the crystal position. Absorption corrections were applied by using *ABSCOR*.<sup>S1</sup> The structures were solved with direct methods and refined with a full-matrix

least-squares technique with the *SHELXTL* program package.<sup>52</sup> Anisotropic atomic displacement parameters were applied to all non-hydrogen atoms, whereas all the hydrogen atoms were generated geometrically. The C-bound H atoms of the disordered trimethylammonium cation are not included in the refinements. Crystallographic data and structural refinements for **3** under two different temperatures are summarized in Table S1. Selected bond lengths and the geometry of hydrogen-bonds are listed in Table S2 and S3, respectively. More details about the crystallographic data have been deposited as ESI.<sup>†</sup>

#### II. Crystal structures of compound 2

The crystal structures of **2** in its three phases can be roughly described as a distorted perovskite-like structure (Fig. S1). The Mn(II) ion is octahedrally coordinated by six nitrogen atoms from six azido ions, all of which act as end-to-end bridging ligands between two Mn(II) ions, thus leading to a three-dimensional cage-like framework. The common structural feature of **2** is the anionic  $[Mn(N_3)_3]^-$  cage enclosed by twelve Mn–N–N–Mn fragments, within which the guest  $[(CH_3)_3NH]^+$  cation resides.

The structural differences among  $2\alpha$ ,  $2\beta$  and  $2\gamma$  phases can mainly be attributed to the order-disorder of the  $[(CH_3)_3NH]^+$  guest accompanying with a deformation of the  $[Mn(N_3)_3]^$ framework. The number of the crystallographically independent  $N_3^-$  ligands in  $2\alpha$  is one and four halves, and it reduces to three halves in  $2\beta$  and one half in  $2\gamma$ . The four half-occupied N<sub>3</sub><sup>-</sup> ligands in  $2\alpha$  and the only half-occupied N<sub>3</sub><sup>-</sup> ligand in  $2\gamma$  each are related by an inversion center; however, one half-occupied N<sub>3</sub><sup>-</sup> ligand in **2** $\beta$  is related by 2-fold symmetry while the other two half-occupied N<sub>3</sub><sup>-</sup> ligands remain related by an inversion center. By and large, the [Mn(N<sub>3</sub>)<sub>3</sub>]<sup>-</sup> cage exhibits a high flexibility in the varieties of symmetry elements, and its volume expands slightly from  $2\alpha$  to  $2\beta$ phase, and further to **2y** phase. On the other hand, the number of crystallographically independent  $[(CH_3)_3NH]^+$  guests in  $2\alpha$  is one and it reduces to half in  $2\beta$ , and to one twelfth in  $2\gamma$ . As required by the imposed crystallographic symmetry, the disordered  $[(CH_3)_3NH]^+$  guests in **2** $\beta$  and **2** $\gamma$  are distributed over two and four positions, respectively, which are related by 2-fold symmetry. What's more, each  $[(CH_3)_3NH]^+$  guest itself in **2** $\gamma$  is simultaneously related by a 3-fold axis and three mirrors. For all three phases, hydrogen-bonding interactions can be found between the [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup> guest and the terminal azido N atoms of the host  $[Mn(N_3)_3]^-$  framework (see reference 24 and Fig. S1). Over all, the host-guest interaction accompanying with the synergic order-disorder transitions of the  $[Mn(N_3)_3]^-$  cage and the  $[(CH_3)_3NH]^+$  guest during the heating/cooling process results in these structural phase transitions.

#### III. Thermal analysis for compound 3

Compound **3** is stable when exposed to air, and the TGA analysis shows that it starts decomposing at 98 °C under a nitrogen atmosphere (Fig. S5). MDSC measurement was used to detect the possible phase transition and to confirm the existence of heat anomaly. As shown in Fig. S6, the total heat flows of MDSC show a pair of heat anomalies at about 339 K for heating run and 336 K for cooling run, revealing that **3** can undergo a reversible phase transition (vide infra). Furthermore, the abnormal signals in the total heat flows are almost contributed by the reversing part for both heating and cooling runs, whereas the non-reversing part related to the latent heat is silent, indicating a second-order nature for the phase transition.<sup>S3</sup> In addition, the structural phase transition was also confirmed by the heat capacity ( $C_p$ ) measurement on PPMS (Fig. S7). The corresponding  $\Delta S$  related to the phase transition does not show a discontinuity, but increased gradually with a small total entropy change of *ca*. **1**.7 J·mol<sup>-1</sup>·K<sup>-1</sup> from 300 K to 340 K, further confiming the second-order phase transition.

Empirical formula	C <sub>3</sub> H <sub>10</sub> N <sub>10</sub> Cd				
Formula weight	298.61				
Temperature (K)	283(2)	348(2)			
Phase type	3α	3β			
Space group	P2 <sub>1</sub> /c	C2/c			
<i>a</i> (Å)	8.6061(5)	8.6276(7)			
b (Å)	9.3656(5)	9.407(1)			
<i>c</i> (Å)	13.0160(8)	13.057(1)			
β/deg	105.803(2)	105.504(3)			
V/Å <sup>3</sup>	1009.5(1)	1021.1(2)			
Z	4	4			
$D_{calcd}$ /g cm <sup>-3</sup>	1.965	1.942			
µ/mm⁻¹	2.146	2.122			
GOF on F <sup>2</sup>	1.006	1.030			
$R_1, wR_2 [l > 2\sigma(l)]^a$	0.0324, 0.0797	0.0312, 0.0898			
$R_1$ , $wR_2$ (all data)	0.0389, 0.0850	0.0396, 0.1150			
$a_{P} = \sum \ E\  \  \sum \ E\  \  \sum \ E\  \  \  \  \  \  \  \  \  \ $					

Table S1 Summary of crystal data and structural refinements for 3 at two different temperatures

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, \ wR_{2} = \{\sum w[(F_{o})^{2} - (F_{c})^{2}]^{2} / \sum w[(F_{o})^{2}]^{2} \}^{\frac{1}{2}}$ 

Table S2 Selected bond lengths (	Å) for <b>3</b> at two different temperatures

283 K								
Cd1–N6	2.302(2)	Cd1–N8	2.310(2)	Cd1–N3A	2.346(3)			
Cd1–N1	2.359(1)	Cd1–N4	2.348(2)	Cd1-N10	2.346(2)			
348 К								
Cd1–N3	2.327(3)	Cd1–N5	2.328(3)	Cd1–N1	2.347(4)			

**Table S3** The geometry (Å, °) of hydrogen-bonds in **3** at two different temperatures

	D–H…A	D–H	Н…А	D…A	D–H…A
283 K	N(12)–H(12A)…N(1)#1	0.910(3)	2.404(3)	3.148(4)	139.0(2)
	N(12)–H(12A)…N(4)#1	0.910(3)	2.473(3)	3.163(4)	132.8(2)
348 K	N(7)–H(7A)…N(1)#2	0.90(1)	2.503(3)	3.24 (1)	139.8(7)
	N(7)–H(7A)…N(3)#2	0.90(1)	2.571(5)	3.26(1)	134.2(6)

Symmetry codes: #1 1 + *x*, *y*, *z*; #2 –1 + *x*, *y*, *z*.



**Fig. S1** Crystal structures of  $2\alpha$  at 298 K (a),  $2\beta$  at 350 K (b), and  $2\gamma$  at 360 K (c). The  $[(CH_3)_3NH]^+$  cation is disordered at  $2\beta$  and  $2\gamma$  phases, and the  $N_3^-$  anions is disordered at  $2\gamma$  phase. The figures are drawn based on the supplementary crystallographic data of reference 24.



**Fig. S2** Symmetry changing in **2** during heating and cooling processes. The space-group diagrams are copied from *International tables for crystallography, Volume A* (5th Edition, T. Hahn *Ed.*, Dordrecht, Netherlands: Springer, 2002).



Fig. S3 Variable-temperature PXRD patterns of 3.



Fig. S4 Heat capacity measurement for 2. The insets show the  $\Delta C_P$  and  $\Delta S$  related to the phase

transition.



**Fig. S6** MDSC measurement for **3** (8.9 mg) at a heating/cooling rate of 3 K min<sup>-1</sup>. The reversing and non-reversing part of total heat flow are translated along vertical ordinate for clarity.



**Fig. S7** Heat capacity measurement for **3**. The insets show the  $\Delta C_P$  and  $\Delta S$  related to the phase transition.



**Fig. S8** The Cd···Cd distances (Å) and Cd···Cd angles (°) within a  $[Cd(N_3)_3]^-$  cage unit of of  $3\alpha$  at 283 K (a) and  $3\beta$  at 348 K (b).

### References

S1 T. Higashi, ABSCOR, Rigaku Corporation, Tokyo, Japan, 1995.

- S2 G. M. Sheldrick, SHELX-96 Program for Crystal Structure Determination, 1996.
- S3 (a) P. S. Gill, S. R. Sauerbrunn and M. Reading, J. Therm. Anal., 1993, 40, 931-939; (b) M. Reading,
  D. Elliott and V. L. Hill, J. Therm. Anal., 1993, 40, 949-955; (c) Z. G. Wei and R. Sandström, Mater.
  Sci. Eng. A, 1999, 273-275, 352-356.