ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 4, pp. 274–277. © Pleiades Publishing, Ltd., 2016.

Synthesis, Crystal Structure, and Luminescent Property of Two Novel Zn/Co(II) Coordination Polymers with a Linear Bis-Imidazole and Dicarboxylate Ligands[1]

J. F. Lu*, H. G. Ge*, J. Shi, and X. H. Guo

Chemical Engineering College, Shaanxi University of Technology, Hanzhong, 723001 P.R. China

**e-mail: jiufulu@163.com, gehg@snut.edu.cn*

Received June 17, 2015

Abstract—The linear linker 1,3-bis(2-methylimidazolyl)propane (Bmip) has been used to construct two new coordination polymers with Zn^{2+} and Co^{2+} ions and carboxylate donor ligand viz., 4,4'-oxydibenzoic acid (H_2Oba). Compounds formed hydrothermally are $[Zn(Bmip)(Oba)]_n$ (**I**), $[Co(Bmip)(Oba)]_n$ (**II**). Complexes **I** and **II** have been characterized by single crystal X-ray diffraction (CIF files CCDC nos. 1033354 (**I**), 1001813 (**II**)), IR spectroscopy, thermogravimetry, elemental analysis and powder X-ray diffraction. Single crystal X-ray analysis revealed that complexes **I** and **II** are isostructural, which exhibit 2D 4^4-sql net. And the adjacent 4^4-sql net are further inforced through weak noncovalent C–H···π and H-bonding to form a 3D supramolecular framework. Furthermore, the photoluminescence property of complexes **I** and **II** in the solid state at room temperature was also investigated.

DOI: 10.1134/S1070328416030064

INTRODUCTION

Metal coordination polymers (MCPs) are rapidly increasing in number because of their wide potential applications in photochemical areas, molecular magnetism, heterogeneous catalysis, and their intriguing structures [1–8]. Rational design and synthesis of desired MCPs with unique structure and function are still a fundamental scientific challenge, since many factors such as the coordination preferences of metal ions, the role of multifunctional bridging ligands can affect the nature of coordination networks and the framework formation. However, the selection of suitable metal ions and organic ligands are crucial for constructing extended coordination frameworks. To the best of our knowledge, the Bmip, bearing alkyl spacers is a good choice of N-donor ligands, the flexible nature of spacers allows the ligands to bend and rotate when it coordinates to metal centers [9, 10], and this often causes the structural diversity. Meanwhile, mixture of carboxylates with N-donor auxiliary ligands is good for construction of new coordination polymers [11, 12]. In particular, carboxylate ligands have been frequently employed in that their ability to engage in diverse bonding modes, allowing wide structural diversity and the tailoring of physical properties [13–15]. In this case, the Oba ligand has been employed in the preparation of metal-organic complexes in possession of multidimensional networks and interesting properties.

In this paper, we have prepared two new complexes using 1,3-bis(2-methylimidazolyl)propane (Bmip) and 4,4'-oxydibenzoic acid (H_2Oba) constructing $[Zn(Bmip)(Oba)]_n$ (**I**) and $[Co(Bmip)(Oba)]_n$ (**II**), their single crystal structures, luminescent property and catalytic property have been investigated.

EXPERIMENTAL

Materials and methods. All reagents used in the syntheses were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen atoms were performed on a Vario EL III elemental analyzer. The infrared spectra (4000–400 cm^{-1}) were recorded by using KBr pellet on an Avatar 360 E.S.P. IR spectrometer. Thermal stability study was carried out on a TA-SDT Q600 thermal analyzer under N_2 atmosphere with a heating rate of 10°C min^{-1} in the range of 30–900°C. Fluorescent analyses were performed on a Hitachi F-4500 analyzer.

Synthesis of I. A mixture of H_2Oba (0.10 mmol, 25.8 mg), Bmip (0.10 mmol, 20.4 mg) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.10 mmol, 30.8 mg) in distilled water (15 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120°C for 3 days and then cooled to room temperature over 24 h. Colorless block crystals of

---

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Fw	525.87	519.41
T, K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a, Å	11.1940(6)	10.9705(5)
b, Å	15.5899(7)	15.7101(6)
c, Å	14.1477(8)	14.0258(6)
β, deg	106.083(6)	101.282(4)
V, Å ^{3}	2372.3(2)	2370.60(17)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.472	1.455
F(000)	1088	1076
GOOF on F^2	1.063	1.021
Reflection/unique	4602/2091	5248/2091
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0631, 0.1288	0.0360, 0.0774
R_1, wR_2 (all data)*	0.0738, 0.1332	0.0477, 0.0774

$*R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Zn(1)–O(2)	1.987(5)	Zn(1)–N(1)	2.049(4)
Zn(1)–O(4)	1.987(5)	Zn(1)–N(4)	2.049(4)
		II	
Co(1)–O(2)	2.0640(18)	Co(1)–N(1)	2.0811(18)
Co(1)–O(4)	2.0640(18)	Co(1)–N(4)	2.0811(18)
Angle	ω, deg	Angle	ω, deg
		I	
O(4)Zn(1)O(2)	138.2(3)	O(2)Zn(1)N(4)	99.0(2)
O(2)Zn(1)N(1)	105.8(2)	N(1)Zn(1)N(4)	106.2(2)
O(4)Zn(1)N(4)	105.8(2)	O(4)Zn(1)N(1)	99.0(2)
		II	
N(1)Co(1)N(4)	101.42(10)	N(2)Co(1)O(4)	91.77(10)
O(4)Co(1)O(2)	150.42(12)	O(4)Co(1)O(2)	150.42(12)
N(1)Co(1)O(4)	91.18(10)	N(1)Co(1)O(2)	97.12(7)

complex **I** was obtained with the yield of 65% base on Zn.

For $C_{25}H_{24}N_4O_5Zn$ (M = 525.87)			
anal. calcd., %:	C, 57.05;	H, 4.56;	N, 10.65.
Found, %:	C, 57.36;	H, 4.12;	N, 10.81.

IR date (ν, cm^{-1}): 1618 ν_{as}(COO$^-$), 1495 ν_s(COO$^-$), 1216 ν_s(C=C$_{Ar}$), 873 ν_s(C–C).

Synthesis of II was carried out similar to **I** by using $Co(NO_3)_2 \cdot 6H_2O$ (0.10 mmol, 29.1 mg) in place of $Zn(NO_3)_2 \cdot 6H_2O$. Purple block crystals of **II** were obtained with the yield of 51% based on Co.

For $C_{25}H_{24}N_4O_5Co$ (M = 421.88)			
anal. calcd. %:	C, 48.35;	H, 4.26;	N, 13.27.
Found, %:	C, 48.61;	H, 4.04;	N, 13.40.

IR date (ν, cm^{-1}): 1602 ν_{as}(COO$^-$), 1489 ν_s(COO$^-$), 1227 ν_s(C=C$_{Ar}$), 868 ν_s(C–C).

X-ray structure determinations. Single cystal X-ray diffraction analyses of the compouneds were carried out on a Burker SMART APEX IICCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) by using the ω-scan mode at room temperature. The collected data were reduced using the SAINT program [16], and multiscan absorption corrections were applied using the SADABS program [17]. The structures were solved by direct methods and refined against F^2 by full matrix least squares methods using the SHELXTL package [18]. Hydrogens were located by geometric calculations, and their positions and thermal parameters were fixed during the structure refinement. Crystallographic data and experimental details of structural analyses for complexes are summarized in Table 1. Selected bond length and angle parameters are listed in Table 2.

Supplementary material for complexes **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre (nos. 1033354 (**I**), 1001813 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.camac.uk).

RESULT AND DISCUSSION

Single X-ray diffraction study revealed that complexes **I** and **II** are isostructural, so complex **II** is employed as a representation to be described in detail. As shown in Fig. 1a, the asymmetric unit contains one Co^{2+} ion, one Bmip ligand, one Oba anion. The Co(1) atom is in a CoN_2O_2 tetrahedral geometry, completed by two N atoms from two Bmip ligand, two O atoms from two Oba anions (Co(1)–O(2)/O(4) 2.0640(18), Co(1)–N(1)/N(4) 2.0811(18) Å). The bond angles for Co are in the range of 99.0(2)°–138.2(3)°. The Bmip and Oba ligands adopt a bidentate bridging mode to extend the Co(II) atoms to the resulting 2D 4^4-sql network (Fig. 1b) incorporating a [$Co_4(Bmip)_2(Oba)_2$] window of 14.02 × 10.97 Å based on the Co···Co dis-

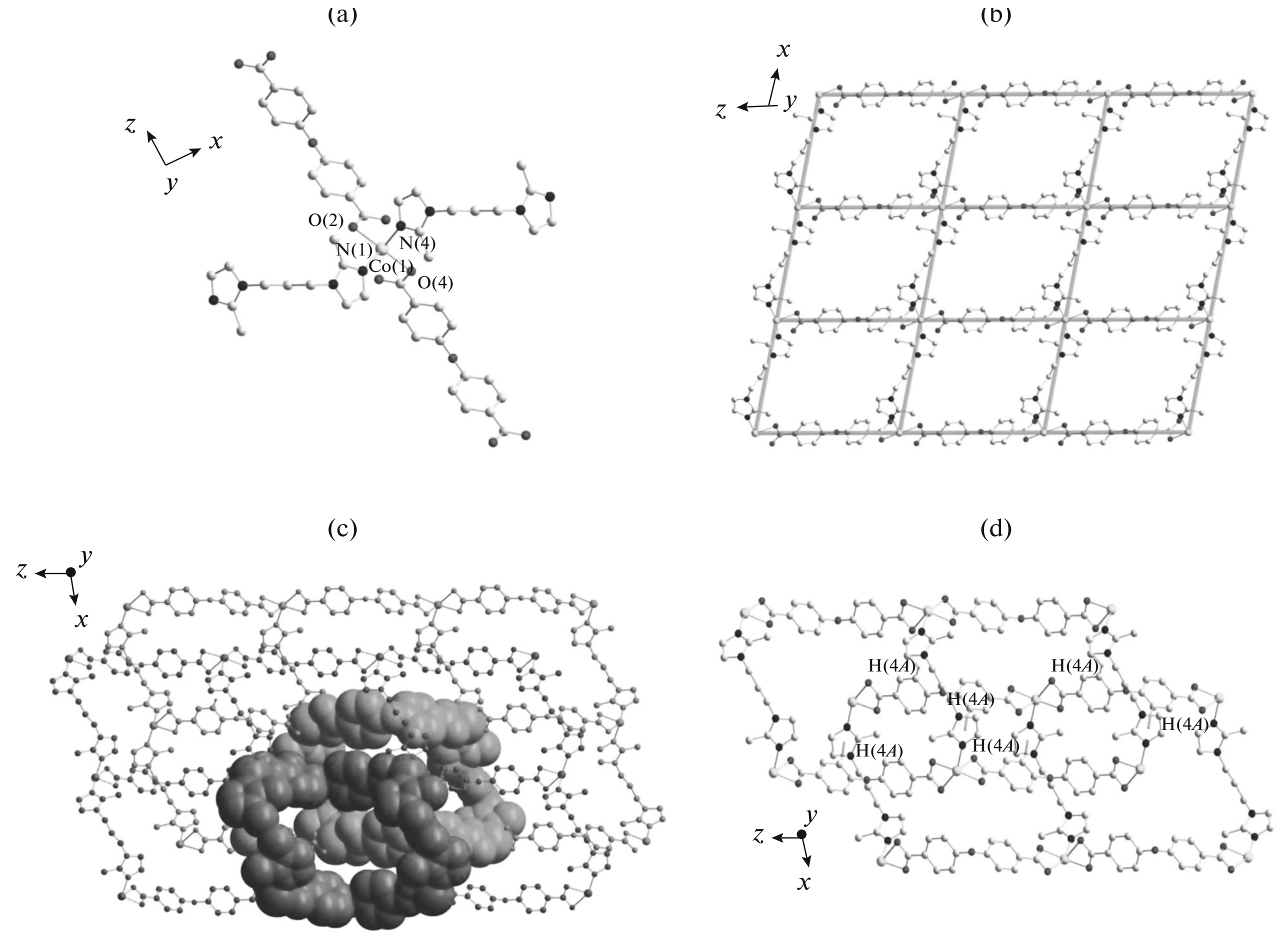

Fig. 1. Coordination environment of Co^{2+} ion in **II** (the hydrogen atoms are omitted for clarity (a); ball and-stick view of the 2D 4^4-sql net in **II** (b); 2D grid layers stacked in —ABAB— fashion in **II** (c); view of 3D supramolecular framework in **II** (d).

tances. The resulting 2D grid layers are further stacked in –ABAB–fashion through weak noncovalent C–H···π (H···π 2.8644(1) Å) between adjacent layers (Fig. 1c), which is further reinforced through H-bonding C(4)–H(4*A*)···C(16) (H(4*A*)···C(16) 2.16 Å) to form an overall 3D supramolecular framework (Fig. 1d).

For confirming the phase purity and stability of complexes **I** and **II**, the original samples were both characterized by powder X-ray diffraction. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison to those simulated from single-crystal models, it can still be considered that the bulk-synthesised materials and as-grown crystals are homogeneous for **I** and **II**.

The thermal stability was measured by thermogravimetric analysis (TGA) on polycrystalline samples in a nitrogen atmosphere heated to 900°C at a rate of 10°C/min, as illustrated in Fig. 2. Complexes **I** and **II** show similar thermal stability owing to their isostructural framework. The framework of complexes **I** and **II** is stable up to 380°C and then the framework begins to collapse, accompanying the release of coordinated Bmip and Oba ligands. Finally, the residue is stable to 900°C, for **I**, the residual weight of 15.9% may be attributed to ZnO and Carbon deposits of ligands, for

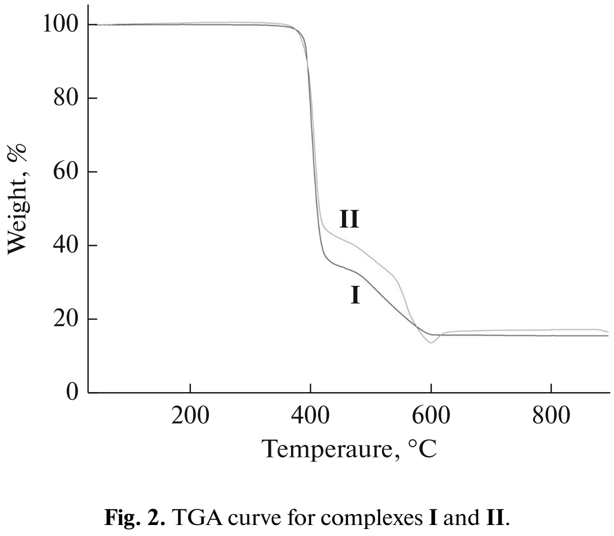

Fig. 2. TGA curve for complexes **I** and **II**.

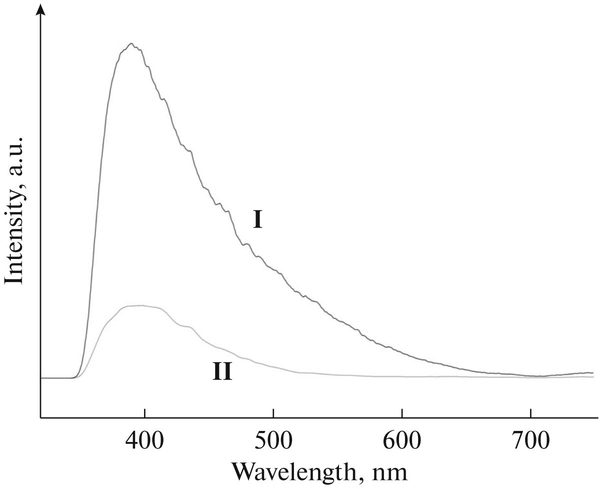

Fig. 3. Emission spectra of complexes **I** and **II**.

II, the residual weight of 17.0% may be attributed to Co_3O_4.

As shown in Fig. 3, the profile of the emission band of **I** and **II** are quite similar to that of the free-organic ligand Bmip which displays photoluminescence with emission maximum at 410 nm (λ_{ex} = 300 nm) [19], but the emission maxima of both of complexes **I** and **II** show slight blue shift in wavelength. It can be presumed that this peak originate from the $\pi^* \to \pi$ transition. To the best of our knowledge, the emission of dicarboxylate belongs to $\pi^* \to n$ transitions which is very weak compared to that of the $\pi^* \to \pi$ transition of the Bmip, so the dicarboxylates almost have no contribution to the fluorescent emission of as-synthesized MOFs [20]. Upon complexation of these ligands with Zn^{2+}/Co^{2+} ions, intense emissions are all observed at 392 nm for complexes **I** and **II** under 300 nm excitation. The blue-shifted emissions of complexes **I** and **II** may be assigned as ligand-to-metal charge transfer (LMCT) transition [21]. This inequality in emission behavior could be due to differences in metal ion. Inimically, quenching of emission intensity is observed in **II** due to presence of paramagnetic metal center [22].

ACKNOWLEDGMENTS

The authors thank financial assistance from the National Natural Science Foundation of China (project no. 21373132), the Project financial support by Shaanxi Province Education Department Scientific Research (project no. 15JK1141) and the foundation of Shaanxi University of Technology (SLGKY15-36).

REFERENCES

1. Lu, J.F., Min, S.T., and Ge, H.G., *J. Chem. Res.*, 2014, vol. 11, no. 3, p. 726.
2. Lu, J.F., Qiao, L.J., Li, L.Q., and Liu, Z.H., *J. Mol. Struct.*, 2015, vol. 1081, no. 2, p. 79.
3. Eddaoudi, M., Moler, D.B., and Li, H., *Acc. Chem. Res.*, 2001, vol. 34, no. 12, p. 319.
4. Seo, J.S., Whang, D., Lee, H., et al., *Nature*, 2000, vol. 404, no. 2, p. 982.
5. Halder, G.J., Kepert, C.J., and Moubaraki, B.K., *Science*, 2002, vol. 298, p. 1762.
6. Takamizawa, S., Yokoyama, H., and Mochizuki, K., *Angew. Chem. Int. Ed.*, 2003, vol. 42, no. 3, p. 4331.
7. Dybtsev, D.N., Chun, H., Yoon, S.H., et al., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 3, p. 32.
8. Kesanli, B., Cui, Y., and Smith, M.R., *Angew. Chem. Int. Ed.*, 2005, vol. 44, no. 2, p. 72.
9. Gao, X.M., Li, D.S., Wang, J.J., et al., *CrystEngComm*, 2008, vol. 10, no. 7, p. 479.
10. Zhang, M.L., Li, D.S., Wang, J.J., et al., *Dalton Trans.*, 2009, vol. 47, no. 3, p. 5355.
11. Wen, L.L., Li, Y.Z., Lu, Z.D., et al., *Cryst. Growth Des.*, 2006, vol. 6, no. 4, p. 530.
12. Fan, J., Slebodnick, C., Angel, R., et al., *Inorg. Chem.*, 2005, vol. 44, no. 3, p. 552.
13. Cui, G.H., Li, J.R., Tian, J.L., et al., *Cryst. Growth Des.*, 2005, vol. 5, no. 1, p. 1775.
14. Habib, H.A., Sanciz, J., and Janiak, C., *Inorg. Chim. Acta*, 2009, vol. 362, no. 2, p. 2452.
15. Wisser, B., Lu, Y., and Janiak, C., *Z. Anorg. Allg. Chem.*, 2007, vol. 633, no. 7, p. 1189.
16. *SMART & SAINT, Software Reference Manuals, Version 6.22*, Madison: Bruker AXS Analytic X-ray Systems Inc., 2000.
17. Sheldrick, G.M., *SADABS, Software for Empirical Absorption Correction*, Göttingen: Univ. of Göttingen, 2000.
18. Sheldrick, G.M., *SHELXTL, Reference Manual, Version 5.1*, Madison: Bruker AXS, Analytic X-ray Systems Inc., 1997.
19. Chen, W.J., Wang, Y., Chen, C., et al., *Inorg. Chem.*, 2003, vol. 42, no. 1, p. 944.
20. Huang, X.Y., Yue, K.F., and Jin, J.C., *Inorg. Chem. Commun.*, 2010, vol. 13, no. 4, p. 338.
21. Hao, H.J., Liu, F.J., and Su, H.F., *CrystEngComm*, 2012, vol. 14, no. 3, p. 6726.
22. Zeng, F., Ni, J., Wang, Q., et al., *Cryst. Growth Des.*, 2010, vol. 10, no. 2, p. 1611.