Structure and Magnetic Properties of a Three-dimensional Metal-organic Framework: $[Co(L)(H_2O)_2]\cdot H_2O$

Man-Sheng Chen, Yi-Fang Deng, Zhi-Min Chen, Chun-Hua Zhang, and Dai-Zhi Kuang

Department of Chemistry and Materials Science, Hengyang Normal University, Hengyang 421008, China

Reprint requests to Dr. Man-Sheng Chen. Fax: +86 734 8484911. E-mail: cmsniu@163.com

Z. Naturforsch. **2011**, *66b,* 355 – 358; received January 23, 2011

A unique 3D fourfold interpenetrated metal-organic framework, $[Co(L)(H_2O)_2]\cdot H_2O$ (**1**), has been synthesized by the solvothermal reaction of H_2L with $Co(NO_3)_2\cdot 6H_2O$ (H_2L = 5-(isonicotinamido)isophthalic acid). Compound **1** crystallizes in the monoclinic space group $P2_1/c$, with the cell parameters: $a = 81301(8)$, $b = 107711(11)$, $c = 167697(16)$ Å, $\beta = 92.656(2)°$, $V = 14669(3)$ Å^3, $R_1 = 0.0325$ and $wR_2 = 0.0833$. Its framework has (10,3)-b topology, where the cobalt atoms are alternately bridged by the pyridyl and the carboxylate groups of the L^{2-} ligands into a three-dimensional network. Compound **1** displays antiferromagnetic interactions. Above 40 K, $\chi_m{}^{-1}$ obeys the Curie-Weiss law with $C = 3.28$ emu K mol^{-1} and $\Theta = -0.66$ K.

Key words: Cobalt(II), Metal-organic Framework, Crystal Structure, Magnetic Property

Introduction

Recently, much interest has been focused on the rapidly expanding field of crystal engineering of metal-organic frameworks (MOFs) [1] due to their intriguing network topologies as well as their potential applications as functional materials in many areas such as separation, catalysis, gas storage, magnetism, and others [2 – 4]. Solvothermal synthesis has been widely employed to generate MOFs with unique structures and special properties [5]. However, solvothermal reactions are often complicated and their course unpredictable [6]. Although such reactions may have their difficulties in targeted material syntheses and rational molecular design, they can also afford some novel functional materials with enchanting structures.

5-(Isonicotinamido)isophthalic acid (H_2L) has remarkable features as a ligand: (a) it contains two carboxylate groups, which can adopt different coordination modes in the formation of MOFs; (b) the carboxamide group can serve as a hydrogen bonding acceptor and / or donor, which may consolidate structures [7 – 9]. So far, most investigations on solvent-induced conformational changes in artificial minimal model systems have simply been performed in solution. In this contribution, we present a 3D metal-organic framework generated from H_2L and $Co(NO_3)_2\cdot 6H_2O$ under solvothermal conditions, $[Co(L)(H_2O)_2]\cdot H_2O$ (**1**). The magnetic interactions between the metal ions have been investigated.

Experimental Section

Measurements of physical properties

All chemicals were commercially available in p. a. grade and were used without further purification. The C, H and N microanalyses were performed with a Perkin-Elmer 2400-CHNS/O elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 400 – 4000 cm^{-1} on a Shimadzu FT-IR-8900 spectrometer. The magnetic susceptibilities were measured using a SQUID magnetometer on crystalline samples in the temperature range of 1.8 to 300 K under 2kOe.

Preparation of $[Co(L)(H_2O)_2]\cdot H_2O$ (1)

A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.365 g, 1 mmol), 5-(isonicotinamido)isophthalic acid (0.287 g, 1.0 mmol) and 8 mL *N*,*N*-dimethylformamide (DMF) was placed in a 15 mL Teflon reactor and kept under autogeneous pressure at 120 °C for 3 d. The mixture was cooled to r. t., and block-shaped red crystals were obtained in 42 % yield (based on the initial $Co(NO_3)_2\cdot 6H_2O$). – Anal. for $C_{14}H_{14}CoN_2O_8$: calcd. C 41.19, H 2.29, N 8.01; found C 41.15, H 1.86, N 7.92. – IR: ν = 3438(s), 1749(s), 1568(s), 1489(w), 1431(s), 1392(s), 1304(s), 1121(s), 1082(w), 941(w), 836(m), 785(s), 755(m), 698(m), 662(m), 603(m) cm^{-1}.

0932–0776 / 11 / 0400–0355 $ 06.00

Table 1. Crystal and refinement data for $[Co(L)(H_2O)_2]\cdot H_2O$ (**1**).

Formula	$C_{14}H_{14}CoN_2O_8$
M_r	397.20
Crystal size, mm^3	$0.20 \times 0.15 \times 0.10$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	8.1301(8)
b, Å	10.7711(11)
c, Å	16.7697(16)
β, deg	92.656(2)
V, $Å^3$	1466.9(3)
Z	4
D_{calcd}, g cm^{-3}	1.80
$\mu(MoK_\alpha)$, cm^{-1}	1.2
$F(000)$, e	812
hkl range	$-6 \rightarrow 9$, ± 12, $-20 \rightarrow 17$
$((\sin\theta)/\lambda)$max, $Å^{-1}$	0.599
Refl. measd. / unique / R_{int}	7246 / 2642 / 0.046
Param. refined	226
$R_1(F)^a$ / $wR_2(F^2)^b$ (all refls.)	0.0358 / 0.0851
A / B values for weighting scheme[b]	0.0503 / 0.4644
GoF $(F^2)^c$	1.030
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	0.45 / −0.36

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0)+2F_c{}^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Selected interatomic distances (Å) and angles (deg) for **1**[a].

Co(1)-O(1W)	2.1208(15)	Co(1)-O(2)	2.0712(16)
Co(1)-O(2W)	2.1205(17)	Co(1)-N(2)[#2]	2.1110(19)
Co(1)-O(3)[#1]	2.0198(16)	Co(1)-O(1)	2.3187(15)
O(3)[#1]-Co(1)-O(2W)	95.86(7)	O(1W)-Co(1)-O(1)	93.37(6)
O(2)-Co(1)-O(3)[#1]	94.63(7)	O(2)-Co(1)-N(2)[#2]	162.32(7)
O(3)[#1]-Co(1)-N(2)[#2]	102.76(7)	O(2W)-Co(1)-O(1)	87.71(6)
O(2)-Co(1)-O(1W)	94.69(9)	O(2)-Co(1)-O(2W)	91.84(7)
O(3)[#1]-Co(1)-O(1W)	86.23(6)	N(2)[#2]-Co(1)-O(2W)	89.57(7)
O(2)-Co(1)-O(1)	59.24(6)	N(2)[#2]-Co(1)-O(1)	103.23(7)
O(3)[#1]-Co(1)-O(1)	153.78(6)	N(2)[#2]-Co(1)-O(1W)	83.42(7)
O(1W)-Co(1)-O(2W)	172.97(6)		

[a] Symmetry codes: [#1]: x, $3/2 - y$, $-1/2 + z$; [#2]: $-1+x$, $-1+y$, z.

X-Ray structure analysis

The reflection intensities of **1** were collected at 293(3) K using a Bruker SMART Apex II CCD area detector single-crystal diffractometer, with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å), using the $\psi/2\vartheta$ scan mode. An absorption correction was applied using the program SADABS [10]. The structure was solved by Direct Methods using SHELXS-97 [11] and refined by full-matrix least-squares methods on F^2 (SHELXL-97 [12]). All hydrogen atoms attached to the carbon and nitrogen atoms were generated geometrically, and the hydrogen atoms of the water molecules were found directly. All non-hydrogen atoms were finally refined with anisotropic displacement parameters. H atoms attached to C atoms were treated as riding, with C–H = 0.93 Å. The H atoms of the water molecules were refined with $U_{iso}(H) = 1.5\ U_{eq}(O)$. Crystal data and further information of the structure determination are summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC 806179 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Synthesis and IR spectra

In the preparation of **1**, it is noteworthy that no DMF molecules were found in the resulting complex, however, the DMF solvent plays a key role in the formation of crystalline products since no crystals were obtained without DMF in the reaction. Repeated experiments have indicated that no crystalline product of **1** can be obtained using the same cobalt salts in other organic solvents or in an aqueous system under the same synthesis conditions.

The IR spectrum of **1** shows the ν(O–H) stretching vibration of water molecules at 3438 cm^{-1}. The absorptions at 1568 and 1392 cm^{-1} can be assigned to the $\nu_{as}(CO_2{}^-)$ and $\nu_s(CO_2{}^-)$ stretching vibrations, respectively. The strong absorptions located at 1568 and 1431 cm^{-1} may be assigned to pyridyl vibrations.

Structure description

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ The asymmetric unit contains one unique

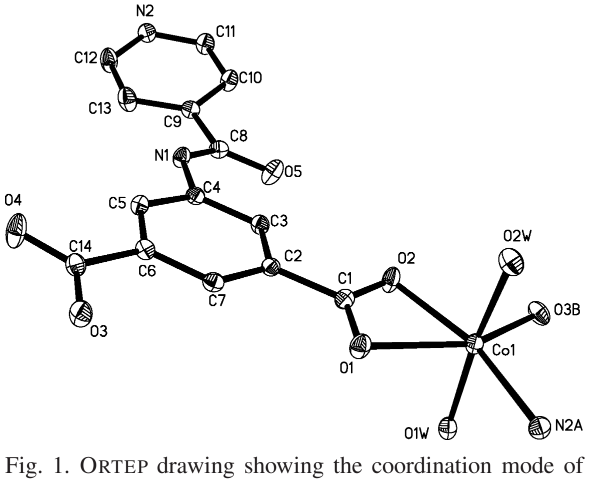

Fig. 1. ORTEP drawing showing the coordination mode of the cobalt atom and the ligand (all the H atoms have been omitted for clarity) in the structure of **1**.

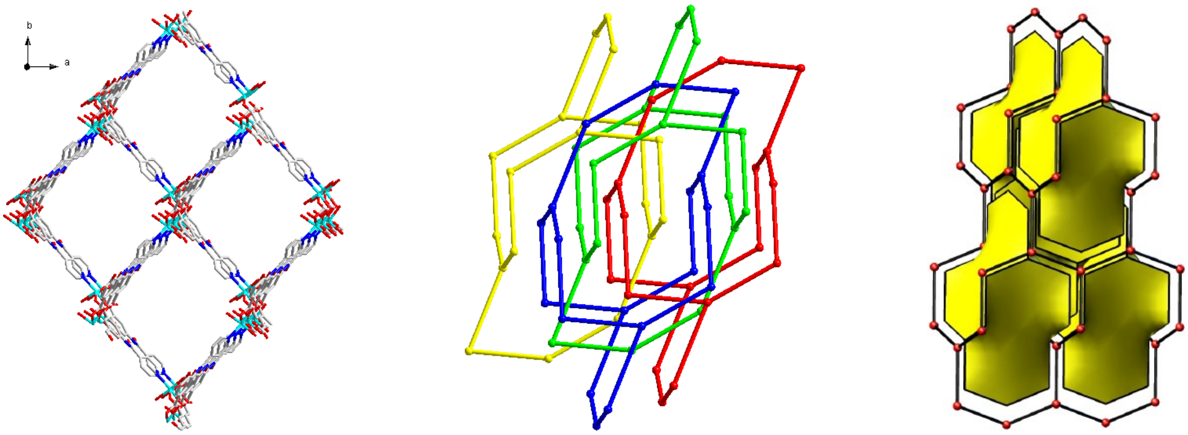

Fig. 2 (color online). View of the 3D framework structure of **1** along the *c* axis (left), the four-fold interpenetration of the $ThSi_2$ net of **1** (middle), and the schematic representation of $ThSi_2$ (right).

Co(II) atom, one L^{2-} ligand, and two coordinated and one free water molecules. The Co1 atom exhibits a significantly distorted octahedral geometry with one N atom of one L^{2-} ligand and three carboxylate O atoms, which come from two different L^{2-} ligands and two coordinated water molecules (Fig. 1). The Co1–O bond lengths range from 2.0198(16) to 2.3187(15) Å, while the Co1–N bond length is 2.1110(19) Å (Table 2). Furthermore, each L^{2-} ligand in **1** employs its one pyridyl and two carboxylate groups to connect three metal atoms. It is noteworthy that the two carboxylate groups of each L^{2-} ligand have different coordination modes, one is μ_1-η^1:η^0-monodentate and the other one acts as a μ_1-η^1:η^1-chelate. Therefore, the coordination interactions between the three-connecting L^{2-} ligands and the six-coordinated Co(II) atoms as described above make **1** a 3D framework (Fig. 2). Firstly, a zigzag chain is formed by the connections between the carboxylate groups and the Co(II) atoms ignoring the coordination of the pyridyl group. Then the chains are linked together by 5-isonicotinamido groups parallel to the *c* axis to give a two-dimensional network in the *bc* plane, which is finally linked by the 5-isonicotinamido groups of L^{2-} paralleling the *a* axis to form the ultimate 3D framework. In order to minimize the big hollow cavities and stabilize the framework, the potential voids formed *via* a single 3D network are combined with three other, identical frameworks, thus giving a four-fold interpenetrated (10,3)-b net.

For a better understanding about the topological structure of the framework, it is necessary to simplify the building units. As discussed above, each L^{2-} ligand and linking three Co(II) atoms can be defined as a three-connecting node, and each metal atom coordinated by three ligands can also be considered as a three-connector. Consequently, according to a calculation of TOPOS [13], the resulting structure of **1** is a uninodal 3-connecting topology with the Schläfli symbol $(10^2\cdot10^4\cdot10^4)$, which corresponds to the $ThSi_2$ structure type with the well-known (10,3)-b net (Fig. 2), but it is somewhat distorted from the standard $ThSi_2$ topology net (Fig. 2).

Magnetic properties

The magnetic susceptibilities were measured on a crystalline sample of **1** in the temperature range from 1.8 to 300 K under 2 kOe using a SQUID magnetometer. At r. t., the observed $\chi_M T$ value is 4.28 emu K mol^{-1} which is larger than the expected value of 1.87 emu K mol^{-1} corresponding to one independent Co(II) (S = 3/2) ion (Fig. 3). Upon cooling from 300 to 40 K the values of $\chi_M T$ decrease slowly, and then rapidly reach a value of 3.52 emu K mol^{-1} at 1.8 K. The $\chi_M{}^{-1}$ *versus* T plot above 40 K follows the Curie-Weiss law with C = 3.28 emu K mol^{-1}, Θ = −0.66 K. The negative θ value suggests that there is a weak antiferromagnetic interaction among cobalt(II) atoms transferred through L^{2-} ligands.

Conclusion

The unique four-fold interpenetrated 3D Co(II) complex (**1**) has been obtained by a solvothermal reac-

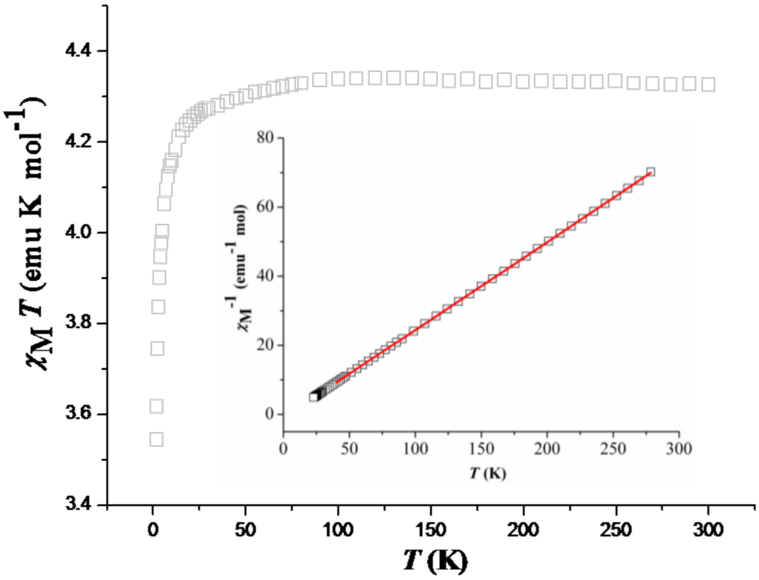

Fig. 3 (color online). Temperature dependence of the magnetic susceptibility of **1**.

tion. It has a rare 3D three-connecting $ThSi_2$-type network with the (10,3)-b topology. The result may promote the exploration of new carboxylate ligands containing amidopyridine groups for the construction of MOFs with useful properties and charming topologies under solvothermal conditions.

Acknowledgement

This work has been funded by the Distinguished Young Cadreman of Hunan Province (2008), the Science Foundation of Hengyang Normal University of China (10B67) and the Scientific Research Fund of Hunan Provincial Education Department of China (10C0473).

[1] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319 – 330.

[2] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982 – 986.

[3] J. L. C. Rowsell, E.C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science* **2005**, *309*, 1350 – 1354.

[4] G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762 – 1765.

[5] S. Höger, D. L. Morrison, V. Enkelmann, *J. Am. Chem. Soc.* **2002**, *124*, 6734 – 6736.

[6] L.Q. Ma, W.B. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 13834 – 13835.

[7] M.S. Chen, Z.S. Bai, T.A. Okamura, Z. Su, S.S. Chen, W. Y. Sun, N. Ueyama, *CrystEngCommun* **2010**, *12*, 1935 – 1944.

[8] M. S. Chen, Z. Su, M. Chen, S. S. Chen, Y. Z. Li, W. Y. Sun, *CrystEngCommun* **2010**, *12*, 3267 – 3276.

[9] M. S. Chen, M. Chen, T. A. Okamura, W. Y. Sun, N. Ueyama, *Micropor. Mesop. Mater.* **2011**, *139*, 25 – 30.

[10] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2003**.

[11] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

[12] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.

[13] V. A. Blatov, Multipurpose crystallochemical analysis with the program package TOPOS, *IUCr CompComm Newsletter* **2006**, *7*, 4 – 38.