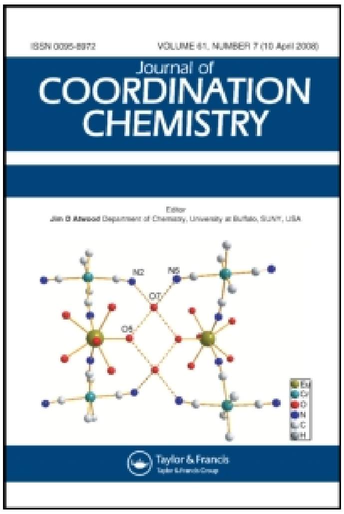

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Synthesis, crystal structure and luminescence of a 3-D coordination polymer based on 4-(1H-tetrazol-5-yl) benzoic acid

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Synthesis, crystal structure and luminescence of a 3-D coordination polymer based on 4-(1H-tetrazol-5-yl) benzoic acid

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A cobalt(II) coordination polymer [Co(4-TZBA^{2-})(H_2O)$_2$] (**1**) was obtained by treatment of $Co(ClO_4)_2 \cdot 6H_2O$ with 4-(1H-tetrazol-5-yl)benzoic acid [H_2(4-TZBA)] under hydrothermal conditions. The X-ray single crystal diffraction analysis reveals that **1** crystallizes in monoclinic $P2_1/c$, with $a = 10.503(2)$ Å, $b = 9.0860(18)$ Å, $c = 10.179(2)$ Å, $\beta = 96.75(3)^\circ$ and $Z = 4$. In **1**, adjacent cobalt(II) atoms are bridged by two 4-TZBA^{2-} ligands to form a dimer, which is linked with six dimers to result in a 3-D structure. **1** exhibits strong luminescence at room temperature in the solid state.

Keywords: Hydrothermal conditions; Tetrazolate; Metal-organic frameworks; Luminescence

1. Introduction

Metal-organic frameworks (MOFs) have received interest because of their topological diversity and potential applications in gas storage [1], catalysis [2], luminescence [3], magnetism [4] and non-linear optics (NLO) [5]. The functions of metal-organic frameworks (MOFs) come from their topological diversity. Compounds with one-, two- or three-dimensional networks can be obtained via a combination of metal centers (or metal clusters) with organic spacers. Organic spacers are of great importance in construction of metal-organic frameworks (MOFs) because of variation in flexibility, length and symmetry. Many types of organic spacers, such as polycarboxylates and heterocycles [6], have been used for metal-organic frameworks. Recently, chemists have focused their interest on ligands containing tetrazolate due to their aromaticity and multiple *N*-donor atoms; a number of metal-organic frameworks based on 5-substituted tetrazoles have been reported [7]. Rarely have metal-tetrazole coordination polymers built by 5-(carboxylatophenyl)-tetrazole been reported [8]. Our previous work showed that 5-substituted tetrazolate ligands could be used to construct coordination

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polymers [9]. In this article, we report the synthesis, crystal structure and luminescence of [Co(4-TZBA^{2-})(H_2O)$_2$] (**1**).

2. Experimental

2.1. *Materials and general methods*

Cobalt perchlorate hexahydrate was prepared by reaction of cobalt carbonate with perchloric acid. 4-(1H-tetrazol-5-yl)benzoic acid [H_2(4-TZBA)] was synthesized according to the literature [10]. All other chemicals were AR grade. Elemental analyses (C, N, H) were performed by using an Elementar Vario ELIII elemental analyzer. IR spectra as KBr discs were recorded with a Bruker VECTOR-22 FT-IR spectrophotometer. Thermal gravimetric analysis was performed with a Shimadzu TGA-50H Thermal Gravimetric Analyzer at a heating of 5°C min^{-1}. Excitation and emission spectra were recorded with a Perkin–Elmer LS55 luminescence spectrometer.

Caution: $Co(ClO_4)_2 \cdot 6H_2O$ is potentially explosive and should be used with care!!

2.2. *Synthesis of [Co(4-TZBA^{2-})(H_2O)$_2$] (1)*

A mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (37 mg, 0.1 mmol), H_2(4-TZBA) (19 mg, 0.1 mmol), H_2O (0.4 mL) and pyridine (0.1 mL) was placed in a heavy-walled Pyrex tube. This tube was frozen in liquid nitrogen, sealed under vacuum, and placed in an oven at 120°C for 12 h. Red shuttle-like crystals of **1** were obtained (60%, based on $Co(ClO_4)_2 \cdot 6H_2O$). $C_8H_8CoN_4O_4$ (283.11): Calcd C, 33.91; H, 2.83; N, 19.78, Found: C, 33.61; H, 2.77; N, 19.31. IR (KBr, cm^{-1}): 3396.43(w), 1590.82(m), 1538.28(s), 1397.61(s), 1010.61(m), 819.14(m), 749.01(m).

2.3. *X-ray crystallography*

X-ray single-crystal diffraction data for **1** were collected on a Siemens SMART CCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature (293 K). The structure was solved using direct methods and refined by full-matrix least-squares using the SHELXTL crystallographic software package [11]. All non-hydrogen atoms were refined by anisotropic thermal parameters. All hydrogen atoms were generated geometrically and treated as riding. CCDC 664482 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. Tables 1 and 2 summarize the crystal details and selected bond distances and angles.

3. Results and discussion

3.1. *Description of the structure*

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in monoclinic $P2_1/c$. The asymmetric unit contains one Co(II), one 4-TZBA^{2-} ligand and two water

Table 1. Crystal data and structure refinement for **1**.

Compound	**1**
Empirical formula	$C_8H_8CoN_4O_4$
Formula weight	283.11
Crystal system	Monoclinic
Space group	$P2_1/c$
Units of cell dimenions (°, Å)	
a	10.503(2)
b	9.0860(18)
c	10.179(2)
β	96.75(3)
V (Å^3)	964.7(3)
Z	4
F(000)	572
ρ_{Calcd} (g cm^{-3})	1.949
T(K)	293(2)
μ(mm^{-1})	1.789
Goodness-of-fit on F^2	1.018
Reflections collected	11779
Independent reflections (R_{int})	1938 (0.0309)
Observed reflections	1999
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0289, 0.0675
Final R_1, wR_2 [all data]	0.0299, 0.0686

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Co(1)–O(1)#B	2.1320(13)	Co(1)–O(4)	2.0805(17)
Co(1)–O(2)	2.1445(16)	Co(1)–N(2)	2.1602(16)
Co(1)–O(3)	2.1260(16)	Co(1)–N(3)#A	2.1155(16)
O(4)–Co(1)–N(3)#A	93.23(7)	O(4)–Co(1)–O(3)	92.07(7)
N(3)#A–Co(1)–O(3)	174.28(7)	O(4)–Co(1)–O(1)#B	9.05(6)
N(3)#A–Co(1)–O(1)#B	2.27(6)	O(3)–Co(1)–O(1)#B	89.96(6)
O(4)–Co(1)–O(2)	174.86(6)	N(3)#A–Co(1)–O(2)	0.89(6)
O(3)–Co(1)–O(2)	83.70(6)	O(1)#B–Co(1)–O(2)	93.87(6)
O(4)–Co(1)–N(2)	88.14(6)	N(3)#A–Co(1)–N(2)	94.92(6)
O(3)–Co(1)–N(2)	83.10(6)	O(1)#B–Co(1)–N(2)	172.41(6)
O(2)–Co(1)–N(2)	88.44(6)		

Symmetry code: #A $-x$, $-y$, $-z$; #B x, $-y-1/2$, $z-1/2$.

molecules (figure 1). Each Co(II) is bound to two water oxygen molecules (O3 and O4), two carboxylate oxygens (O1^B and O2) and two tetrazolate nitrogens (N3^A and N4) from three different 4-TZBA^{2-} ligands, completing a distorted octahedral coordination geometry. The Co–O bond distances range from 2.0805(17) to 2.1445(16) Å and Co–N bond distances are 2.1155(16) Å and 2.1602(16) Å, respectively. The bond angles around cobalt vary from 83.70(6) to 174.86(6)°. Each 4-TZBA^{2-} coordinates three different cobalt atoms through its carboxylate 2- and 3-nitrogens, so 4-TZBA^{2-} can be regarded as a tridentate ligand.

Adjacent cobalt(II) atoms are bridged by two 2-nitrogens and two 3-nitrogens from two 4-TZBA^{2-} to form a dimer with a Co-Co distance of 4.169 Å. This dimer can be regarded as a secondary building unit (SBU) (figure 2). Each SBU is interconnected with the other SBU via the carboxylate oxygen of 4-TZBA^{2-}. Four SBUs in the *bc* plane bind to the central SBU through the carboxylate (O1) while the other two SBUs

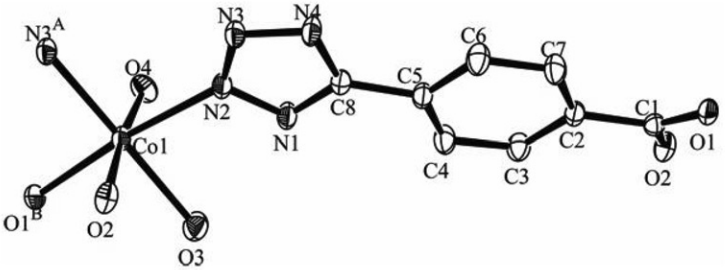

Figure 1. ORTEP drawing at the 50% probability level showing the coordination environment of Co(II) in **1**. Hydrogen atoms are omitted for clarity. Symmetry code: A $= -x$, $y + 1/2$, $-z + 1/2$; B $= x$, $-y - 1/2$, $z - 1/2$.

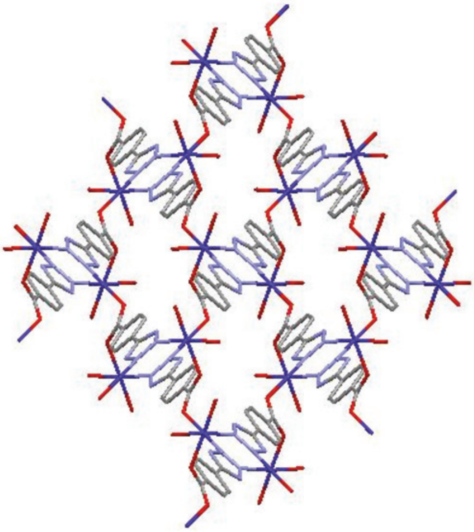

Figure 2. The 2-D sheet of **1** in the *bc* plane.

quasi-perpendicular connect the central SBU to carboxylate (O2). In this way, a 3-D structure is formed as shown in figure 3.

3.2. *Thermal analyses*

The TG curve of **1** was measured from room temperature to 800°C at a heating of 5°C min^{-1} under nitrogen (see Supplementary Material). The first weight loss of 11.9% (Calcd 12.7%) occurred between 112 and 304°C, which corresponds to loss of two coordinated waters. The remaining weight of 37.1% could probably be ascribed to $Co_2(OH)_2CO_3$ (Calcd 37.4%).

3.3. *Magnetic property*

The magnetic behavior of **1** in the temperature range 5–350 K under an applied field of 100 Oe (figure 4) showed paramagnetic behavior. The $\chi(T)$ value above 25 K was fitted

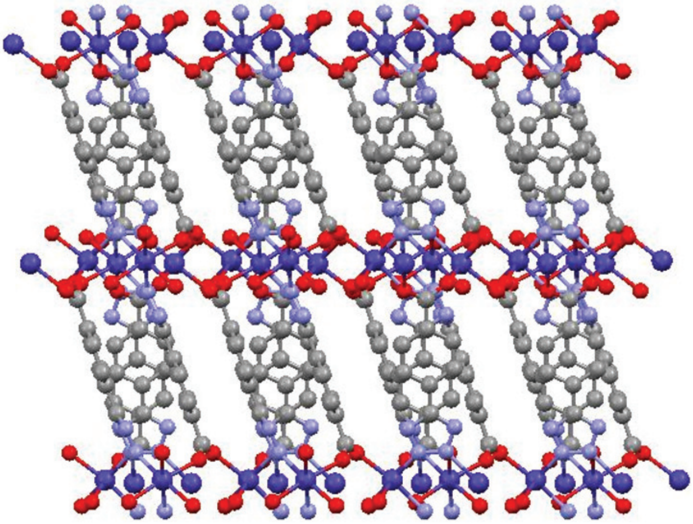

Figure 3. The 3-D structure of **1** (color code online: Co blue; N light blue; O red; C grey).

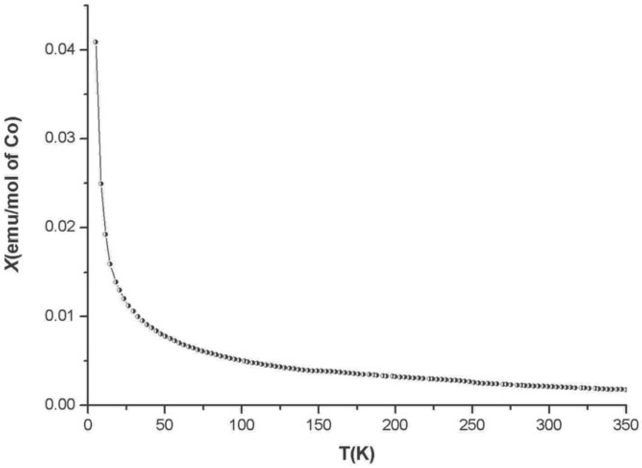

Figure 4. Temperature dependence of the magnetic susceptibility of **1** (H = 100 Oe).

to the Curie–Weiss law: $\chi(T) = C/(T - \theta)$, yielding $\theta = -34.1$ K. The negative θ value indicates antiferromagnetic interactions among the Co ions in **1**.

3.4. *Luminescent properties*

The luminescent properties of free H_2(4-TZBA) and **1** were investigated in the solid state at room temperature. Free H_2(4-TZBA) shows a strong emission peak at 327 nm upon excitation at 300 nm. Compared to free H_2(4-TZBA), the emission peak of **1** is bathochromic shifted to 377 nm (excitation at 340 nm) (figure 5), which can probably be assigned to the ligand-to-metal charge transfer (LMCT). In **1**, a very broad

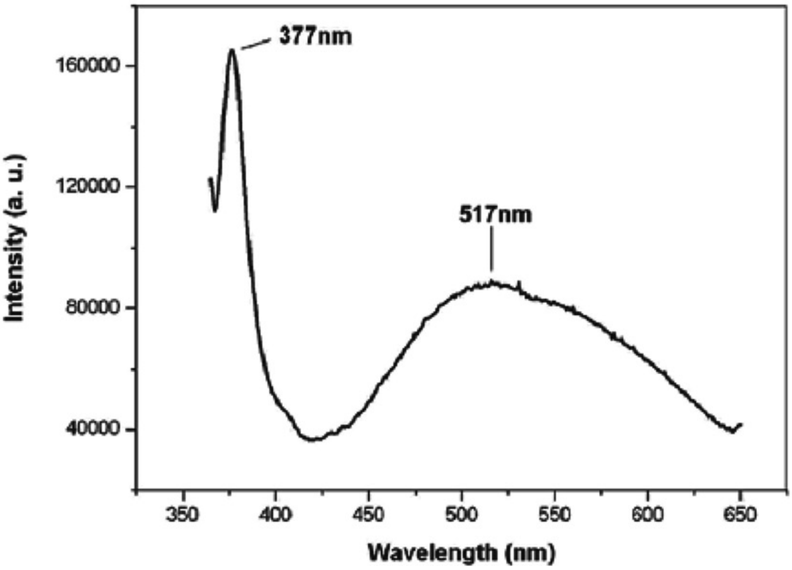

Figure 5. The emission spectra of **1** in the solid state at room temperature.

emission peak centered at 517 nm can also be observed, possibly due to a phosphorescent emission.

4. Conclusions

In conclusion, we have synthesized a new 3-D coordination polymer from 5-(carboxylatophenyl)-tetrazole (H_2(4-TZBA)). **1** exhibits strong luminescence in the solid state at room temperature.

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