$\{[In_3(pzdc)_6]^{3-}\}_\infty$: A Metal–Organic Framework of Distorted NbO-like Net (pzdc = Pyrazine-2,3-dicarboxylato)

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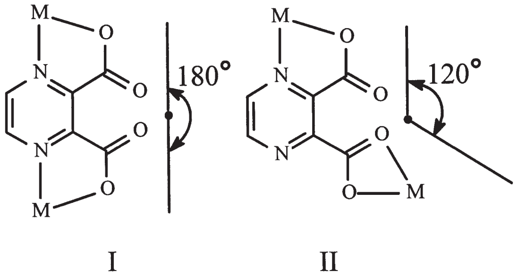
(Received May 27, 2003; CL-030469)

Molecular spontaneous assembly of In(III) and bidentate ditopic ligand (pzdc) gives a novel compound with four-connected 3D framework which demonstrates a NbO-like net.

Polymeric coordination network is a topical area of current research.[1] Design and construction of novel coordination frameworks are of great interest because of their potential application[2] such as molecular inclusion, electrochemical, magnetic, and photophysical properties. In order to create such novel materials, rational structural designs[3] and logical synthetic strategies are often the key issues. It is a common knowledge that for linkers of a given length the frameworks built of tetrahedral nodes generate much bigger cavities and access openings than those based on octahedral nodes. Consequently we are interested in the 4-connected networks. As we know, nets of zeolites, quarts, diamond, lonsdalite, and NbO are made of 3D frameworks based on 4-connected topologies.[4] Among them the diamondoid nets appear more frequently in the metal–organic networks.[5] However, the nets with quarts-,[6] zeolite-like[7] or NbO[8] topologies are not so commonly found in the coordination polymers. Here we report a 4-connected distorted NbO-net, which is generated by a strategy of reacting 8-coordinate metals with bidentate ditopic ligand. For the 8-coordinate metals, we initially chose lanthanides and for the bidentate ditopic ligand we chose pyrazine-2,3-dicarboxylato (pzdc). As linker of the 8-coordinate metals, pzdc shows two different possible coordinate modes (see mode I and II), in which the ligand bridges adjacent metals together and to each metal it (Scheme 1) provides two coordinate sites. Thus, an 8-coordinate metal center is connected by the four ligands and a four-connected net of distorted square or tetrahedral nodes could be, therefore, generated. There have been many reports[9] on the transition metal complexes of pzdc. Although some of them do exhibit three-dimensional frameworks; however, they are neither the open frameworks nor the 4-connected nets.

Our experiments demonstrate that reaction of lanthanides with pzdc do not form the expected ordered crystalline arrangements and only amorphous solids with indefinite compositions were obtained. However, the use of indium (III) has led to production of colorless rhombus crystals $\{[In(H_2O)_6][In_3(Pzdc)_6]\cdot 15(H_2O)\}_\infty$ (**1**). They were prepared by mixing solutions of pzdc (0.6-mmol pzdc in 20 mL H_2O) and $InCl_3$ (0.4 mmol in 20 mL H_2O) at 10 °C and standing the reaction mixture at RT for ca. a week. X-ray single crystal studies[10] reveal that the indiums (III) are 8-coordinated in the framework of **1** and that a negatively charged three-dimensional framework with D_{3d} symmetry includs cations of hexaaquaindium (III) (Figue 1). In the framework, each indium(III) is coordinated by two nitrogen atoms of a pair pzdcs and six oxygen atoms of four carboxylates of four pzdcs (Figure 2) which are fully deprotonated. The adjacent indium atoms in the framework separated by about 8 Å are linked by the pzdcs to the chair-like 6-rings, eight of which build up of a distorted 6^8-cage unit (Figures 3a and 3b) of NbO-like net. Because of the distortion of the 4-connected nods that deviate far from the tetrahedral or square-planar configurations, the crystal symmetry $Im\bar{3}m$ of NbO net is declined to $R\bar{3}c$ and affords the structure with relatively large hexagonal channels of effective cross-section of ca. 6.5 × 6.5 Å in the [0 0 1] direction and relatively small elliptical channels of ca. 5.3 × 4.2 Å in the [1 2 0], [2 1 0] and [1 $\bar{1}$ 0] directions. The water-clusters accommodated in the cage units are hexaaquaindium(III) complexes associated with another 15 water molecules via hydrogen bonding. Furthermore, they are hydrogen-bonded to the metal-organic framework via oxygen atoms of the pzdcs carboxylates.



Scheme 1.

Thermal analysis (TGA)[11] of the compound **1** shows ca.

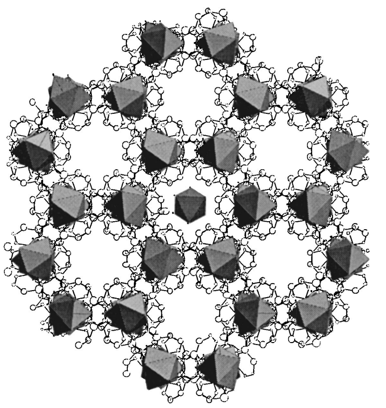


Figure 1. Polyhedral packing diagram of **1** to show the hexagonal channels running in [0 0 1]. The dodecahedra: indium in the framework, octahedra: $[In(H_2O)_6]^{3+}$ (For clarity only one of the channels is plotted with $[In(H_2O)_6]^{3+}$ and the lattice waters are omitted).

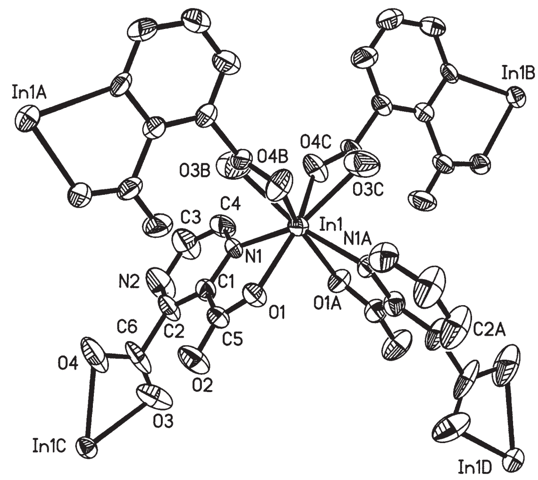


Figure 2. The indium(III) coordination geometry in the metal-organic framework of **1**. Thermal ellipsoids are at 50% probability. Selected bond lengths [Å] and angles [°]: In1–N1 2.339(5), In1–O1 2.165(4), In1–O3c 2.237(5), In1–O4c 2.447(6). O3c–In1–O4c 55.34(11), O3c–In1–O4b 81.38(17), N1–In1–O1 72.57(14), N1–In1–O1a 79.17(15), N1–In1–O3b 77.47(19), N1–In1–O4b 77.83 (16), N1–In1–N1a 140.9(2), O1–In1–O186.6(2). Symmetry transformations used to generate equivalent atoms: a) $y + 1/3$, $x + 2/3$, $-z + 7/6$; b) $x - y$, x, $-z$; c) $x + 1/3$, $x - y + 2/3$, $z + 1/6$.

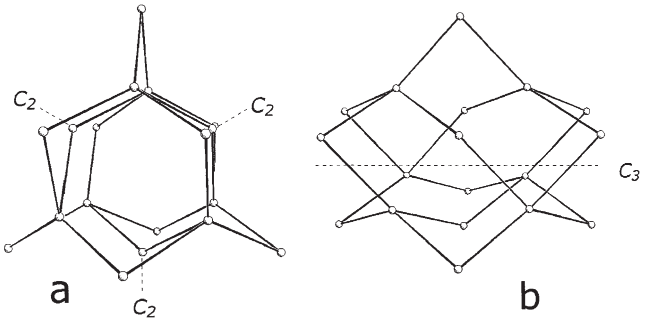


Figure 3. Ball- and stick-representation of the cage-unit in **1** to show the 6^8 unit: **a**. View down the [0 0 1] along the C_3-axis; **b**. View down the [2 1 0] (Sphere: Indium; stick: pzdc).

14.4% weight-loss below 100 °C corresponding to the all lattice waters, and about 6% weight-loss between 100 and 210 °C corresponding to all coordinate waters of the guest indium ion. By 270 °C decomposition of the compound occurs and beyond 400 °C the compound loses its organic component completely. Accordingly we heated the crystalline samples to 120 °C and 200 °C in air for 5 h, respectively. The sample heated to 120 °C became to microcrystals and its XRD demonstrates a new crystalline phase indicating that **1** loses its original structure if the lattice waters do not exist, while the sample heated to 200 °C turned pale-brown and its XRD results evidenced that **1** has completely lost the crystallinity.

In order to prepare isostructural compounds of **1** containing counterions of rare-earth metals, we have managed to proportionally add lanthanides(III) to the reaction mixture. However, the approaches resulted in nothing of the expected product or, sometimes, resulted in generation of a small amount of **1**. This forced us to realize that the six-coordinated hexaaquaindium $[In(H_2O)_6]^{3+}$ may play the template[12] role by forming the metal–organic framework **1**, whereas the lanthanide ions are most likely coordinated by more than six waters in the aqueous solution. On the other hand, by approach to use $[M(H_2O)_6]^{3+}$ (M = Cr, Fe) as templates we have obtained the following isostructural compounds of **1**:

$\{[Cr_{0.7}In_{0.3}(H_2O)_6][In_3(pzdc)_6]\cdot 15(H_2O)\}_\infty$(**2a**),
$\{[Fe_{0.3}In_{0.7}(H_2O)_6][In_3(pzdc)_6]\cdot 15(H_2O)\}_\infty$(**2b**).

X-ray single structure studies[10] demonstrate that the compounds **2a** and **2b** are isostructural. The above formulas are determined according to the element analyses,[13] which are consistent with the crystal structures. More interestingly **2b** is light sensitive: its color turns from pale yellow to brown under radiation of sunlight while the crystal transparency keeps unchanged. To explain this phenomenon, the further studies are encouraged.

This work was supported by the State Key Project Fundamental Research (No. G200077500) and the Natural Science Foundation of China. We thank also Prof. Ren-Gen Xiong for production of Figure 1.

References and Notes

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10 Crystal data of **1**, **2a**, and **2b** for X-ray structural analyses were collected on a Bruker SMART CCD diffractometer at 293(2) K with Mo Kα radiation. **1** ($C_{36}H_{54}In_4N_{12}O_{45}$): colorless rhombus 0.35 × 0.35 × 0.20 mm, trigonal, $R\bar{3}c$, $a = 17.727(3)$, $c = 32.803(7)$ Å, $V = 8927(3)$ Å^3, $Z = 12$. 17272 measured ($2\theta_{max} = 56.18°$), 2355 unique, 1404 observed ($I > 2\sigma(I)$). $wR_2 = 0.1161$, $R_1 = 0.0482$, GOF = 1.045; **2a** ($C_{36}H_{54}In_{3.3}Cr_{0.7}N_{12}O_{45}$): pale-violet rhombus 0.30 × 0.30 × 0.20 mm, trigonal, $R\bar{3}c$, $a = 17.7099(14)$, $c = 32.977(3)$ Å, $V = 8957.1(12)$ Å^3, $Z = 12$. 14650 measured ($2\theta_{max} = 50.0°$), 1761 unique, 1409 observed ($I > 2\sigma(I)$) $wR_2 = 0.1148$, $R_1 = 0.0358$, GOF = 1.070; **2b**: ($C_{36}H_{54}In_{3.7}Fe_{0.3}N_{12}O_{45}$): pale-yellow rhombus 0.35 × 0.35 × 0.20 mm, trigonal, $R\bar{3}c$, $a = 17.6740(10)$, $c = 33.140(3)$, $V = 8965.0(11)$ Å^3, $Z = 12$, 17416 measured ($2\theta_{max} = 56.04°$), 2328 unique, 1834 observed ($I > 2\sigma(I)$), $wR_2 = 0.0895$, $R_1 = 0.0318$, GOF = 0.996. CCDC-176758(**1**), CCDC-176759(**2a**), CCDC-176760(**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

11 Thermal analysis was carried out using TA-SDT 2960 with heating rate of 5 °C/min from 20 to 600 °C under a flux of nitrogen. 5.72 mg of the sample **1** was used for the measurement.

12 To illustrate the templating effect of $[M(H_2O)_6]^{n+}$, several experiment evidences are given in the supporting information.

13 Element analyses, Calcd for **2a**: C, 24.14; H 0.67, N 9.39, In 21.17, Cr 2.03. Found: C 23.88, H 0.44, N 8.93, In 21.0, Cr 2.0. Calcd for **2b**: C 23.79, H 0.66, N 9.25, In 23.40, Fe, 0.92. Found: C 23,45, H 0.33, N 8.90, In 23.0, Fe 1.0.

Published on the web (Advance View) August 4, 2003; DOI 10.1246/cl.2003.796