ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 8, pp. 549–552. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © S.A. Sapchenko, E.S. Saparbaev, D.G. Samsonenko, D.N. Dybtsev, V.P. Fedin, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 8, pp. 451–455.

Synthesis, Structure, and Properties of a New Layered Coordination Polymer Based on Zinc(II) Carboxylate

S. A. Sapchenko[a], E. S. Saparbaev[b], D. G. Samsonenko[a, b], D. N. Dybtsev[a, b, c], and V. P. Fedin[a, b, *]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*
[c] *Pohang University of Science and Technology, Pohang, 790784 Korea*
**e-mail: cluster@niic.nsc.ru*

Received January 24, 2013

Abstract—Heating of zinc(II) nitrate and 2,5-thiophenedicarboxylic acid (H_2Tdc) in the presence of hexamethylenetetramine in *N*-methylpyrrolidone (Nmp) gave the crystals of a layered coordination polymer $[Zn_2(Nmp)_2(Tdc)_2] \cdot 2Nmp \cdot 0.5H_2O$, which were studied by X-ray diffraction. The compound was characterized by IR spectroscopy, elemental and thermogravimetric analyses, and luminescence measurements.

DOI: 10.1134/S1070328413080071

INTRODUCTION

Metal-organic coordination polymers are compounds composed of metallic centers (single atom, cluster, or polynuclear complex) combined by organic bridging ligands to one-, two-, or three-dimensional periodic structures. The considerable interest in these items is related to both the extensive opportunities for the controlled design they provide and the presence of a series of valuable functional properties such as sorption and selective separation of gas mixtures [1, 2], catalytic [3, 4] and luminescence properties [5], etc.

The effective synthetic strategy for the preparation of these compounds is the use of polycarboxylic acids, which are made to react with transition metal salts in nonaqueous media under solvothermal conditions. The structure and properties of the final coordination polymer are determined by numerous factors: the coordinating ability of the metal, the solvent used for the reaction, and especially by the geometry of the carboxyl groups of the organic ligand, the ligand size, and the stereochemistry as a whole [6].

2,5-Thiophenedicarboxylic acid is a widely used ligand for the preparation of coordination polymers. The five-membered aromatic system ensures the steric rigidity of Tdc^{2-}, while the angular arrangement of the carboxylate groups (144°) allows the design of structures with unusual topologies [7]. It is also important for the design that H_2Tdc can be coordinated in different modes: 2,5-thiophenedicarboxylate can function as monodentate [8, 9], bridging bidentate [8–11], bridging tridentate [9, 12], and even tetradentate ligand; both symmetric [11, 13] and unsymmetric [14] coordination is possible. There are examples of one-, two-, and thee-dimensional different-ligand Mn(II), Co(II), Cu(II), and Zn(II) coordination polymers based on thiophenedicarboxylates and N-donor ligands [11, 12]. Two- and three-dimensional coordination polymers based only on thiophenedicarboxylates were prepared for lanthanides (Tb(III) [13, 15], Dy(III), Ho(III), Er(III) [16], etc.) and 3*d* metals (for example, Cu(II) [17], Co(II) [14], and Mn(II) [11]). Some of the coordination polymers show interesting luminescence and magnetic properties [14, 16, 18].

This communication reports the synthesis, structure, and thermal and luminescence properties of a new two-dimensional coordination polymer based on zinc(II) thiophenedicarboxylate $[Zn_2(Nmp)_2(Tdc)_2] \cdot 2Nmp \cdot 0.5H_2O$ (**I**).

EXPERIMENTAL

The starting compounds, zinc nitrate hexahydrate, 2,5-thiophenedicarboxylic acid, urotropine (Ur), *N*-methylpyrrolidone, and acetone were at least reagent grade commercial chemicals. IR spectra were recorded in the 4000–400 cm^{-1} range in KBr pellets on a Scimitar FTS 2000 FT IR spectrometer. Thermogravimetric analysis (TGA) was performed in a He atmosphere on a Netzch TG 209 F1 thermal analyzer, the samples being heated at a linear rate of 10°C/min. Elemental analysis of carried out at the analytical laboratory of the Nikolaev Institute of Inorganic Chemistry using a Euro EA 3000 instrument. Powder X-ray diffraction data were obtained on a Shimadzu XRD 7000S powder diffractometer (CuK_α radiation). The fluorescence spectra were measured on a Varian Cary Eclipse instrument.

Synthesis of I. A mixture of zinc nitrate hexahydrate (300 mg, 1 mmol), 2,5-thiophenedicarboxylic acid (170 mg, 1 mmol), urotropine (140 mg, 1 mmol),

Table 1. Crystallographic data and X-ray experiment details for structure **I**

Parameter	Value
Molecular formula	$C_{33.5}H_{43.5}N_{4.5}O_{12.5}S_2Zn_2$
M	904.09
System	Tetragonal
Space group	$P4/ncc$
a, Å	20.3027(5)
c, Å	20.1273(7)
V, Å^3	8296.5(4)
Z	8
ρ_{calcd}, g/cm^3	1.448
μ, mm^{-1}	2.906
F(000)	3744
Crystal size, mm	0.10 × 0.06 × 0.04
Scan range on θ, deg	3.08–67.66
Ranges of indices h, k, l	$-14 < h < 24$, $-20 < k < 25$, $-24 < l < 24$
The number of measured/independent reflections	34790/3720
R_{int}	0.0811
The number of reflections with $I > 2\sigma(I)$	2825
T_{max}/T_{min}	0.8926/0.7598
GOOF on F^2	1.042
R-factors ($I > 2\sigma(I)$)	$R_1 = 0.0471$, $wR_2 = 0.1363$
R-factors (for all reflections)	$R_1 = 0.0663$, $wR_2 = 0.1524$
Residual electron density (max/min), e/Å^3	0.775/–0.558

and *N*-methylpyrrolidone (25 mL) were sonicated for 10 min and heated at 100°C in a glass vial with screw cap for 48 h. The resulting crystals were washed with *N*-methylpyrrolidone (2 × 10 mL) and acetone (2 × 10 mL) and dried in air. Yield 152 mg (17% in relation to Zn).

For $C_{32}H_{41}N_4O_{12.5}Zn_2$				
anal. calcd. (%):	C, 43.8;	H, 4.7;	N, 6.44;	S, 7.3.
Found (%):	C, 44.1;	H, 4.9;	N, 6.7;	S, 6.9.

IR (ν, cm^{-1}): 3442, 3095, 2956, 2883, 1675, 1618, 1529, 1473, 1375, 1262, 1113, 1021, 987, 852, 805, 773, 682, 562, 514.

TGA. Found: $\Delta m = 44\%$.Calculated for the loss of 4Nmp + $0.5H_2O$ in **I**: $\Delta m = 46\%$.

X-ray diffraction. X-ray diffraction data were collected at 100 K on a Bruker Apex Duo four-circle automated diffractometer equipped with a two-coordinate detector (φ and ω scan modes, $\lambda(CuK_\alpha) = 1.54178$ Å, graphite monochromator). The crystal data and X-ray experiment details are summarized in Table 1. The absorption corrections were applied based on divergence of equivalent reflections (SADABS) [19]. The structure was solved by the direct method and refined by full-matrix least squares method in the anisotropic (except for hydrogen atoms) approximation (SHELX-97) [20]. The positions of hydrogen atoms of the organic ligands were calculated geometrically and refined by the riding model. Selected interatomic distances and bond angles are summarized in Table 2. Full tables of interatomic distances and bond angles, atom coordinates, and atom displacement parameters are deposited with the Cambridge Crystallographic Data Centre (no. 920495; deposit@ccdc.cam.ac.uk or

Table 2. Selected bond lengths and bond angles in **I***

Bond	d, Å	Bond	d, Å
Zn(1)–O(11)	2.051(3)	Zn(1)–O(14)^{iii}	2.059(3)
Zn(1)–O(12)^{i}	2.016(3)	Zn(1)–O(1)	1.976(3)
Zn(1)–O(13)^{ii}	2.013(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(11)Zn(1)O(14)^{iii}	162.28(12)	O(13)^{ii}Zn(1)O(14)^{iii}	87.11(13)
O(12)^{i}Zn(1)O(11)	88.35(12)	O(1)Zn(1)O(11)	98.70(12)
O(12)^{i}Zn(1)O(14)^{iii}	87.97(13)	O(1)Zn(1)O(12)^{i}	106.65(12)
O(13)^{ii}Zn(1)O(11)	88.16(12)	O(1)Zn(1)O(13)^{ii}	100.91(12)
O(13)^{ii}Zn(1)O(12)^{i}	152.43(12)	O(1)Zn(1)O(14)^{iii}	98.96(12)

* The coordinates of dependent atoms were obtained with the following symmetry codes: ^{i} $y + 1/2, x - 1/2, -z + 1/2$; ^{ii} $y + 1, -x + 1/2, z$; ^{iii} $-x + 1, y + 1/2, -z + 1/2$.

http://www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

RESULTS AND DISCUSSION

Zinc nitrate hexahydrate served as the source of zinc in the synthesis of coordination polymer **I**. This starting compound reacted with 2,5-thiophenedicarboxylic acid, which functioned as the bridging ligand. As solvents, *N,N*-dimethylformamide, dimethyl sulfoxide, *N,N*-dimethylacetamide, *N*-methylpyrrolidone, and *N,N*-diethylformamide were tested. Good-quality light yellow crystals were obtained in *N*-methylpyrrolidone. Urotropine was also added to the reaction mixture ($Zn(NO_3)_2 \cdot 6H_2O : H_2Tdc : Ur = 1 : 1 : 1$), although it is not present in the structure of the final compound. We attempted to reproduce the experiments without uropropine, which yielded poor-quality irregular coarse crystals.

According to X-ray diffraction data, the zinc coordination polyhedron is a tetragonal pyramid formed by five oxygen atoms of four Tdc^{2-} and Nmp ligands (Fig. 1). The Zn(1)–O bond lengths (1.976(3)–2.059(3) Å) fit in the normal bond length distribution for Zn(II) complexes with C.N. 5. The zinc atoms combined by four bidentate carboxyl groups form the paddle-wheel secondary building block $\{Zn_2(COO)_4(Nmp)_2\}$. These blocks combined with the Tdc^{2-} ligands (type of coordination $(\kappa^1\text{-}\kappa^1)\text{-}(\kappa^1\text{-}\kappa^1)\text{-}\mu_4$) form layers in the *xy* plane containing square windows with dimensions 6 × 6 Å (Fig. 2). The mutual orientation of the layers gives rise to a system of channels of two types along the *z* axis. Channels of the first type are occupied by guest Nmp molecules, the space

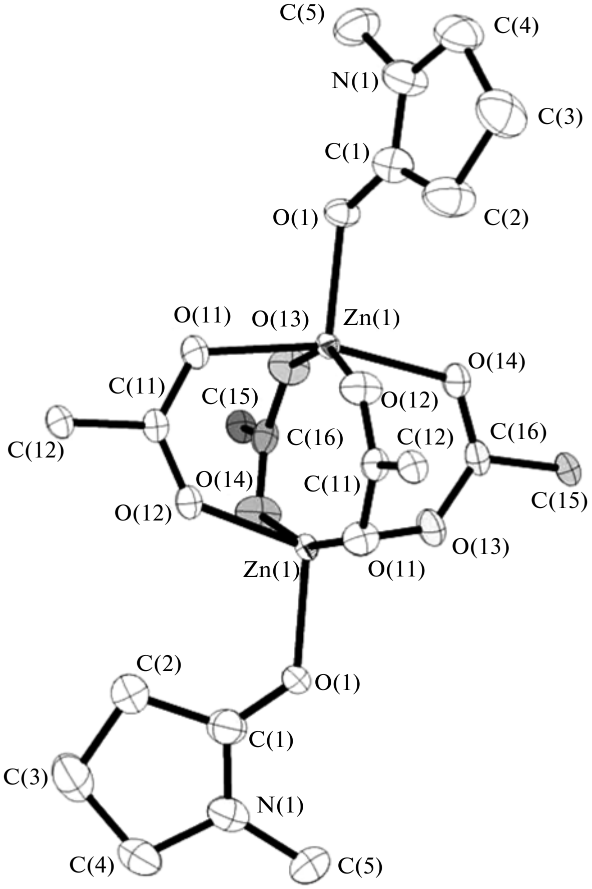

Fig. 1. Structure of the secondary building block, “Chinese lantern” in **I** (50% probability ellipsoids). The hydrogen atoms are omitted.

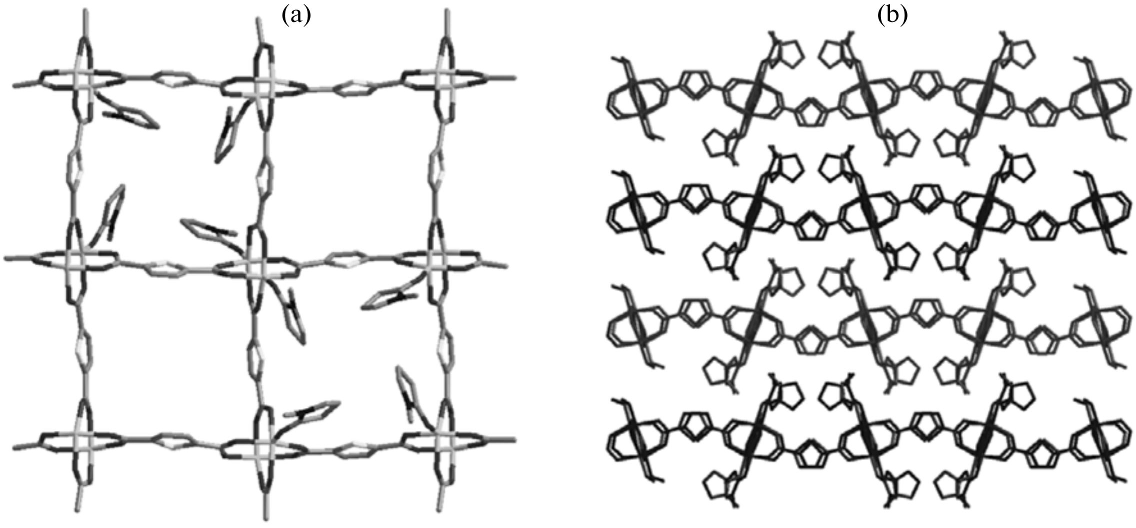

Fig. 2. (a) Fragment of the structure of compound **I**. (b) View along the *z* axis; schematic view of the mutual arrangement of layers in the structure of **I**. The hydrogen atoms and the guest Nmp molecules are omitted.

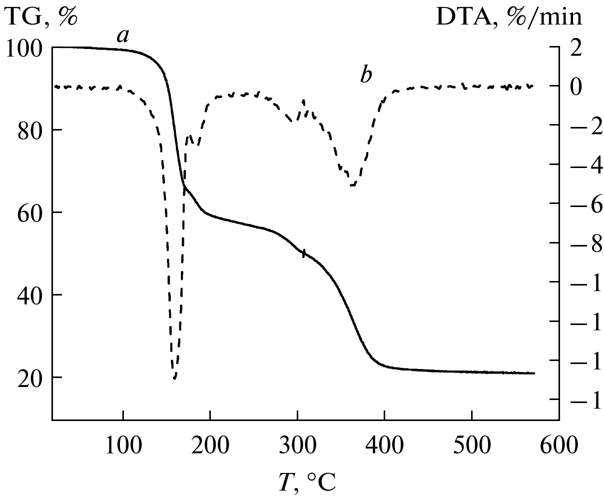

Fig. 3. (*a*) TG and (*b*) DTA curves for compound **I**; heating rate 10°C min^{-1}.

of the second-type channels is occupied by coordinated Nmp molecules and solvation water (Fig. 2).

The IR spectrum of compound **I** exhibits C=O stretching bands for *N*-methylpyrrolidone at 1675 cm^{-1}. A very weak band occurs at 3342 cm^{-1} and corresponds to O—H(H_2O) symmetric stretching vibrations, which attests to almost complete absence of water in the coordination polymer. The 1618 and 1375 cm^{-1} bands are due to asymmetric and symmetric stretching vibrations of the Tdc^{2-} carboxyl group [21, 22].

The TGA of compound **I** performed in a helium atmosphere showed a 44% weight loss in the range from room temperature to 250°C, which may be attributed to the removal of four Nmp molecules (both coordinated and guest molecules) and $0.5H_2O$ (the calculated value is 46%). The subsequent weight loss is associated with decomposition of the coordination polymer (Fig. 3). The elemental analysis data (C, H, N) are consistent with X-ray diffraction and TGA data, and, hence, compound **I** can be identified as $[Zn_2(Nmp)_2(Tdc)_2] \cdot 2Nmp \cdot 0.5H_2O$.

The phase purity of compound **I** was confirmed by powder X-ray diffraction. The experimental X-ray diffraction pattern of compound **I** coincides with that calculated from single crystal X-ray diffraction data.

For investigation of the luminescence properties of solid compound **I**, its fluorescence spectrum at room temperature was recorded. The photoluminescence spectrum of compound **I** was measured in the range of 300—800 nm with $\lambda_{\text{excit}} = 340$ nm. The spectrum shows a strong broad emission band with a maximum at 480 nm, which can be assigned to ligand to metal charge transfer.

Thus, we developed a method for the synthesis of an intricate coordination polymer $[Zn_2(Nmp)_2(Tdc)_2] \cdot 2Nmp \cdot 0.5H_2O$ based on 2,5-thiophenedicarboxylate. The structure of the polymer was determined by X-ray diffraction and its thermal and luminescence properties were studied. These compounds are of interest for further studies as regards their sorption characteristics.

ACKNOWLEDGMENTS

This work was supported by the Russia Foundation for Basic Research (projects nos. 11-03-00112, 12-03-31329) and the State Contract (no. 1729.2012.3).

REFERENCES

1. Li, J.-R., Kuppler, R.J., and Zhou, H.-C., *Chem. Soc. Rev.*, 2009, vol. 38, no. 5, p. 1477.
2. Chen, B.L., Xiang, Sh.Ch., and Qian, G.-D., *Acc. Chem. Res.*, 2010, vol. 43, no. 8, p. 1115.
3. Liu, Y., Xuan, W.M., and Cui, Y., *Adv. Mater.*, 2010, vol. 22, no. 37, p. 4112.
4. Lee, J.Y., Farha, O.K., Roberts, J., et al., *Chem. Soc. Rev.*, 2009, vol. 38, no. 5, p. 1450.
5. Allendorf, M.D., Bauer, C.A., Bhakta, R.K., et al., *Chem. Soc. Rev.*, 2009, vol. 38, no. 5, p. 1330.
6. Yahgi, O.M., Li, H., Davis, C.E., et al., *Acc. Chem. Res.*, 1988, vol. 31, no. 8, p. 474.
7. Znang, J., Chen, Sh., Wu, T., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, p. 12882.
8. Chen, B.L., Mok, K.F., Ng, S.-C., et al., *Polyhedron*, 1998, vol. 17, p. 4237.
9. Chen, B.L., Mok, K.F., Ng, S.C., and Drew, M.G.B., *Polyhedron*, 1999, vol. 18, p. 1211.
10. Sun, X.Z., Sun, Y.F., Ye, B.H., and Chen, X.M., *Inorg. Chem. Commun.*, 2003, vol. 6, p. 1412.
11. Chen, B.L., Mok, K.F., Ng, S.C., and Drew, M.G.B., *New J. Chem.*, 1999, vol. 23, p. 877.
12. Jia, H.P., Li, W., Ju, Z.F., and Zhang, J., *Eur. J. Inorg. Chem.*, 2006, p. 4264.
13. Rosi, N.L., Kim, J., Eddaoudi, M., et al., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 1504.
14. Demessence, A., Rogez, G., Welter, R., and Rabu, P., *Inorg. Chem.*, 2007, vol. 46, no. 9, p. 3423.
15. Huang, W., Wu, D., Zhou, P., et al., *Cryst. Growth Des.*, 2009, vol. 9, no. 3, p. 1361.
16. Wang, J.G., Huang, Ch.C., Huang, X.H., and Liu, D.Sh., *Cryst. Growth Des.*, 2008, vol. 8, no. 3, p 795.
17. Eddaoudi, M., Kim, J., Vodak, D., Sudik, A., et al., *Proc. Natl. Acad. Sci. USA*, 2002, vol. 99, p. 4900.
18. Demessence, A., Rogez, G., and Rabu, P., *Chem. Mater.*, 2006, vol. 18, p. 3005.
19. *Bruker Advanced X-Ray Solutions*, Madison (WI, USA): Bruker AXS Inc., 2004.
20. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
21. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1963.
22. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.

Translated by Z. Svitanko