Structure and Magnetic Properties of a Three-dimensional Cobalt Metal-Organic Framework

Man-Sheng Chen[a], Wei Li[a], Man-Bo Zhang[b],
Rui-Xiang Hu[b], Chun-Hua Zhang[a], and
Zhi-Min Chen[a]

[a] Key Laboratory of Functional Organometallic Materials,
Department of Chemistry and Materials Science,
Hengyang Normal University, Hengyang, Hunan 421008,
China
[b] College of Chemistry and Chemical Engineering,
Hunan Normal University, Changsha 410081, China

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

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A new 3D fourfold interpenetrated metal-organic framework, $[Co(L)_2(SO_4)]\cdot H_2O$ (**1**), has been synthesized by the solvothermal reaction of L with $CoSO_4\cdot 6H_2O$ (L = 1,4-bis(imidazolyl)benzene). Compound **1** crystallizes in the monoclinic space group $P2_1/n$, with the cell parameters: a = 9.943(2), b = 21.7104(15), c = 13.2658(18) Å, β = 97.638(3)°, V = 2838.2(8) Å^3, R_1 = 0.0566 and wR_2 = 0.1035. It represents a novel **dia** net, in which the cobalt atoms are alternately bridged by the imidazolyl N atoms of the ligands L into a three-dimensional network. Compound **1** displays antiferromagnetic interactions. From 2 to 300 K, χ_m^{-1} it obeys the Curie-Weiss law with C =2.68 emu K mol^{-1} and Θ = −2.59 K.

Key words: Metal-Organic Framework, Crystal Structure, Magnetic Properties

Introduction

Recently, metal-organic frameworks (MOFs) have attracted much attention owing to their intriguing architectures and topologies and potential applications in catalysis, luminescent probes, ion exchange, and magnetic materials [1 – 7]. It is well known that the origin of interpenetration can be ascribed to the presence of large free voids in a single framework, and that interpenetration will occur to fill the void space, which benefits the stability of the frameworks [8, 9]. Furthermore, long spacer ligands, particularly rigid *N*,*N*′-bidentate donors, are efficient building blocks, which favor the formation of interpenetrated motifs. Therefore, many reports show a boom in the exploratory synthesis and construction of interpenetrated porous frameworks to establish the feasibility for selective gas sorption by long spacer ligands [10, 11].

Compared with common *N*-heterocyclic ligands, like 4,4′-bipyridine, 1,4-bis(imidazolyl)benzene (L) can show richer coordination modes due to the flexility of its imidazolyl groups. Accordingly, it is an excellent candidate for the construction of metalorganic frameworks [12 – 15]. In this paper, we report on the solvothermal synthesis, crystal structure and magnetic behavior of a new coordination polymer, $[Co(L)_2(SO_4)]\cdot H_2O$ (**1**).

Experimental Section

Measurements of physical properties

The reagents were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer using KBr discs. The magnetic susceptibilities were measured using a SQUID magnetometer on crystalline samples in the temperature range of 1.8 to 300 K under 2 kOe (1 kOe = 7.96×10^4 A m^{-1}).

Preparation of $[Co(L)_2(SO_4)]\cdot H_2O$ *(**1**)*

The title complex was prepared under solvothermal conditions. A mixture of L (0.043 g, 0.2 mmol), $CoSO_4\cdot 7H_2O$ (0.028 g, 0.1 mmol) and *N*,*N*-dimethylformamide (DMF) (10 mL) was placed in a Teflon-lined stainless-steel vessel, heated to 120 °C for 3 d, and then cooled to r. t. over 24 h. Red block-shaped crystals of **1** were obtained. – IR (KBr pellet, cm^{-1}): ν = 3419 (s), 2842 (w), 1625 (w), 1518 (m), 1487 (m), 1386 (s), 1135 (s), 1071(s), 836 (w), 624 (w), 599 (w). – Anal. for $C_{24}H_{22}CoN_8O_5S$ (593.49): calcd. C 48.53, H 3.71, N 18.87; found C 48.49, H 3.77, N 18.85.

X-Ray structure analysis

The reflection intensities of **1** were collected at 291(2) K using a Bruker SMART Apex II CCD area detector single-crystal diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å), using the $\psi/2\vartheta$ scan mode. An absorption correction was applied using the program SADABS [16]. The structure was solved by Direct Methods using SHELXS-97 [17] and refined by full-matrix least-squares methods on F^2 (SHELXL-97 [18]). All hydrogen atoms attached to the carbon and nitrogen atoms were generated geometrically, and the hydrogen atoms of

Table 1. Crystal and refinement data for $[Co(L)_2(SO_4)]\cdot(H_2O)$ (**1**).

Formula	$C_{24}H_{22}CoN_8O_5S$
M_r	593.49
Crystal size, mm^3	$0.28 \times 0.22 \times 0.20$
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	9.943(2)
b, Å	21.7104(15)
c, Å	13.2658(18)
β, deg	97.638(3)
V, $Å^3$	2838.2(8)
Z	4
D_{calcd}, $g\,cm^{-3}$	1.39
$\mu(MoK_\alpha)$, cm^{-1}	0.7
$F(000)$, e	1220
hkl range	$-12 \le h \le 11$, $-26 \le k \le 14$, $-16 \le l \le 16$
$((\sin\theta)/\lambda)$ max, $Å^{-1}$	0.595
Refl. measured / unique / R_{int}	15174 / 5575 / 0.0671
Param. refined	358
$R_1(F)$ / $wR_2(F^2)^{a,b}$ (all refls.)	0.0817 / 0.1075
A / B values (weighting scheme)[b]	0.0421 / 0.0000
GoF $(F^2)^c$	1.077
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	0.67 / −0.41

[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 bond lengths (Å) and bond angles (deg) for $\mathbf{1}^a$.

Co(1)–O(1)	2.177(2)	Co(1)–N(5)	2.081(3)
Co(1)–O(2)	2.219(2)	Co(1)–$N(4)^{\#1}$	2.030(3)
Co(1)–N(1)	2.058(2)	Co(1)–$N(8)^{\#2}$	2.052(3)
O(1)–Co(1)–O(2)	64.75(8)	N(5)–Co(1)–O(2)	87.81(9)
N(1)–Co(1)–O(2)	88.61(9)	N(1)–Co(1)–O(1)	88.48(9)
N(5)–Co(1)–O(1)	91.05(10)	N(1)–Co(1)–N(5)	176.23(10)
$N(4)^{\#1}$–Co(1)–$N(8)^{\#2}$	103.43(11)	$N(4)^{\#1}$–Co(1)–N(1)	92.35(11)
$N(8)^{\#2}$–Co(1)–N(1)	90.60(10)	$N(4)^{\#1}$–Co(1)–N(5)	91.42(11)
$N(8)^{\#2}$–Co(1)–N(5)	88.64(11)	$N(4)^{\#1}$–Co(1)–O(1)	95.27(10)
$N(8)^{\#2}$–Co(1)–O(1)	161.30(10)	$N(4)^{\#1}$–Co(1)–O(2)	159.98(9)
$N(8)^{\#2}$–Co(1)–O(2)	96.55(9)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-1/2+x$, $1/2-y$, $-1/2+z$; #2 $-1/2+x$, $3/2-y$, $1/2+z$.

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 d(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 841588 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

Regarding 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 mixture. Repeated experiments have indicated that crystalline **1** is not obtained using the same cobalt salts in other organic solvents or in an aqueous system under the same conditions.

The IR spectrum of **1** shows the ν(O–H) stretching vibration of water molecules at 3419 cm^{-1}. The absorptions at 1135 and 1071 cm^{-1} can be assigned to the $SO_4{}^{2-}$ stretching vibrations, and the strong absorptions located at 1518 and 1487 cm^{-1} may be assigned to imidazolyl vibrations.

Structure description

The results of the structure analysis revealed that complex **1** crystallizes in the monoclinic space group $P2_1/n$ and exhibits a novel 3D four-fold interpenetrated coordination framework. The asymmetric unit contains one unique Co(II) atom, two L ligands, one coordinated $SO_4{}^{2-}$ anion and one free water molecule. The Co1 atom exhibits a significantly distorted octahedral geometry with four N atoms of four L ligands, and two O atoms from one chelating sulfate (Fig. 1). The Co1–O bond lengths are 2.177(2) and 2.219(2) Å, while the Co1–N bond lengths are in the range 2.030(3)–2.081(3) Å (Table 2). It is noteworthy that each L ligand in **1** employs its two imidazolyl groups to connect two metal atoms, and each Co atom bridges four L ligands, which is entirely different from the connectivity reported for the complex $[Cu(L)_{1.5}(SO_4)]\cdot3H_2O$ [14]. Therefore, the co-

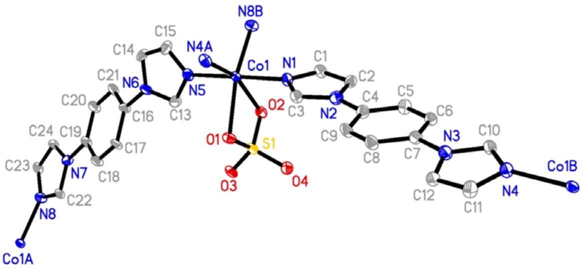

Fig. 1 (color online). ORTEP drawing showing the coordination mode of the cobalt atom and the ligands (all H atoms omitted for clarity).

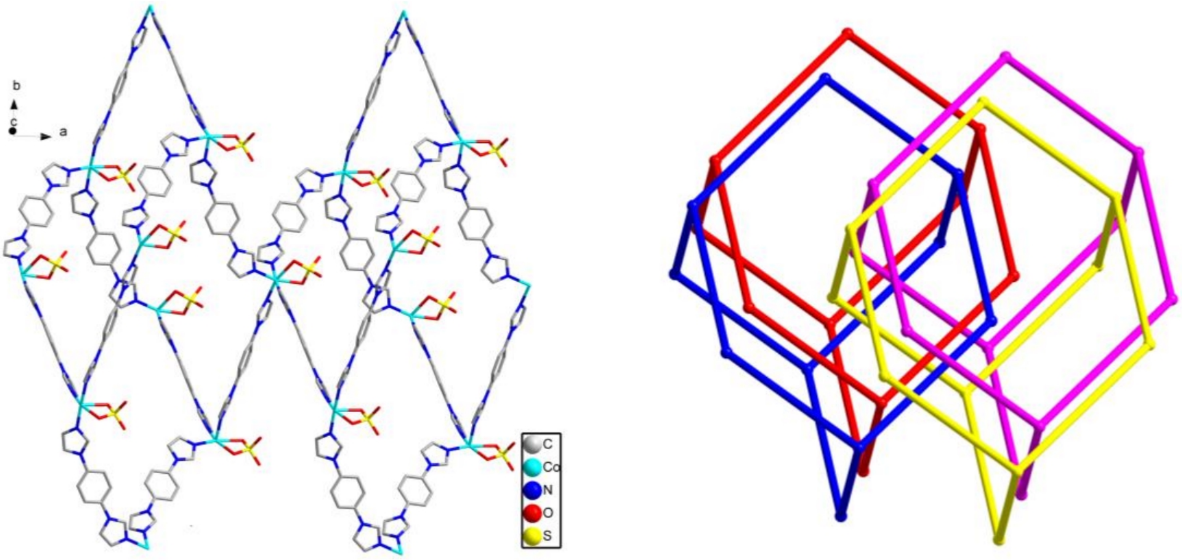

Fig 2 (color online). View of the 3D framework structure of **1** along the crystallographic *a* axis (left), and the four-fold interpenetration of the **dia** net of **1** (right).

ordination interactions between the difunctional ligands L and the six-coordinated Co(II) atoms as described above make **1** a 3D framework (Fig. 2). 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 **dia** net with the short and long Schläfli symbols 6^6 and $(6_2.6_2.6_2.6_2.6_2.6_2)$, respectively (Fig. 2) [19]. Moreover, the four-fold interpenetrated **dia** nets are linked *via* C–H···O hydrogen bonds with C···A distances in the range of 2.712(3)–3.262(4) Å and C–H···A angles ranging from 155 to 169° to generate a stable 3D supramolecular structure.

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 3.20 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 100 K the values of $\chi_M T$ decrease slowly, and then rapidly reach a value of 2.24 emu K mol^{-1} at 1.8 K. The $\chi_M{}^{-1}$ *versus* T plot follows the Curie-Weiss law with C = 2.68 emu K mol^{-1}, $\Theta = -2.59$ K. The negative θ value suggests that there is a weak antiferromagnetic interaction among cobalt(II) atoms transferred through L ligands.

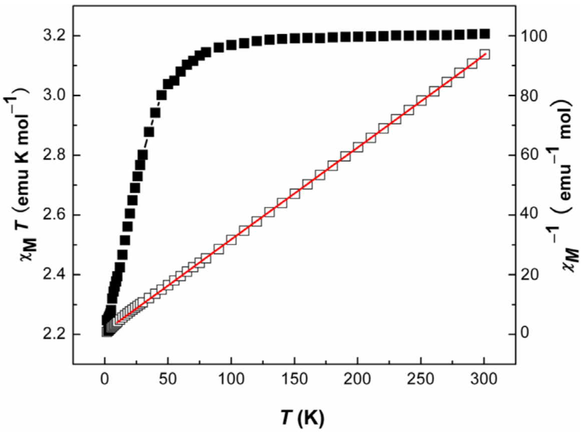

Fig. 3 (color online). Temperature dependence of the magnetic susceptibility of **1**.

Conclusion

A new four-fold interpenetrated 3D Co(II) complex with 1,4-bis(imidazolyl)benzen ligands and a sulfate anion has been obtained by a solvothermal reaction. Complex **1** has a rare 3D **dia**-type network. The result may enhance the exploration of rigid multi-imidazolyl ligands for the construction of MOFs with useful properties and charming topologies under solvothermal conditions.

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