DALTON
FULL PAPER

A unique open inorganic–organic framework with alternate hexa- and penta-coordinate cobalt(II) sites. Synthesis, crystal structure and magnetic properties of $[Co_3(C_4H_4O_4)_{2.5}(OH)]_n \cdot 0.5nH_2O$

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Received 20th June 2001, Accepted 3rd August 2001
First published as an Advance Article on the web 12th September 2001

A three-dimensional open-framework with unprecedented alternate hexa- and penta-coordinate cobalt(II) sites was obtained from the hydrothermal reaction of cobalt nitrate and succinate in a basic solution. Of the four crystallographically independent Co(II) atoms in the crystal structure of this compound, three are hexa-coordinated and one penta-coordinated. The cobalt(II) atoms are linked by edge-sharing CoO_n (n = 5 or 6) polyhedrons. The temperature dependence of the magnetic susceptibility of this compound shows strong antiferromagnetic interaction between the metal atoms.

Introduction

Inorganic–organic hybrid frameworks are widely regarded as promising materials for applications in catalysis, separation, gas storage and molecular recognition.[1–3] Compared to conventional microporous inorganic zeolite materials, the organic components offer great potential for chemical and structural diversity, including the direct incorporation of catalytic sites.[4] To date, considerable progress has been made on the control of the resulting coordination polymers which are often plagued by interpenetration[5] or framework breakdown upon the removal of absorbates.[6] However, the selectivities, especially in separation, catalysis and molecular recognition for the reported materials are still poor, limiting their practical applications. One of the possible strategies to improve the selectivity and reactivity is to synthesize inorganic–organic hybrid frameworks with unsaturated metal sites, as has been observed in penta-coordinate cobalt(II) complexes and metalloenzymes.[7] However, reports of open inorganic–organic frameworks with unsaturated metal sites have been largely absent from the literature.[8] As for cobalt complexes, only a few such structures have been reported in three-dimensional hybrid frameworks up to now,[9] apparently because these polymeric structures are difficult to control. Therefore, synthesis of this kind of material can not only help us understand how the open inorganic–organic framework with unsaturated metal sites is formed, but also provide frameworks with higher selectivity, in catalysis. In particular, the Co(II) ion may be used, for its coordinational flexibility and additional magnetic properties, in a polymeric structure as a metal template for the preparation of multi-dimensional hybrid inorganic–organic materials.[10] We now report the synthesis and crystal structure of an open framework containing mixed coordination metal centres, namely $[Co_3(C_4H_4O_4)_{2.5}(OH)]_n \cdot 0.5nH_2O$ (**1**).

Experimental

All reagents used were commercially available and were used as received. All samples were thoroughly dried prior to elemental analyses.

Physical measurements

The C, H and N elemental analyses were performed on a Perkin-Elmer 204 elemental analyzer. The magnetic data of **1** were measured (Maglab 2000, Oxford) over the temperature range 2–300 K at 10 kOe applied field.

Preparation

A mixture composed of cobalt(II) nitrate hydrate, succinic acid, sodium hydroxide and water in the molar ratio 1 : 2 : 1 : 600 was heated at 180 °C in a stainless steel autoclave for 5 days. Pink crystals of **1** suitable for X-ray crystallography were isloated (yield 0.152 g, 31%). Anal. calc. for $C_{10}H_{12}Co_3O_{11.5}$ **1**: C, 24.19; H, 2.47. Found: C, 24.57; H, 2.35%.

Crystallography

Diffraction intensities of **1** (crystal size 0.32 × 0.20 × 0.15 mm) were collected at 295 K on an Enraf-Nonius CAD4 diffractometer. Lorentz-polarization and absorption corrections were applied. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages, respectively.[11,12] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H = 0.96 Å) and those of the aqua ligands were located from the difference maps; all the hydrogen atoms were assigned the same isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[13] Crystal data, as well as details of data collection and refinement, are summarised in Table 1. Selected bond lengths of **1** are given in Table 2.

CCDC reference number 156110.

See http://www.rsc.org/suppdata/dt/b1/b105482c/ for crystallographic data in CIF or other electronic format.

 DOI: 10.1039/b105482c

Results and discussion

Crystal structure

The crystal structure shows that the three-dimensional open-network of **1** consists of $[Co_3(succinate)_{2.5}(OH)]_n$ layers and succinate pillars. The layer structure in **1** features a honeycomb network constructed from edge-sharing CoO_n (n = 5 or 6) polyhedrons, as shown in Fig. 1,[14] in which every 14 polyhedrons are interconnected to form a rhombic ring. The layer structure is consolidated by both μ_3-hydroxy and bis-tridentate succinate groups. Adjacent layers are covalently linked by bis-tridentate succinate groups as molecular pillars to furnish a three-dimensional open framework with hourglass-shaped channels running along the *a*-axis, as shown in Fig. 2. Lattice water molecules are located in the hourglass-shaped channels, forming relatively weak hydrogen bonds with the carboxy oxygen atoms [O(2w)···O(3a) 2.857(3) Å]. There are four

Table 1 Crystal data for complex **1**

Formula	$C_{10}H_{12}Co_3O_{11.5}$
FW	492.99
Crystal system	Triclinic
Space group	*P*-1 (no. 2)
a/Å	8.750(2)
b/Å	9.112(2)
c/Å	10.350(2)
β/°	68.69(3)
V/Å^3	745.1(3)
Z	2
D_c/g cm^{-3}	2.197
μ(Mo-Kα)/mm^{-1}	3.362
Unique data	2918
Data with $I \geq 2\sigma(I)$	3122
R_1 [$I \geq 2\sigma(I)$]	0.0321
wR_2 (all data)	0.0857
Goodness-of-fit on F^2	1.040

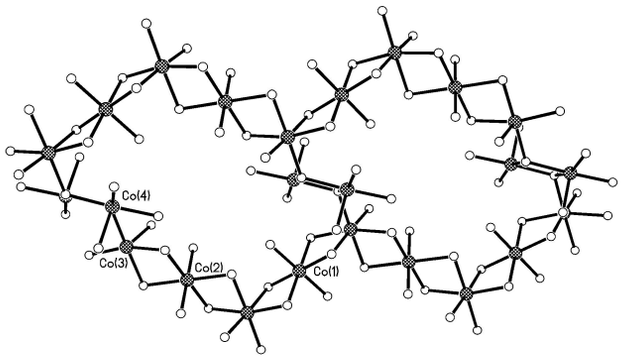

Fig. 1 Perspective view of the coordination environments of the metal atoms and the interconnection of the CoO_5 and CoO_6 polyhedrons viewed along the *b*-axis.

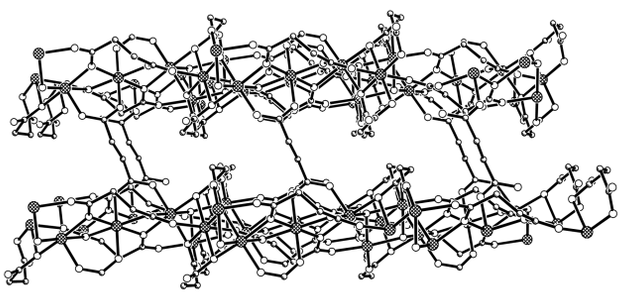

Fig. 2 Perspective view of the 3D structure of **1** along the *a*-axis.

Table 2 Selected bond lengths (Å) and bond angles (°) for complex **1**[a]

Co(1)–O(1a)	2.052(2)	Co(1)–O(1)	2.052(2)
Co(1)–O(5)	2.063(2)	Co(1)–O(4)	2.098(2)
Co(2)–O(10)	2.023(2)	Co(2)–O(7)	2.121(2)
Co(2)–O(6)	2.133(2)	Co(3)–O(9b)	2.047(2)
Co(3)–O(1w)	2.038(2)	Co(3)–O(7)	2.111(2)
Co(3)–O(1c)	2.114(2)	Co(3)–O(4b)	2.127(2)
Co(3)–O(6b)	2.118(2)	Co(4)–O(8)	2.026(2)
Co(4)–O(3d)	2.001(2)	Co(4)–O(1w)	2.014(2)
Co(4)–O(1we)	2.103(2)	Co(4)–O(2c)	2.027(2)
O(1a)–Co(1)–O(1)	180.00(18)	O(1a)–Co(1)–O(5)	93.16(8)
O(1)–Co(1)–O(5)	86.84(8)	O(1a)–Co(1)–O(5a)	86.84(8)
O(1)–Co(1)–O(5a)	93.16(8)	O(5)–Co(1)–O(5a)	180.00(17)
O(1a)–Co(1)–O(4)	83.36(8)	O(1)–Co(1)–O(4)	96.64(8)
O(5)–Co(1)–O(4)	89.61(8)	O(5a)–Co(1)–O(4)	90.39(8)
O(1a)–Co(1)–O(4a)	96.64(8)	O(1)–Co(1)–O(4a)	83.36(8)
O(5)–Co(1)–O(4a)	90.39(8)	O(5a)–Co(1)–O(4a)	89.61(8)
O(4)–Co(1)–O(4a)	180.00(11)	O(10)–Co(2)–O(10b)	180.0
O(10)–Co(2)–O(7)	91.71(9)	O(10b)–Co(2)–O(7)	88.29(9)
O(10)–Co(2)–O(7b)	88.29(9)	O(10b)–Co(2)–O(7b)	91.71(9)
O(7)–Co(2)–O(7b)	180.0	O(10)–Co(2)–O(6)	90.73(9)
O(10b)–Co(2)–O(6)	89.27(9)	O(7)–Co(2)–O(6)	99.76(8)
O(7b)–Co(2)–O(6)	80.24(8)	O(10)–Co(2)–O(6b)	89.27(9)
O(10b)–Co(2)–O(6b)	90.73(9)	O(7)–Co(2)–O(6b)	80.24(8)
O(7b)–Co(2)–O(6b)	99.76(8)	O(6)–Co(2)–O(6b)	180.00(4)
O(1w)–Co(3)–O(9b)	88.04(9)	O(1w)–Co(3)–O(7)	98.49(8)
O(9b)–Co(3)–O(7)	88.78(9)	O(1w)–Co(3)–O(1c)	94.96(9)
O(9b)–Co(3)–O(1c)	176.93(8)	O(7)–Co(3)–O(1c)	90.15(8)
O(1w)–Co(3)–O(6b)	178.05(8)	O(9b)–Co(3)–O(6b)	90.12(9)
O(7)–Co(3)–O(6b)	80.81(8)	O(1c)–Co(3)–O(6b)	86.87(8)
O(1w)–Co(3)–O(4b)	94.46(8)	O(9b)–Co(3)–O(4b)	99.23(9)
O(7)–Co(3)–O(4b)	165.00(7)	O(1c)–Co(3)–O(4b)	81.19(8)
O(6b)–Co(3)–O(4b)	86.48(8)	O(3d)–Co(4)–O(1w)	156.48(8)
O(3d)–Co(4)–O(8)	89.27(10)	O(1w)–Co(4)–O(8)	95.74(10)
O(3d)–Co(4)–O(2c)	96.07(9)	O(1w)–Co(4)–O(2c)	106.45(9)
O(8)–Co(4)–O(2c)	93.93(11)	O(3d)–Co(4)–O(1we)	93.29(10)
O(1w)–Co(4)–O(1we)	80.19(10)	O(8)–Co(4)–O(1we)	174.92(10)
O(2c)–Co(4)–O(1we)	90.17(10)		

[a] Symmetry codes: a: $-x, -y, -z$; b: $-x, -y, -z+1$; c: $x, y, z+1$; d: $x-1, y, z+1$; e: $-x-1, -y, -z+2$; f: $x, y, z-1$; g: $x+1, y, z-1$.

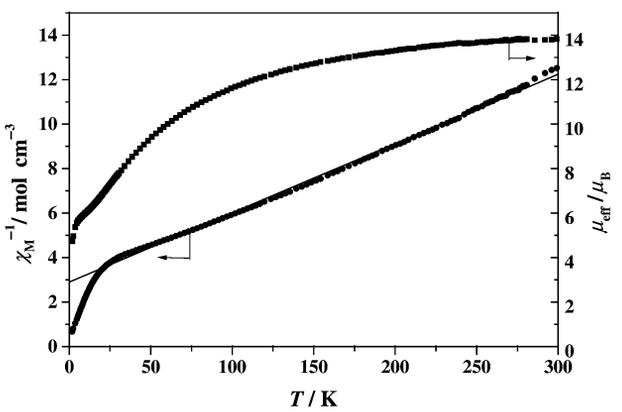

Fig. 3 Temperature dependence of the effective magnetic moment (μ_{eff}) and the reciprocal molar magnetic susceptibility (χ_M^{-1}) for **1**.

crystallographically independent Co(II) atoms. Co(1) is located at an inverse centre and octahedrally coordinated by six oxygen atoms from three bis-tridentate succinate groups in the layer; Co(2) is octahedrally coordinated by four oxygen atoms from two bis-tridentate succinate groups and two oxygen atoms from the two bis-tridentate succinate groups. Co(3) is also octahedrally coordinated by six oxygen atoms, with four from four bis-tridentate succinate groups and one from a bis-bidentate succinate group and one from a hydroxyl group. Co(4) is square-pyramidally coordinated by three oxygen atoms from three succinate groups and two oxygen atoms from two μ_3-hydroxy groups. The Co–O(carboxy) and Co–O(hydroxy) bond lengths are in the ranges 2.001(2)–2.133(2) and 2.014(2)–2.103(2) Å, respectively. Co(II) atoms usually exhibit an octahedral geometry in their coordination polymers,[10] in particular, the Co(II) atoms in a related hybrid open framework consisting of both carboxylate bridges and μ_3-hydroxy bridges found[10c] in $[Co_5(C_4H_4O_4)_4(OH)_2]_n$ exhibit uniquely octahedral coordinations. Although cobalt(II) atoms in alternative octahedral and tetrahedral geometries or octahedral and square-pyramidal geometry have been reported in one-dimensional chain,[15] two-dimensional[9] and three-dimensional structures,[9] to the best of our knowledge, **1** is the first example of a three-dimensional open framework with both carboxylate bridges and μ_3-hydroxy bridges adopting different coordination geometries. The penta-coordination of Co(4) in **1** may be, at least in part, attributed to the two μ_3-OH bridges, which are stronger donors than carboxylate oxygen atoms, hence decreasing the coordination number. Meanwhile, the molar ratio of metal : succinate : hydroxide is also important, the higher molar ratio for **1** compared to those in the related complexes (4 : 3 : 2 and 5 : 4 : 2)[10c,d] may play a role in the formation of the penta-coordination.

Magnetic properties

The temperature dependence of the magnetic susceptibility in the temperature range 2–300 K under a 10 kOe applied field was studied for **1**. As illustrated in Fig. 3, the effective magnetic moment per mol (μ_{eff}) for **1** at room temperature is 13.81 μ_B, which is significantly higher than the spin-only number of 11.61 μ_B for a high-spin d^7 trimer, indicates that the cobalt(II) atoms experience substantial orbital contribution to the magnetic moment.[10a] On lowering the temperature, μ_{eff} decreases from 13.81 μ_B at 300.1 K to 4.77 μ_B at 1.96 K per trimer complex. Above 26 K, the magnetic data follow the Curie–Weiss law with C = 32.08 cm^3 K mol^{-1}, and θ = −93.33 K. The facts suggest that there is a strong antiferromagnetic interaction between the cobalt(II) ions. The magnetic behaviour is different from a related cobalt(II) coordination polymer with carboxylate and hydroxide ligands, which exhibits both strong antiferromagnetic interactions within the layer and weak ferromagnetic interactions within the tetranuclear subunit.[10c,d]

In conclusion, we report here a three-dimensional inorganic–organic hybrid material with mixed hexa- and penta-coordinate cobalt(II) sites, in which the metal atoms are strongly antiferromagnetically coupled. We also show that both two μ_3-OH bridges and the high metal : succinate : hydroxide ratio are important for the formation of penta-coordinate cobalt(II) sites in the material.

Acknowledgements

This work was supported by NFSC and Xiamen University (Y07015).

References

1 M. J. Zaworotko, *Nature*, 1997, **386**, 220; T. E. Mallouk, *Nature*, 1997, **387**, 350; G. B. Gardner, D. Venkataraman, J. S. Moore and S. Lee, *Nature*, 1995, **374**, 729; O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703; H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.
2 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; C. R. Kagan, D. B. Mitzi and C. D. Dimitrakopoulos, *Science*, 1999, **286**, 954.
3 C. L. Bowes and G. A. Ozin, *Adv. Mater.*, 1996, **8**, 13; P. S. Halasyamani, M. J. Drewitt and D. O'Hare, *Chem. Commun.*, 1997, 867; P. J. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2634.
4 B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727; M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
5 T. Soma, H. Yuge and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1665; R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.
6 S. Subramanian and M. Zaworotoko, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2127.
7 D. E. De Vos, F. Thibault-Starzyk and P. A. Jacobs, *Angew. Chem., Intl. Ed. Engl.*, 1994, **33**, 431; A. L. Balch, M. Mazzanti, T. M. St. Claire and M. M. Olmstead, *Inorg. Chem.*, 1995, **34**, 2194; A. L. Balch, M. Mazzanti and M. M. Olmstead, *J. Chem. Soc., Chem. Commun.*, 1994, 269.
8 B. L. Chen, M. Eddaoudi, T. M. Reinke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559.
9 A. Disler, D. L. Lohse and S. C. Sevov, *J. Chem. Soc., Dalton Trans.*, 1999, 1085.
10 (*a*) S. O. H. Guts, M. Molinier, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 991; (*b*) A. Distler and S. Sevov, *Chem. Commun.*, 1998, 959; (*c*) C. Livage, C. Egger and G. Férey, *Chem. Mater.*, 1999, **11**, 1546; (*d*) C. Livage, C. Egger, M. Nogus and G. Férey, *J. Mater. Chem.*, 1998, **8**, 2743.
11 G. M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination, University of Göttingen, Germany, 1997.
12 G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinment, University of Göttingen, Germany, 1997.
13 *International Tables for Crystallography*, Kluwer Academic Publishers, Dordrecht, 1992, vol. C, 4.2.6.8 and 6.1.1.4.
14 G. M. Sheldrick, SHELXTL-PC, Program Package for X-ray Crystal Structure Determination, Siemens Analytical X-ray Instruments, Inc., Karlsruhe, Germany, 1990.
15 J.-C. Hierso, D. D. Ellis, A. L. Spek, E. Bouwman and J. Reedijk, *Chem. Commun.*, 2000, 1359.