Synthesis and Structure of a 3D Cobalt(II) Coordination Polymer with 1,4-Bis(imidazole-1-ylmethyl)benzene

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Treatment of 1,4-bis(imidazole-1-ylmethyl)benzene (bix) with $Co(OAc)_2$ in organic/inorganic solution gives the complex $[Co(bix)_3]\cdot 2OH\cdot CH_3OH\cdot 3H_2O$ (**1**), which forms an open three-dimensional framework. The specific channels in **1** occupied by solvent molecules, indicate that **1** might be an attractive functional microporous solid materials.

Coordination polymer frameworks have been much studied in recent years.[1] A major reason for this interest is that these polymers have shown some potential applications such as selective guest absorption, gas storage, ion exchange, nanoporous materials and heterogeneous catalysis.[2] Many such crystalline coordination polymers with one-, two- and three-dimensional structures are already known for polyamines coordinated to a variety of transition metals.[2–5] In general, the multiple coordination sites of the longer chain ligands may form structures of higher dimensions with various sizes and shapes of cavities or channels in the assembly reaction of the bridging ligand with metal ions. In this paper, we explore the use of conformationally flexible bridging ligands to generate 3D large-ring frameworks which have the ability to 'breathe', and thereby generate more adaptable arrays.

During the last few years, a particularly promising class of ligand in which two imidazoles units are interconnected by chains or groups of different types have been explored to form some open frameworks. However, only very few complexes with imidazole ligands have been structurally characterized because of difficulties involving modification of the imidazole moiety and its the extremely low solubility.[6–10] 1,4-bis(imidazole-1-ylmethyl)benzene, which has a longer linker, is a good candidate for formation of open structures or interpenetrated lattices. To the best of our knowledge, only three examples of polymers of 1,4-bis(imidazole-1-ylmethyl)benzene have been reported: two-dimensional polyrotaxanes, $[Zn(bix)_2(NO_3)_2]\cdot 4.5H_2O$[11] and $[Ag_2(bix)_3(NO_3)]$,[12] and a quasi-two-dimensional polymer $[Mn(bix)_3(NO_2)_2\cdot 4H_2O]$.[13] In the two formers, Zn^{II} and Ag^{I} have the d^{10} configuration. The cobalt complex with bix (bix=1,4-bis(imidazole-1-ylmethyl)benzene) ligand has never been isolated and characterized. We report here a coordination polymeric compound with bix ligand having an open 3D framework structure, $[Co(bix)_3]\cdot 2OH\cdot CH_3OH\cdot 3H_2O$,[14] which is the first cobalt polymer structurally characterized with long chain imidazole ligands. This organic molecule can be expected to exhibit the characteristic bidentate-bridging through incorporation of the two imidazole nitrogen donor functions. The large channels in the title complex were defined by the bridging bix. It is interesting to note that guest molecules, which are OH^- anions, methanol and water molecules, were found inside these channels.

Bix was prepared as described in the reference[12] by the use of α,α'-dibromo-*p*-xylene instead of α,α'-dichloro-*p*-xylene in the synthesis processing.

The reaction of bix with $Co(OAc)_2$ in organic/inorganic solution yields crystal suitable for X-ray diffraction.[14] The crystallographic analyses[15] reveal that the complex is composed of noninteracting OH^- anions and a $[Co(bix)_3]^{2+}$ macrocation. The Co atoms are located on an inversion center with an octahedral geometry (Figure 1). Selected bond lengths and angles are listed in Figure 1. Each cobalt atom is coordinated by six imidazole nitrogen atoms from six individual bix ligands with Co–N distances of 2.135(2), 2.176(3) and 2.210(2) Å, respectively. The N(1)–Co–N(1b), N(3)–Co–N(3b) and N(5)–Co–N(5b) angles are 180.0°. Other N–Co–N angles around Co centers range from 87.42(10)° to 92.58(10)°. Each bix ligand

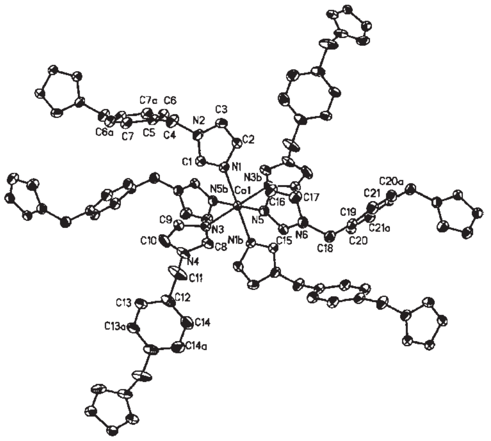

Figure 1. ORTEP view of the $[Co(bix)_3]^{2+}$ unit with thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Co(1)–N(3) 2.135(2), Co–N(1b) 2.210(2), Co(1)–N(3b) 2.135(2), Co(1)–N(5) 2.176(3), Co(1)–N(1) 2.210(2), Co(1)–N(5b) 2.176(3), N(3)–Co(1)–N(3b) 180.0, N(3b)–Co(1)–N(1b) 91.66(10), N(5)–Co(1)–N(5b) 180.0, N(5)–Co(1)–N(1b) 90.44(10), N(1)–Co(1)–N(1b) 180.0, N(5b)–Co(1)–N(1b) 89.56(10), N(3)–Co(1)–N(5) 92.58(10), N(3)–Co(1)–N(1) 91.66(10), N(3b)–Co(1)–N(5) 87.42(10), N(3b)–Co(1)–N(1) 88.34(10), N(3)–Co(1)–N(5b) 87.42(10), N(5)–Co(1)–N(1) 89.56(10), N(3b)–Co(1)–N(5b) 92.58(10), N(5b)–Co(1)–N(1) 90.44(10), N(3)–Co(1)–N(1b) 88.34(10).

adopts a *trans-gauche* conformation in which the three-rings (two-imidazole rings and one benzene) are not in a plane. In each bridging bix, the dihedral angle between the plane of the coordinated imidazole and the benzene plane is 89.4°. The adjacent Co^{II} ions are linked by bridging bix ligands, building up polymers to an open three-dimensional network with some channels, which are filled guest OH^- anions, methanol and water molecules (Figure 2). The Co···Co longer separation across the bridging bix is 13.558 Å, which is similar to the corresponding metal-metal separation in the complexs $[Zn(bix)_2(NO_3)_2]\cdot 4.5H_2O$ (15.037(2) Å),[11] $[Ag_2(bix)_3(NO_3)_2]$ (14.626(2) Å),[12] $[Mn(bix)_3(NO_2)_2\cdot 4H_2O]$ (12.659 Å).[13] The effective dimension of the diamond-shaped cavity in **1** is approximately 8.43 × 8.43 Å. Solvent molecules are located inside these channels. The specific channels indicate that the complex **1** might be an attractive functional microporous solid materials.

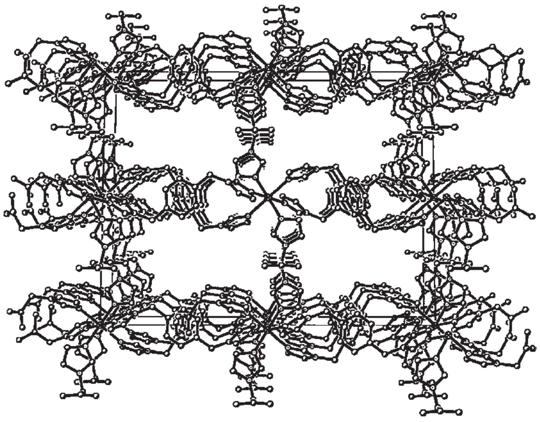

Figure 2. Side view of the packing of complex **1**, showing the three-dimensional framework and the channels.

Interesting conclusions can be extracted when examining the structures of bix with Zn^{2+}, Ag^+, Co^{2+} and Mn^{2+} cations. It is noteworthy that only Zn^{2+} and Ag^+ which have the d^{10} configuration are able to form polyrotaxanes complexes with bix ligand and only when the counterion is nitrate. In the comparison with the complexes Co-bix and Mn-bix, the different coordination modes of bix groups with metal cations lead to different final structures. In the former, Co^{2+} is coordinated with six bridging bix groups to form a 3D network. In the latter, however, Mn^{2+} cation is coordinated with two terminal bix groups, two bridging bix groups and two coordinating waters. The bridging bix groups link the metal cations to form a chain, and the two NO_2^- ions, two coordination waters and the two crystal waters form hydrogen bonds to produce a two-dimensional network. We can then conclude that both the nature of the metal and the counterion are fundamental in determining the final structure.

The magnetic susceptibilities (χ_M) of **1** were measured in the temperature range 2–300 K. The $\chi_M T$ value is equal to 5.05 $cm^3 mol^{-1} K$ at room temperature, which is greater than the spin-only value of 4.37 $cm^3 mol^{-1} K$ for Co^{II} ($S = 5/2$). The $\chi_M T$ value exhibits continuous decrease upon cooling to 1.52 $cm^3 mol^{-1} K$ at 2 K. This result supports the presence of a weak antiferromagnetic interactions in complex **1**.

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References and Notes

1 a) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990). b) "Comprehensive Supramolecular Chemistry," ed. by J. L. Atwood, J. E. D. Davies, D. D. MacNicol, and F. Vogtle, Pergamon Press, New York (1996), Vols. 6 and 7. c) S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, **71**, 1739 (1998). d) M. J. Zaworotko, *Chem. Soc. Rev.*, **23**, 284 (1994). e) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, **1994**, 2755. f) D. M. L. Goodgame, S. Menzer, A. M. Smith, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, **1997**, 3213. g) M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, and M. Schroder, *Angew. Chem., Int. Ed. Engl.*, **36**, 2327 (1997).

2 a) O. M. Yaghi, C. E. Davies, G. Li, and H. Li, *J. Am. Chem. Soc.*, **119**, 2861 (1997). b) O. M. Yaghi, G. Li, and H. Li, *Nature*, **378**, 703 (1995). c) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, **117**, 10401 (1995). d) S. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, *Science*, **283**, 1148 (1999). f) M. Fujita, Y. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994).

3 a) H. K. Fun, S. S. Raj, R. G. Xiong, J.-L. Zuo, Z. Yu, and X.-Z. You, *J. Chem. Soc., Dalton Trans.*, **1999**, 1915. b) J. Cano, G. D. Munno, J. L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve, and A. Caneshi, *J. Chem. Soc., Dalton Trans.*, **1997**, 1915.

4 a) H. Li, M. Eddaoudi, M. O'keeffe, and O. M. Yaghi, *Nature*, **402**, 276 (1999). b) H. Li, C. E. Davis, T. L. Groy, D. G. Kelley, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 2186 (1998). c) H. Li, M. Eddaoudi, T. L. Groy, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 8571 (1998).

5 a) L. Deakin, A. M. Arif, and J. S. Miller, *Inorg. Chem.*, **38**, 5072 (1999). b) C. S. Hong, S. K. Son, Y. S. Lee, M. J. Jun, and Y. Do, *Inorg. Chem.*, **38**, 5602 (1999). c) R. H. Groeneman, L. R. MacGillivray, and J. L. Atwood, *Inorg. Chem.*, **38**, 208 (1999).

6 L. P. Wu, Y. Yamagiwa, T. Kuroda-Sowa, T. Kamikawa, and M. Munakata, *Inorg. Chim. Acta*, **256**, 155 (1997).

7 M. Sato, S. Nagae, K. Ohmae, J. Nakaya, K. Miki, and N. Kasai, *J. Chem. Soc., Dalton Trans.*, **1986**, 1949.

8 B. K. S. Lundberg, *Acta Chem. Scand.*, **26**, 3902 (1972).

9 P. C. M. Duncan, D. M. L. Goodgame, S. Menzer, and D. J. Williams, *Chem. Commun.*, **1996**, 2127.

10 H. Y. Shen, D. Z. Liao, Z. H. Jiang, S. P. Yan, and G. L. Wang, *Synth. React. Inorg. Met.-Org. Chem.*, **28**, 1331 (1999).

11 B. F. Hoskins, R. Robson, and D. Slizys, *Angew. Chem., Int. Ed. Engl.*, **36**, 2336 (1997).

12 B. F. Hoskins, R. Robson, and D. Slizys, *J. Am. Chem. Soc.*, **119**, 2952 (1997).

13 H. Y. Shen, D. Z. Liao, Z. H. Jiang, S. P. Yan, G. L. Wang, X. K. Yao, and H. G. Wang, *Acta Chem. Scand.*, **53**, 387 (1999).

14 Synthesis complex **1**: Bix (0.073 g, 0.3 mmol) in methanol (10 ml) was added dropwise to a stirred aqueous solution (5 ml) of $Co(OAc)_2\cdot 4H_2O$ (0.025 g, 0.1 mmol); then $NaNO_2$ (0.014 g, 0.2 mmol) dissolved in water (5 ml) was added slowly. The resulting mixture was refluxed for 3 hours. Cooled to room temperature, some red precipitate was formed. Filtered off the solid, the filtrate was left to stand at room temperature. A month later, red crystals suitable for X-ray diffraction were obtained (yield 61%). The crystals of **1** have a good stability after the crystals are removed from mother solution. IR for **1** (KBr, cm^{-1}): 3479(m), 3123(m), 1642(m), 1518(s), 1444(m), 1426(m), 1395(m), 1351(m), 1285(m), 1230(s), 1102(s), 1090(s), 1034(m), 935(m), 828(m), 747(m), 726(m), 718(m), 673(m), 666(m). UV-vis-NIR (in solid state): The bands at 240 nm, 285 nm and 360 nm may be attributed to the π–π^* transitions of bix, while the band at 560 nm may be attributed to the d–d transitions of Co(II) ions. Anal. Calcd. for **1** (%): C, 58.96; H, 5.98; N, 19.19. Found: C, 58.65, H, 5.74, N, 19.35.

15 Crystal data for **1**: $C_{21.50}H_{27}Co_{0.50}N_6O_3$, fw = 446.96, monoclinic, space group $C2/c$, $a = 9.334(2)$, $b = 25.458(5)$, $c = 19.822(4)$ Å, $\beta = 99.86(3)°$, $V = 4640.6(16)$ Å^3, $Z = 8$, $D_{calcd} = 1.279$ Mg m^{-3}, Crystal size 0.50× 0.30 × 0.20 mm^3, λ(Mo Kα) = 0.71073 Å, $T = 293(2)$ K. Absorption coefficient is 0.428 mm^{-1}, 2.35°, $< 2\theta <$ 27.48°, $R_1[I > 2\alpha(I)] = 0.0602$, $_wR$(all data) = 0.1716, $GOF = 1.015$. Deposited in No. CCDC-188219. The crystal structure was solved by direct methods and refined on F^2 using full matrix least squares with SHELXL-97 program package.