A Novel Three-dimensional Rhombic Network Self-assembled by the First Reported *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ Cations through Hydrogen Bonding Interactions

Baolong Li,* Baozong Li, Jianping Lang, and Yong Zhang
School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 21500, P. R. China

(Received February 3, 2003; CL-030098)

A novel complex $[Mn(4,4'\text{-azpy})_2(H_2O)_4](ClO_4)_2 \cdot 2(4,4'\text{-azpy}) \cdot 0.5(H_2O)$ was synthesized and characterized. It is composed of the first example *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cations. Three-dimensional rhombic network is formed through hydrogen bonding interactions between coordinated water and mono-coordinated 4,4′-azpy and noncoordinated 4,4′-azpy.

Pronounced interest in the crystal engineering of coordinated frameworks stems from, not only for their potential applications as zeolite-like material in molecular section, ion exchange, and catalysis, but also their intriguing variety of architectures and topologies.[1] Up to now, the most important driving forces in crystal engineering are coordination bonding and hydrogen bonding interactions.[2] Extended networks possessing higher dimensionalities can be obtained by assembly of coordination polymers (or complexes) with lower dimensionalies via hydrogen-bonding interaction.[2–5] However, normally the higher dimensional networks are constructed by one-dimensional chains via hydrogen-bonding interactions.[2,3] Only a few are formed by self-assembly of hydrated metal ion building blocks.[4,5] Up to now, some metal-ions $[M(L1)_2(H_2O)_4]^{2+}$ (L1 = monodentate)[4] and one-dimensional chains $[M(L2)(H_2O)_4]_n^{2n+}$ (L2 = bidentate)[3] compounds are reported, all of these compounds adopt *trans* geometry. We have been pursing the synthetic strategies for the preparation of non-interpenetrating open framework and new architectures and topologies, in which the rod-like rigid spacers such as 4,4′-azpy (4,4′-azpy = 4,4′-azobispyridine), 4,4′-bipy (4,4′-bipy = 4,4′-bipyridine) are chosen as building blocks.[2c,2d,2f,3c,3d] In the present work, we have synthesized a new complex $[Mn(4,4'\text{-azpy})_2(H_2O)_4](ClO_4)_2 \cdot 2(4,4'\text{-azpy}) \cdot 0.5(H_2O)$ (**1**)[6], novel three-dimensional rhombic network constructed by hydrogen-bonding interactions involving the first reported *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cations.

Compound **1** was synthesized by the reactions of a water solution (20 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.362 g, 1 mmol) and an ethanol solution (20 mL) of 4,4′-azpy (0.184 g, 1 mmol)). The red single crystals suitable for X-ray diffraction were obtained after about two weeks. Elemental analysis confirmed the organic content. (Found: C, 44.56; H, 3.75; N, 20.73 Calcd. for $C_{40}H_{41}Cl_2MnN_{16}O_{12.50}$: C, 44.83; H, 3.86; N, 20.92%). As these perchlorates are potential explosives safety precaution should be taken in handing these materials.

1 contains *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cations, uncoordinated 4,4′-azpy molecules, H_2O and disordered ClO_4^- anions. The Mn(II) is in a distorted octahedral geometry, being coordinated by four oxygen atoms from coordinated water molecules and two nitrogen atoms from two monodentate 4,4′-azpy (Figure 1). The bond angle N(1)–Mn(1)–N(5) is 93.99(6)°. This geometry is quite different from the geometry found in metal ions $[M(L1)_2(H_2O)_4]^{2+}$ (L1 = monodentate)[4] and one-dimensional chains $[M(L2)(H_2O)_4]_n^{2n+}$ (L2 = bidentate),[3] in which two L1 (or L2) ligands adopt *trans* geometry. The *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation is the first example of *cis* geometry.

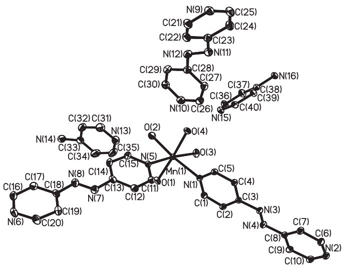

Figure 1. The local coordination of *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation. Selected distances (Å) and angles (°): Mn(1)–O(1), 2.1698(13); Mn(1)–O(2), 2.1475(19); Mn(1)–O(3), 2.2059(15); Mn(1)–O(4), 2.1417(14); Mn(1)–N(1), 2.2937(19); Mn(1)–N(5), 2.3023(15); O(1)–Mn(1)–O(2), 89.32(7); O(1)–Mn(1)–O(3), 90.83(6); O(1)–Mn(1)–O(4), 175.63(5); O(2)–Mn(1)–O(3), 90.95(7); O(3)–Mn(1)–O(4), 88.62(6); N(1)–Mn(1)–O(1), 93.50(6); N(5)–Mn(1)–O(1), 85.96(5); N(1)–Mn(1)–N(5), 93.99(6).

Each *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation acts as a hydrogen-bonding acceptor, forming two equivalent N···H–O hydrogen bondings between the two terminal nitrogen atoms [N(6) and N(2)] of two 4,4′-azpy ligands and hydrogen atoms from two coordinated water molecules [O(1) and O(3)] per Mn center on two neighboring *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cations [N(6)···O(1) $(-x+1,\ -y+2,\ -z)$, 2.833 Å; O(3)···N(2) $(-x-1,\ -y+1,\ -z)$, 2.842 Å]. The same *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation acts also as a hydrogen-bonding donor, forming two additional equivalent O–H···N hydrogen bonding per Mn center with two terminal nitrogen atoms of two 4,4′-azpy ligands from two neighboring *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cations. The structure, therefore, features a complementary binary hydrogen-bonding system. Through hydrogen-bonding interactions inter *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cations, one-dimensional double-stranded chain structure is formed (Figure 2). The pyridyl rings of 4,4′-azpy ligands stack with face to face separation ca. 3.3–3.6 Å in chain, indicating significant π-π interactions.[7] These comple-

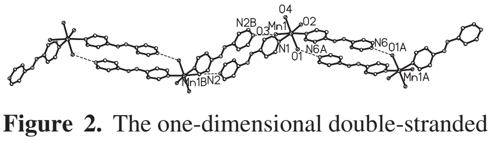

Figure 2. The one-dimensional double-stranded chain structure along the *c* direction.

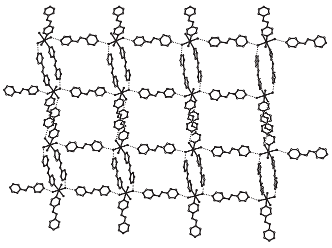

Figure 3. Viewing the two-dimensional rhombic network from the *a* direction.

mentary binary hydrogen-bonding systems are few. Two examples reported previously are $[Cd_2(H_2O)_4(4,4'\text{-bipy})_5(NO_3)_2](PF_6)_2$[2e] and $\{[Co_2(4,4'\text{-azpy})_5(H_2O)_6](ClO_4)_4 \cdot 10(H_2O) \cdot 4(4,4'\text{-azpy})$.[2f] But an obvious difference is that there are four N···H–O hydrogen bondings between coordinated water molecules and four monocoordinated 4,4′-bipy or 4,4′-azpy of "H-shaped" dimeric cations. But *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation only has two monocoordinated 4,4′-azpy, so two N···H–O hydrogen bondings are formed in *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation in **1**.

Interchain connections are formed through O–H···N hydrogen bonding involving coordinated water molecules and uncoordinated 4,4′-azpy ligands. The hydrogen bonding can be formulated as $Mn–H_2O \cdots 4,4'\text{-azpy} \cdots H_2O–Mn$. One-dimensional chains are linked through hydrogen-bonding interactions between coordination water [O(1) and O(4)] and uncoordinated 4,4′-azpy ligand [O(1)···N(9), $(x-1,\ y+1,\ z)$, 2.788 Å; O(4)···N(10), 2.792 Å], to form a two-dimensional rhombic network with dimensions 14.8 Å × 17.8 Å (Figure 3). Hydrogen-bonding interactions between coordinated water and uncoordinated 4,4′-azpy ligand [O(2)···N(13), 2.730 Å; O(4)···N(15), 2.749 Å] further link the two-dimensional networks to construct a three-dimensional rhombic network with channel 12.2 Å × 15.2 Å (Figure 4). The disordered ClO_4^- anions and water molecules lie in the channel and form hydrogen bonding with coordinated water. These three-dimensional hydrogen-bonding network are rare. One example reported previously is $[Mn(H_2O)_4(4,4'\text{-bipy})_2](ClO_4)_2 \cdot 4(4,4'\text{-bipy})$[5b] when 4,4′-bipy instead of 4,4′-azpy was used. But the obvious differences are *cis* geometry of *cis*-$[Mn(4,4'\text{-azpy})_2(H_2O)_4]^{2+}$ cation and three-dimensional rhombic network in the title complex, and *trans* geometry of *trans*-$[Mn(4,4'\text{-bipy})_2(H_2O)_4]^{2+}$ cation and three-dimensional trangular network in the latter. Another example is $[Mn(H_2O)_4(\mu\text{-bpe})](ClO_4)_2 \cdot 4(\text{bpe}) \cdot 2H_2O$.[3e] Which also is of *trans* geometry and forms an infinite chain with the bridged bpe ligand. The four other bpe molecules are hydrogen bonded to the aqua ligands and form an extensive interpenetrating three-dimensional network. **1** is a successful example for regulating architectures and topologies by regulating the lengths of ligands through hydrogen bonding.

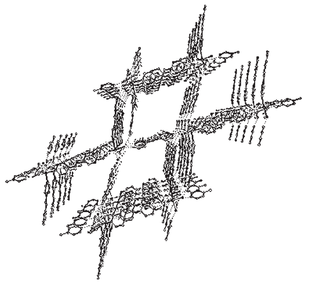

Figure 4. Viewing the three-dimensional rhombic network from the *b* direction.

Thermal analysis shows that water was lost in a continuous fashion (Obsd., 7.4%; Calcd., 7.6%) in 80–122 °C. Uncoordinated 4,4′-azpy ligand was lost (Obsd., 32.5%; Calcd., 34.3%) in 122–264°C. Then coordinated 4,4′-azpy ligand was lost and explosion happened at 324 °C.

We thank Funds of the Key Laboratory of Organic Synthesis Chemistry, the Education Committee of Jiansu Province.

References and Notes

1 a) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, and J. Liu, in "Supramolecular Architecture," American Chemical Society, Washington, D.C. (1992), p 526. b) M. Fujita, Y. J. Kwon, S. Washiza, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994). c) P. J. Hagrman, D. Hagrman, and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, **38**, 2638 (1999). d) M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, and K. Seki, *Angew. Chem., Int. Ed. Engl.*, **38**, 140 (1999). e) L.-M. Zheng, X. Fang, K.-H. Lii, H.-H. Song, X.-Q. Xin, H.-K. Fun, K. Chinnakali, and I. A. Razak, *J. Chem. Soc., Dalton Trans.*, **1999**, 2311.

2 a) A. J. Blake, S. J. Hill, P. Hubberstey, and W.-S. Li, *J. Chem. Soc., Dalton Trans.*, **1997**, 913. b) S. Noro, M. Kondo, S. Kitagawa, T. Ishii, and H. Matsuzaka, *Chem. Lett.*, **1999**, 727. c) B.-L. Li, H.-B. Liu, J.-T. Chen, Y. Xu, and Z. Xu, *Chem. Lett.*, **2001**, 902. d) B.-L. Li, H.-B. Liu, Y. Xu, G. Yin, J.-T. Chen, and Z. Xu, *Chem. Lett.*, **2001**, 214. e) Y.-B. Dong, M. D. Smith, R. C. Layland, and H.-C. zur M. Loye, *J. Chem. Soc., Dalton Trans.*, **2000**, 775. f) B.-L. Li, H.-B. Liu, Y. Xu, J.-T. Chen, H.-Q. Wang, and Z. Xu, *J. Mol. Struct.*, **597**, 21 (2001).

3 a) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Chem. Soc., Dalton Trans.*, **1997**, 1801. b) B.-Q. Ma, S. Gao, H.-L. Sun, and G.-X. Xu, *J. Chem. Soc., Dalton Trans.*, **2001**, 130. c) B.-L. Li, Y. Xu, Y. Dong, J.-T. Chen, and Z. Xu, *J. Chem. Crystallogr.*, **31**, 357 (2001). d) B.-L. Li, Z.-B. Cao, S.-W. Wang, Z. Xu, and K.-B. Yu, *Chin. J. Struct. Chem.*, **21**, 292 (2002). e) F. D. Rochon, M. Andruh, and R. Melanson, *Can. J. Chem.*, **76**, 1564 (1998).

4 a) L. J. Barbour, L. R. MacGillivary, and J. L. Atwood, *Supramol. Chem.*, **7**, 167 (1996). b) G. R. Lewis and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, **1998**, 1873. c) C. V. K. Sharma and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, **1996**, 2655.

5 a) G. Jovanovski, P. Naumov, O. Grupce, and B. Kaitner, *Eur. J. Solid State Inorg. Chem.*, **35**, 579 (1998). b) M.-L. Tong, H. K. Lee, X.-M. Chen, R.-B. Huang, and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, **1999**, 3657. c) R. K. Barman and B. K. Das, *CrystEngComun*, **4**, 80 (2002).

6 Crystal data for **1**: $C_{40}H_{41}MnN_{16}O_{12.5}$, triclinic, space group $P\bar{1}$, $a = 10.792(2)$, $b = 14.421(3)$, $c = 18.014(4)$ Å, $\alpha = 65.79(3)$, $\beta = 71.46(3)$, $\gamma = 88.94(3)°$, $V = 2403.9(8)$ Å^3, $Z = 2$, $M_r = 1071.73$, $D_{\text{calcd}} = 1.481\ \text{g cm}^{-1}$, $\lambda = 0.71073$ Å. The data collection was performed at 193.2 K on a Rigaku CCD. The structure was solved by direct methods and refined by full-matrix least-squares analysis (SHELXTL97), giving a final $R1$ value of 0.0466 for 726 parameters and 10083 independent reflections [$I_{\text{obs}} > 2\sigma(I)$] and $wR2$ of 0.1243.

7 a) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, **112**, 5525 (1990). b) I. Dance and M. Scudder, *J. Chem. Soc., Chem. Commun.*, **1995**, 1039.