

Ionothermal Synthesis and Crystal Structure of a Neutral 2D Metal-Organic Framework Based on Cobalt(II) 1,2,3-Benzenetricarboxylate

Shun Shun Liu, Rui Min Zhou, Shuai Chen, Yan Bai, and Dong Bin Dang

Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China

Reprint requests to Yan Bai or Dong Bin Dang. Fax: +86-371-23881589.

E-mail: baiban@henu.edu.cn or dangdb@henu.edu.cn

Z. Naturforsch. **2014**, *69b*, 864–870 / DOI: 10.5560/ZNB.2014-4091

Received April 13, 2014

A neutral metal-organic framework [CoNa₃(1,2,3-H₃btb)(1,2,3-btb)] (**1**) has been synthesized through an ionothermal method using 1-ethyl-3-methylimidazolium bromide as solvent (1,2,3-H₃btb = 1,2,3-benzenetricarboxylic acid). The complex has been characterized by IR spectroscopy, elemental analysis, PXRD and single-crystal X-ray diffraction. The structure of **1** exhibits a layer network structure in which Co(II) is five-coordinated forming a distorted trigonal bipyramid. Na1 and Na3 are surrounded by seven oxygen atoms, and Na2 is six-coordinated. In the structure, the anions of 1,2,3-H₃btb are embedded in two bridging μ_8 coordination modes. The luminescence properties of **1** have been investigated in the solid state at room temperature.

Key words: Metal-Organic Framework, Ionothermal Reaction, Crystal Structure, Luminescence Properties

Introduction

In coordination chemistry, the synthesis and exploitation of metal-organic frameworks (MOFs) with various intriguing structures constitute one of the most exciting developments during the past decades because of their special functional properties such as chirality, luminescence, redox activity, and magnetism [1–4]. In comparison with aqueous solutions and/or typical organic solvents, ionic liquids (ILs) have many outstanding physicochemical properties, such as non-flammability, negligible vapor pressure, high ionic conductivity, excellent dissolving capacity, and thermostability [5–7]. Since the first three-dimensional MOF [Cu₃(tpt)₄](BF₄)₃·(TPT)_{2/3}·5H₂O (TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine) was reported by Kim *et al.* in 2004 using [BMIm][BF₄] (BMIm = 1-butyl-3-methylimidazolium) as solvent [8], ionothermal syntheses as promising methods to prepare functional MOFs have received remarkable attention. The ILs function as reaction media, structure templates or charge-compensating groups [9, 10].

By means of ionothermal synthesis, although a number of monometal MOFs have been re-

ported in the literature, the preparation of heteronuclear MOFs is rare because of the versatile coordination behavior. In two cases of ionothermal synthesis, the heterometallic organic frameworks {[EMIM]₂[InK(1,2,4,5-btc)_{1.5}·(H₂O)₂]}_n [11] reported in 2012, and [(EMIM)NaCu(1,4-ndc)₂]_n [12] reported in 2013, the [EMIM]⁺ cations act as extra charge-balancing species occupying the channels of the 3D anionic frameworks. For most MOFs synthesized by the ionothermal method, the ILs function as solvents, templates and reactants at the same time. Their structures always consist of anionic coordination frameworks with the cations of the ILs playing a charge-compensating and space-filling role. So far, it is still a challenge to design and construct neutral frameworks under ionothermal condition [13].

Multicarboxylate ligands as suitable spacers, especially arene-multicarboxylate ligands, are frequently chosen for constructing MOFs with fascinating aesthetically pleasing structures. So far, investigations have been mainly devoted to the use of benzene-multicarboxylate ligands with high symmetry, such as 1,4-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, or 1,2,4,5-benzenetetracarboxylate [14–16]. In

comparison, there are only few examples of coordination frameworks derived from the less symmetrical 1,2,3-benzenetricarboxylic acid (1,2,3-H₃btb) due to the steric hindrance of the three carboxylate groups and the multiplicity of the dihedral angles between the planes of the carboxylate groups and the phenyl ring plane [17–23]. All of 1,2,3-H₃btb-based metal-organic frameworks were synthesized in hydrothermal reactions or through evolution methods, but none in ionothermal synthesis. Moreover, heterometallic frameworks based on 1,2,3-H₃btb are generally rather rare [17]. In this manuscript, we report the preparation of a neutral heterometallic framework [CoNa₃(1,2,3-H₃btb)(1,2,3-btb)] (**1**) using 1-ethyl-3-methylimidazolium bromide ([EMIM]Br) as the solvent, which is in sharp contrast to the above two anionic heterometallic frameworks [11, 12].

Results and Discussion

Complex **1** was synthesized from a mixture of 1,2,3-benzenetricarboxylic acid, Co(NO₃)·6H₂O, NaOH, and [EMIM]Br sealed in a Teflon-lined stainless-steel bomb and heated to 160° for 120 h.

IR spectra

The IR spectrum of **1** exhibits the characteristic bands of carboxylate groups. Two strong broad bands at 1623 and 1580 cm⁻¹ show the antisymmetric stretching $\nu_{as}(\text{CO}_2)$, and the bands at 1459 and 1386 cm⁻¹ are assigned to the symmetric stretching frequencies $\nu_s(\text{CO}_2)$. This result indicates that the carboxylate groups of the ligands function in different coordination modes, which agrees well with the data of other relevant compounds [18, 19]. The bands which appear at 1708 and 1264 cm⁻¹ can be attributed to $\nu(\text{C}=\text{O})$ and $\nu(\text{CO})$, respectively, indicating the existence of a non-coordinated carboxylate group. Their identity was finally confirmed by X-ray crystallography.

Crystal and molecular structure

Single-crystal X-ray diffraction analysis has revealed that the structure of **1** exhibits a crystalline 2D metal-organic framework, in which the di- and the tri-anion of 1,2,3-H₃btb are embedded in two different coordination modes. Complex **1** crystallizes in the mono-

clinic space group $P\bar{1}$. An ORTEP diagram of **1** with the atomic numbering scheme and coordination environments of the Co(II) and Na(I) centers is depicted in Fig. 1. The asymmetric unit consists of one Co(II) ion, three Na(I) ions, one 1,2,3-btb³⁻ and one 1,2,3-H₃btb²⁻ ligand. The Co1 atom is coordinated by five oxygen atoms (O1A, O2A, O3, O9, O12B) of two 1,2,3-btb³⁻ and two 1,2,3-H₃btb²⁻ ligands forming a distorted trigonal bipyramid with the value of the topological parameter τ of 0.70 [24]. The average Co1-O distance is 2.09 Å, and the bond angles of adjacent donors around Co1 are in the range from 101.6° to 121.4°.

As a significant aspect of the structure of **1**, there are three crystallographically independent Na(I) centers, of which Na1 and Na3 are surrounded by seven oxygen atoms, while Na2 is six-coordinated. The seven neighbors around the Na1 atom include two chelating carboxylate groups from two 1,2,3-btb³⁻ anions (O3, O4, O5C, O6C), one monodentate carboxylate oxygen atom (O8E), and two oxygen atoms (O10D, O11D) of two adjacent carboxylate groups from two 1,2,3-H₃btb²⁻ ligands. The Na(1)-O distances are in the range of 2.2907(16) to 2.7354(16) Å. The Na2 atom is located in a distorted octahedral coordination geometry with an O₆ set from three 1,2,3-btb³⁻ ligands (O2E, O4E, O4F, O5F, O5D) and one 1,2,3-H₃btb²⁻ ligand (O10). Na3 binds to seven oxygen atoms from one 1,2,3-H₃btb²⁻ ligand (O2E, O3E) and three 1,2,3-btb³⁻ ligands (O9, O10, O9D, O11B, O11D). The Na2-O and Na3-O bond lengths

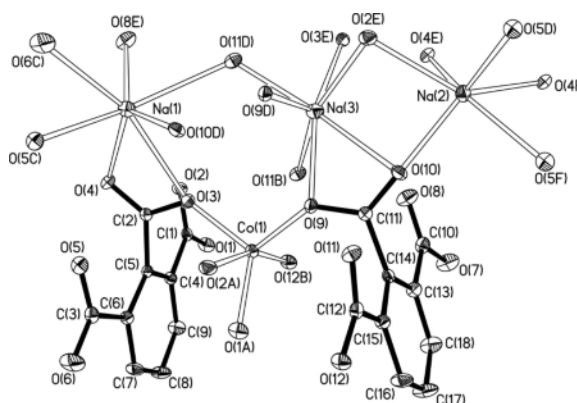


Fig. 1. ORTEP drawing of **1** with the atom numbering scheme. The atoms are represented by 30% probability displacement ellipsoids, and all hydrogen atoms are omitted for clarity. Symmetry codes as given in Table 2.

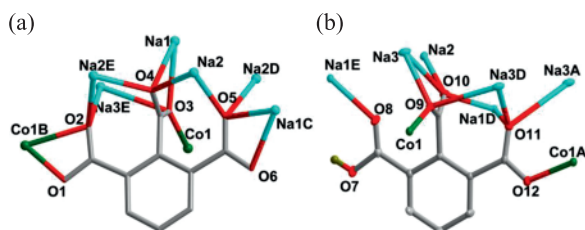


Fig. 2 (color online). Two kinds of the μ_8 coordination modes of the ligands in **1**: (a) 1,2,3- btb^{3-} , (b) 1,2,3-H btb^{2-} . Symmetry codes as given in Table 2.

are in the ranges of 2.3534(15)–2.5209(16) Å and 2.2809(16)–2.8527(17) Å, respectively.

In the asymmetric unit of **1**, the anions of 1,2,3- H_3btb serve as bridging ligands, $\mu_8\text{-}\kappa^1, \kappa^3, \kappa^3, \kappa^3, \kappa^3, \kappa^1$ (1,2,3- btb^{3-}) and $\mu_8\text{-}\kappa^1, \kappa^3, \kappa^3, \kappa^3, \kappa^1$ (1,2,3-H btb^{2-}) (Fig. 2). In 1,2,3- btb^{3-} , O1 and O2 are coordinated to Co1B forming a bidentate chelate structure; besides, O2 is also bound to Na2E and Na3E centers. O3 and O4 of the middle carboxylate group not only chelate the Na1 center, but are also connected with Co1 and Na3E (for O3), and with Na2 and Na2E (for O4). The two oxygen donors O5 and O6 of the third carboxylate group are bound to three different metal centers (Na1C, Na2 and Na2D). In the 1,2,3-H btb^{2-} ligand, only two of the three carboxylate groups are deprotonated. The dianion links two Co atoms (Co1, Co1A) with a Co···Co distance of 6.32 Å and six Na atoms (Na1D, Na1E, Na2, Na3, Na3A, Na3D). The

carboxyl group containing O7 and O8 is not deprotonated and is bound to the Na1E center using only the O8 atom. The coordination mode of the deprotonated carboxylate group with O9 and O10 is similar to that of O3 and O4. From the last deprotonated carboxylate group, O11 is coordinated to three Na centers (Na1D, Na3A and Na3D), and O12 is only bound to Co1A. To sum up, two 1,2,3- btb^{3-} and 1,2,3-H btb^{2-} ligands both exhibit unique bridging coordination modes.

Based on these connection modes, all Co(II) and Na(I) centers are linked by seven kinds of $\mu_3\text{-O}$ atoms (O2, O3, O4, O5, O9, O10, O11) of the two ligands to form a 2D coordination network (Fig. 3). Adjacent Co1, Na2 and Na3 atoms are linked through $\mu_3\text{-O2}$. Co1, Na1 and Na3 centers are bridged by $\mu_3\text{-O3}$, while Co1, Na3 and Na3 centers are bridged by $\mu_3\text{-O9}$. Adjacent Na centers are bridged by four kinds of $\mu_3\text{-O}$ atoms (O4, O5, O10, O11) with two kinds of $\mu_3\text{-O}$ atoms (O4, O5) linking one Na1 and two Na2 atoms. The atom $\mu_3\text{-O10}$ links Na1, Na2 and Na3 atoms while $\mu_3\text{-O11}$ links one Na1 and two Na3 atoms. The average Na···Na distances are 3.65, 3.92, 3.47, and 3.78 Å for Na(1)···Na(2), Na(1)···Na(3), Na(2)···Na(3) and Na(3)···Na(3), respectively. Hydrogen bonds O(7)–H(7C)···O(6) also play a role in stabilizing the network.

There are four types of intramolecular C–H···O hydrogen bonds in the crystal structure of **1** with the average C···O separations of 2.73 Å and C–H···O angles of 101.5° (Fig. 4). Although these interactions

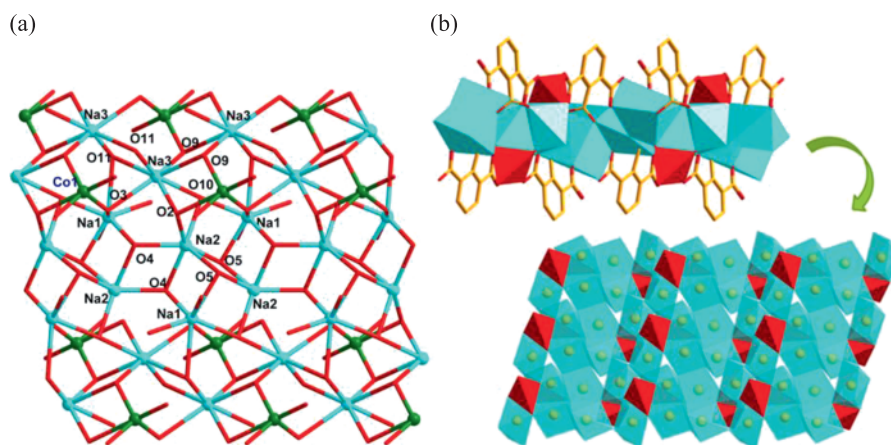


Fig. 3 (color online). (a) View of a Co-Na-H btb^{2-} - btb^{3-} layer, all hydrogen atoms and carbon atoms are omitted for clarity. Color codes: Co, green; Na, turquoise; O, red. (b) Views of a Co-Na-H btb^{2-} - btb^{3-} layer (top) and a Co/Na layer (bottom). Color codes: Co, red polyhedra; Na, turquoise polyhedra.

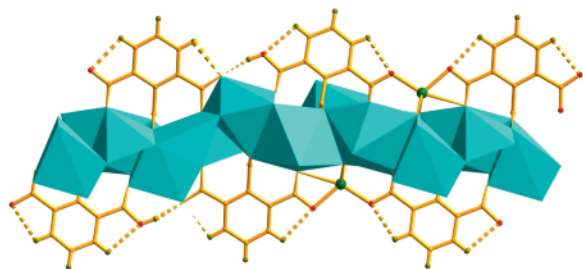


Fig. 4 (color online). Illustration of a layer in **1** with hydrogen bonds in dashed lines. Color code: Co, green; Na, turquoise polyhedra.

are weak compared to the metal-oxygen coordination bonds and O-H...O hydrogen bonds, it is suggested that these interactions are relevant for the molecular packing [25, 26].

Powder X-ray diffraction

The structure of the bulk materials was studied by powder X-ray diffraction (PXRD). As shown in Fig. 5, the experimental PXRD pattern of the bulk product of **1** is in good agreement with the PXRD pattern simulated from single-crystal X-ray diffraction data, indicating the phase purity of the sample. The intensity difference between experimental and simulated PXRD patterns is due to the variations in the preferred orientations of the powder sample during collection of the experimental PXRD.

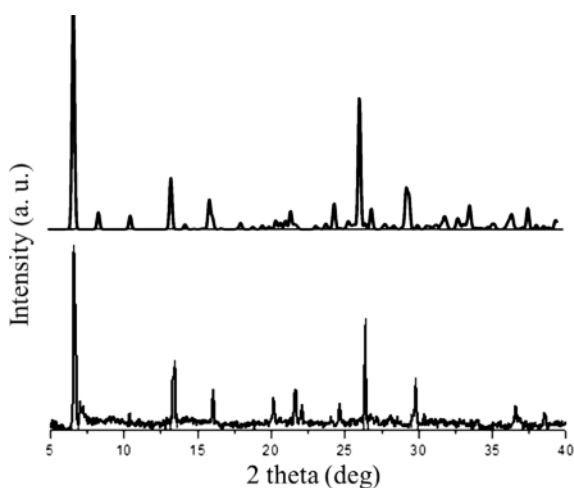


Fig. 5. Powder X-ray diffraction pattern as calculated from the single-crystal data for **1** (top) and experimental pattern of a sample (bottom).

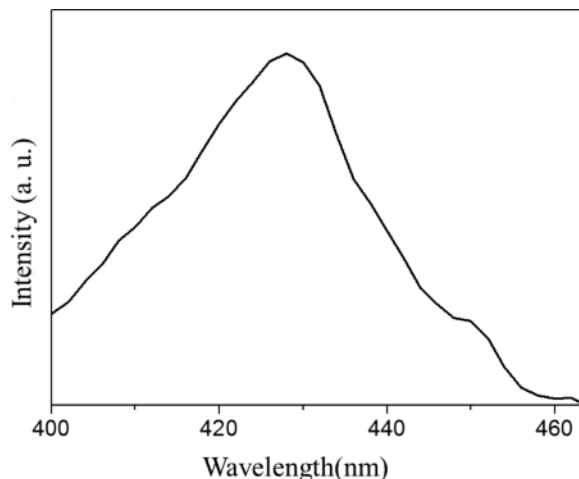


Fig. 6. The emission spectrum of **1** in the solid state at room temperature ($\lambda_{\text{ex}} = 312$ nm).

Luminescence properties

The solid-state luminescence properties of **1** were investigated at room temperature (Fig. 6). Upon excitation at 312 nm, the maximum emission peak at 427 nm is comparable to that of related complexes,

Table 1. Summary of crystal data and data collection and structure refinement results of **1**.

Empirical formula	$\text{C}_{18}\text{H}_7\text{CoNa}_3\text{O}_{12}$
M_r	543.14
Crystal size, mm^3	$0.46 \times 0.31 \times 0.12$
Crystal system	triclinic
Space group	$P\bar{1}$
a , Å	6.3218(3)
b , Å	10.7689(5)
c , Å	13.2433(7)
α , deg	90.876(1)
β , deg	93.451(1)
γ , deg	102.480(1)
Volume, Å ³	878.32(7)
Z	2
$D_{\text{calcd.}}$, $\text{g}\cdot\text{cm}^{-3}$	2.05
μ , mm^{-1}	1.7
$F(000)$, e	542
θ range data collection	1.94–25.05
hkl range	$-6 \leq h \leq 7; -12 \leq k \leq 10; -15 \leq l \leq 14$
Refl.s collected/unique/ R_{int}	4577/2918/0.0176
Param. refined	307
$R(F)/wR(F^2)^a$ (all refls.)	0.0246/0.0645
GoF (F^2) ^a	1.049
$\Delta\rho_{\text{fin}}$ (max/min), $\text{e}\cdot\text{Å}^{-3}$	0.30/−0.35

Bond lengths (Å)				Table 2. Selected bond lengths (Å) and bond angles (deg) of 1 ^a .
Co(1)–O(1A)	1.9997(14)	Co(1)–O(3)	2.0124(13)	
Co(1)–O(2A)	2.4808(18)	Co(1)–O(9)	1.9971(13)	
Co(1)–O(12B)	1.9805(13)	Na(1)–O(3)	2.6663(15)	
Na(1)–O(4)	2.4304(15)	Na(1)–O(5C)	2.4859(15)	
Na(1)–O(6C)	2.5445(18)	Na(1)–O(8E)	2.2907(16)	
Na(1)–O(10D)	2.3209(15)	Na(1)–O(11D)	2.7354(16)	
Na(2)–O(2E)	2.5209(16)	Na(2)–O(4E)	2.3610(15)	
Na(2)–O(4F)	2.4385(15)	Na(2)–O(5D)	2.3534(15)	
Na(2)–O(5F)	2.4782(16)	Na(2)–O(10)	2.3817(15)	
Na(3)–O(2E)	2.3071(17)	Na(3)–O(3E)	2.7766(16)	
Na(3)–O(9)	2.2929(15)	Na(3)–O(9D)	2.7935(16)	
Na(3)–O(10)	2.7227(16)	Na(3)–O(11D)	2.2809(16)	
Na(3)–O(11B)	2.8527(17)			
Bond angles (deg)				
O(1A)–Co(1)–O(3)	121.43(6)	O(1A)–Co(1)–O(9)	111.71(6)	
O(1A)–Co(1)–O(12B)	106.65(5)	O(3)–Co(1)–O(9)	110.07(5)	
O(3)–Co(1)–O(12B)	101.61(6)	O(9)–Co(1)–O(12B)	103.20(6)	
O(3)–Na(1)–O(4)	50.98(4)	O(3)–Na(1)–O(5C)	107.98(5)	
O(3)–Na(1)–O(6C)	159.94(5)	O(3)–Na(1)–O(8E)	116.61(6)	
O(3)–Na(1)–O(10D)	76.76(5)	O(3)–Na(1)–O(11D)	80.91(4)	
O(4)–Na(1)–O(5C)	87.67(5)	O(4)–Na(1)–O(6C)	121.34(6)	
O(4)–Na(1)–O(8E)	94.23(6)	O(4)–Na(1)–O(10D)	120.95(5)	
O(4)–Na(1)–O(11D)	116.12(6)	O(5C)–Na(1)–O(6C)	51.99(5)	
O(5C)–Na(1)–O(8E)	123.36(6)	O(5C)–Na(1)–O(10D)	84.01(5)	
O(5C)–Na(1)–O(11D)	151.85(5)	O(2E)–Na(2)–O(4E)	71.22(5)	
O(2E)–Na(2)–O(4F)	137.08(5)	O(2E)–Na(2)–O(5D)	86.93(5)	
O(2E)–Na(2)–O(5F)	147.63(5)	O(2E)–Na(2)–O(10)	137.08(5)	
O(4E)–Na(2)–O(4F)	73.60(5)	O(4E)–Na(2)–O(5D)	120.81(6)	
O(4E)–Na(2)–O(5F)	140.77(5)	O(4E)–Na(2)–O(10)	110.83(5)	
O(4F)–Na(2)–O(5D)	90.56(5)	O(4F)–Na(2)–O(5F)	72.53(5)	
O(4F)–Na(2)–O(10)	138.33(6)	O(5D)–Na(2)–O(5F)	78.76(6)	
O(5D)–Na(2)–O(10)	117.46(6)	O(5F)–Na(2)–O(10)	82.93(5)	
O(2E)–Na(3)–O(3E)	77.42(5)	O(2E)–Na(3)–O(9)	120.81(6)	
O(2E)–Na(3)–O(9D)	69.90(5)	O(2E)–Na(3)–O(10)	75.39(5)	
O(2E)–Na(3)–O(11B)	149.70(6)	O(2E)–Na(3)–O(11D)	97.80(6)	
O(3E)–Na(3)–O(9)	149.26(6)	O(3E)–Na(3)–O(9D)	132.85(5)	
O(3E)–Na(3)–O(10)	122.04(5)	O(3E)–Na(3)–O(11B)	77.01(5)	
O(3E)–Na(3)–O(11D)	76.83(5)	O(9)–Na(3)–O(9D)	77.86(5)	
O(9)–Na(3)–O(10)	51.32(4)	O(9)–Na(3)–O(11B)	77.01(5)	
O(9)–Na(3)–O(11D)	120.20(6)	O(9D)–Na(3)–O(10)	81.59(5)	
O(9D)–Na(3)–O(11B)	140.38(5)	O(9D)–Na(3)–O(11D)	75.05(5)	
O(10)–Na(3)–O(11B)	105.23(5)	O(10)–Na(3)–O(11D)	156.57(6)	
O(11B)–Na(3)–O(11D)	91.95(5)			

^a Symmetry codes: A, $1+x, y, z$; B, $-1+x, y, z$; C, $1-x, 1-y, -z$; D, $1-x, -y, -z$; E, $-x, -y, -z$; F, $x, -1+y, z$.

and can be assigned to ligand-to-metal charge transfer (LMCT) [17].

Conclusion

In summary, a novel neutral 2D metal-organic framework [CoNa₃(1,2,3-H₃btb)(1,2,3-btb)] **1** has been obtained by a ionothermal reaction in an imidazolium-based ionic liquid as solvent. The structure of **1**

displays an intriguing layer network in which the anions of 1,2,3-H₃btb are embedded in two μ_8 -bridging coordination modes. The Co atom is five-coordinated forming a distorted trigonal bipyramid; Na1 and Na3 are surrounded by sets of seven oxygen atoms, and Na2 is six-coordinated. Because ionothermal syntheses are efficient and environmentally benign, we believe that this strategy is very promising in the design and construction of functional metal-

D-H...A	D-H	H...A	D...A	∠(DHA)	Symmetry transformation for A
O(7)–H(7C)···O(6)	0.85	1.78	2.614(2)	168	$-1+x, -1+y, z$
C(7)–H(7A)···O(6)	0.93	2.41	2.736(3)	100	
C(9)–H(9A)···O(1)	0.93	2.41	2.749(2)	101	
C(16)–H(16A)···O(12)	0.93	2.41	2.732(3)	100	
C(18)–H(18A)···O(7)	0.93	2.39	2.718(3)	101	

Table 3. Hydrogen bond parameters (Å, deg) of **1**.

organic frameworks. Further such studies are currently underway.

Experimental Section

General

Materials: All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

Instrumentation: Elemental analysis (C, H) was carried out on a Perkin-Elmer 240C analytical instrument. The IR spectrum was recorded in a KBr pellet with a Nicolet 170 SXFT-IR spectrophotometer in the $4000 \sim 400 \text{ cm}^{-1}$ region. The powder X-ray diffraction pattern was recorded on a D/max- γ A rotating anode X-ray diffractometer with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$). The luminescence spectrum was recorded on a Hitachi F-7000 fluorescence spectrophotometer.

Synthesis of **1**

Compound **1** was synthesized by the ionothermal method. A mixture of 1,2,3-benzenetricarboxylic acid (0.103 g, 0.5 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.852 g, 3.0 mmol), NaOH (0.066 g, 1.5 mmol), and [EMIM]Br (0.996 g) was sealed in a 30-mL Teflon-lined stainless-steel bomb and heated at $160 \text{ }^\circ\text{C}$ for 120 h. Then the autoclave was cooled to room temperature, and blue-purple block-shaped crystals were isolated and washed with ethanol. Yield: 62%. – Anal. for $\text{C}_{18}\text{H}_7\text{CoNa}_3\text{O}_{12}$ (543.14): calcd. C 39.80, H 1.30; found C 39.67, H 1.25. – IR (cm^{-1} , KBr pellet): $\nu = 3419(\text{m}), 3050(\text{w}), 2980(\text{w}), 2921(\text{w}), 1708(\text{m}), 1623(\text{s}), 1580(\text{s}),$

$1459(\text{s}), 1408(\text{m}), 1386(\text{s}), 1384(\text{s}), 1264(\text{m}), 1167(\text{w}), 1070(\text{m}), 934(\text{m}), 884(\text{w}), 801(\text{m}), 764(\text{w}), 715(\text{m}), 680(\text{w}), 570(\text{w}), 473(\text{w}).$

X-Ray crystallographic studies

A suitable single crystal of size $0.46 \times 0.31 \times 0.12 \text{ mm}^3$ was chosen for the crystallographic study and mounted on a Bruker Smart APEX II CCD diffractometer with ω and ϕ scan mode in the range of $1.94^\circ < \theta < 25.05^\circ$. All diffraction measurements were performed at room temperature using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by Direct Methods and refined on F^2 by using full-matrix least-squares methods with the SHELXS/L-97 program system [27, 28]. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. Space group, lattice parameters and other relevant information are presented in Table 1. Important bond lengths and bond angles are summarized in Table 2.

CCDC 978749 (**1**) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

This work was supported by Innovation Scientists and Technicians Troop Construction Projects of Henan Province, the Natural Science Foundation of Henan Province and the Foundation of the Education Department of Henan Province of China.

- | | |
|---|--|
| <p>[1] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, <i>Chem. Rev.</i> 2012, <i>112</i>, 1105–1125.</p> <p>[2] M. O’Keeffe, O. M. Yaghi, <i>Chem. Rev.</i> 2012, <i>112</i>, 675–702.</p> <p>[3] G. Q. Kong, S. Ou, C. Zou, C. D. Wu, <i>J. Am. Chem. Soc.</i> 2012, <i>134</i>, 19851–19857.</p> | <p>[4] D. B. Dang, B. An, Y. Bai, G. S. Zheng, J. Y. Niu, <i>Chem. Commun.</i> 2013, <i>49</i>, 2243–2245.</p> <p>[5] D. Freudenmann, S. Wolf, M. Wolff, C. Feldmann, <i>Angew. Chem. Int. Ed.</i> 2011, <i>50</i>, 11050–11060.</p> <p>[6] E. Ahmed, M. Ruck, <i>Dalton Trans.</i> 2011, <i>40</i>, 9347–9357.</p> <p>[7] E. R. Parnham, R. E. Morris, <i>Acc. Chem. Res.</i> 2007, <i>40</i>, 1005–1013.</p> |
|---|--|

- [8] D. N. Dybtsev, H. Chun, K. Kim, *Chem. Commun.* **2004**, 1594–1595.
- [9] Z. Q. Jiang, G. Y. Jiang, D. C. Hou, F. Wang, Z. Zhao, J. Zhang, *CrystEngComm* **2013**, *15*, 315–323.
- [10] W. J. Ji, Q. G. Zhai, S. N. Li, Y. C. Jiang, M. C. Hu, *Chem. Commun.* **2011**, *47*, 3834–3836.
- [11] W. J. Ji, Q. G. Zhai, S. N. Li, Y. C. Jiang, M. C. Hu, *Inorg. Chem. Commun.* **2012**, *24*, 209–211.
- [12] Q. Y. Liu, W. L. Xiong, C. M. Liu, Y. L. Wang, J. J. Wei, Z. J. Xiahou, L. H. Xiong, *Inorg. Chem.* **2013**, *52*, 6773–6775.
- [13] T. Hogben, R. E. Douthwaite, L. J. Gillie, A. C. Whitwood, *CrystEngComm* **2006**, *8*, 866–868.
- [14] O. Kozachuk, K. Khaletskaya, M. Halbherr, A. Bétard, M. Meilikhov, R. W. Seidel, B. Jee, A. Pöpl, R. A. Fischer, *Eur. J. Inorg. Chem.* **2012**, 1688–1695.
- [15] C. Dey, R. Das, B. K. Saha, P. Poddar, R. Banerjee, *Chem. Commun.* **2011**, *47*, 11008–11010.
- [16] S. S. Chen, Y. Zhao, J. Fan, T. A. Okamura, Z. S. Bai, Z. H. Chen, W. Y. Sun, *CrystEngComm* **2012**, *14*, 3564–3576.
- [17] L. Xu, B. Liu, G. Guo, J. S. Huang, *Inorg. Chem. Commun.* **2006**, *9*, 220–222.
- [18] H. A. Habib, J. Sanchiz, C. Janiak, *Dalton Trans.* **2008**, 4877–4884.
- [19] K. Akhbari, A. Morsali, *Inorg. Chim. Acta* **2009**, *362*, 1692–1700.
- [20] S. O. H. Gutschke, D. J. Price, A. K. Powell, P. T. Wood, *Angew. Chem. Int. Ed.* **2001**, *40*, 1920–1923.
- [21] L. F. Ma, C. P. Li, L. Y. Wang, M. Du, *Cryst. Growth Des.* **2011**, *11*, 3309–3312.
- [22] L. F. Ma, J. H. Qin, M. L. Han, L. Y. Wang, M. Du, *Inorg. Chem. Commun.* **2011**, *14*, 1584–1587.
- [23] W. Liu, J. Yu, J. Jiang, L. Yuan, B. Xu, Q. Liu, B. Qu, G. Zhang, C. Yan, *CrystEngComm* **2011**, *13*, 2764–2773.
- [24] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955–964.
- [25] D. B. Dang, M. M. Li, Y. Bai, R. Q. Ning, *Synth. Met.* **2012**, *162*, 2075–2080.
- [26] L. Y. Jin, M. M. Li, D. B. Dang, Y. Bai, Y. N. Zheng, *Z. Naturforsch.* **2013**, *68b*, 284–288.
- [27] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**.
- [28] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.