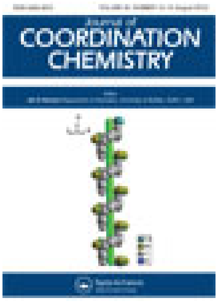
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:37
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

The synthesis, structure, and magnetic studies of one supramolecular PtS net

Yu-Mei Song [a], Xue-Feng Feng [a] & Feng Luo [a]

[a] College of Biology, Chemistry, and Material Science, East China Institute of Technology, Fuzhou, Jiangxi, China

Accepted author version posted online: 08 Jun 2012.Published online: 21 Jun 2012.

To cite this article: Yu-Mei Song, Xue-Feng Feng & Feng Luo (2012) The synthesis, structure, and magnetic studies of one supramolecular PtS net, Journal of Coordination Chemistry, 65:15, 2705-2712, DOI: 10.1080/00958972.2012.701007

To link to this article: http://dx.doi.org/10.1080/00958972.2012.701007

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry
Vol. 65, No. 15, 10 August 2012, 2705–2712

The synthesis, structure, and magnetic studies of one supramolecular *PtS* net

YU-MEI SONG, XUE-FENG FENG and FENG LUO*

College of Biology, Chemistry, and Material Science, East China Institute of Technology, Fuzhou, Jiangxi, China

(*Received 16 February 2012; in final form 1 May 2012*)

A new 2-D coordination polymer, $Co(H_2O)_2(Hoba)_2$ (**1**) [$H_2oba = 4,4'$-oxybis(benzoic acid)], was synthesized under hydrothermal conditions. Polymer **1** has been characterized by single-crystal X-ray diffraction and TG analysis. Through hydrogen bonds **1** shows a supramolecular four-connecting 3-D matrix with 4^28^4 PtS topology. Magnetic studies reveal antiferromagnetic interactions.

Keywords: 4,4′-Oxybis(benzoic acid); Hydrothermal synthesis; Hydrogen bond; Topological matrix; Antiferromagnetic interactions

1. Introduction

Metal-organic coordination polymers have applications as functional materials in magnetism, gas sorption, optics, catalysis, etc. [1–3]. Choice of ligand is the first factor for constructing coordination polymers. For example, in construction of magnetic materials, using short organic bridging ligands to connect ions, as the short bridging ligand benefits magnetic exchange; for porous materials, long rigid linear ligands are favored. 4,4′-Oxybis(benzoic acid) (H_2oba) is an example of long V-shaped, flexible ligands [4–7]. It can connect metal ions with bidentate, tridentate, tetradentate, pentadentate, and hexadentate modes. Its coordination chemistry has been extensively studied and proven to be efficient in synthesis of coordination polymers [8, 9]. The double ligand approach containing both O-donor H_2oba and N-donor such as 4,4′-bipyridine, azide and cyanide were productive. Only a few examples of coordination polymers have been prepared with just H_2oba. The cases include a 3-D In(III) polymer based on a 1-D inorganic rod-like substructure, a 1-D U(VI) compound with tape-like array, a 3-D Cd(II)–Li(I) polymer built on 1-D inorganic rod-like substructures, a 3-D Na(I) layer-pillared net based on Na(I)–O inorganic layer substructures and a porous 3-D In(III) polymer synthesized by ionic liquid [10–14]. However, there is no Co(II) compound only

---

*Corresponding author. Email: ecitluofeng@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2012.701007

constructed by H_2oba. For this ligand, magnetic studies are less developed. Here, we report a cobalt complex based on only H_2oba ligands and its synthesis, structure, thermal analysis, and magnetic properties.

2. Experimental

2.1. *Materials and methods*

All reagents were obtained commercially and used without purification; water was deionized in our laboratory. Analyses for C, H, and N were carried out on a Perkin-Elmer analyzer. Thermogravimetric analysis was carried out on a TA Instruments TGA 2050. Magnetic measurements were performed on a Quantum Design (SQUID) magnetometer MPMS-XL-5.

2.2. *Synthesis of 1*

A mixture of $CoCl_2 \cdot 6H_2O$ (237.9 mg, 1 mmol), H_2oba (258.2 mg, 2 mmol), and H_2O (8 mL) was placed in 23-mL Teflon-lined stainless-steel acid digestion bomb. The solution was heated to 160°C for 4 days, then cooled to room temperature, giving red crystals which were washed with mother liquid. The yield based on Co is 86%. The phase purity of the bulk samples are confirmed by both EA and XRD (figure 1). EA (%): Calcd C 55.18, H 3.63, exp. C 55.12, H 3.67.

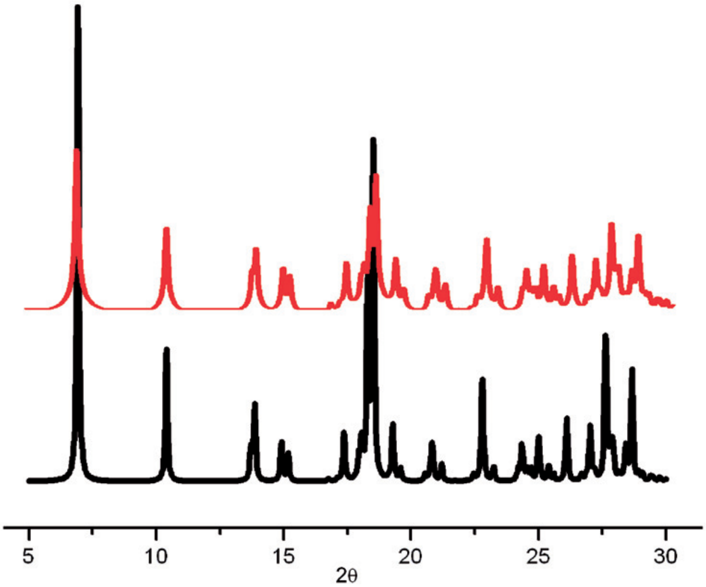


Figure 1. The experimental XRD pattern/red of the bulk samples and the simulated XRD pattern/black from single-crystal data.

2.3. *Crystal structure determination*

The crystallographic data of **1** were collected on a Bruker Apex Smart CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71076$ Å) at 296 K. The structure of **1** was solved by direct methods and refined on F^2 using the SHELXTL-97 software [15]. Non-hydrogen atoms were located from the trial structure and refined anisotropically. Hydrogen atoms were refined isotropically and assigned to calculated geometric positions. A summary of crystal data and the relevant structure refinement results are summarized in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of 1*

Single-crystal X-ray diffraction reveals the triclinic *P*-1 space group. Within **1**, the asymmetric unit contains two crystallography-independent Co(II) ions (figure 2).

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

Parameter	**1**
Empirical formula	$C_{56}H_{44}Co_2O_{24}$
Formula weight	1218.77
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions (Å, °)	
a	6.6337
b	7.3556
c	25.5297
β	91.204
Volume (Å^3), *Z*	1244.89(5), 1
Calculated density (Mg m^{-3})	1.626
F(000)	626
Goodness-of-fit	1.110
R indices (all data)	$R_1 = 0.062$, $wR_2 = 0.1663$

Table 2. Bond lengths (Å) and angles (°) for **1**.

Polymer		**1**	
Co(1)–O(1)	2.068(2)	O(1)#1–Co(1)–O(3)	90.32(9)
Co(1)–O(2)	2.125(2)	O(1)#1–Co(1)–O(3)#1	89.68(9)
Co(2)–O(6)	2.074(2)	O(2)–Co(1)–O(2)#1	180.00(11)
Co(2)–O(5)#3	2.106(2)	O(6)–Co(2)–O(6)#2	180.00(11)
O(3)–Co(1)–O(3)#1	180.00(13)	O(6)–Co(2)–O(5)#3	89.93(8)
O(1)–Co(1)–O(2)	91.26(8)	O(6)#2–Co(2)–O(5)#3	90.07(8)
O(3)–Co(1)–O(2)	92.83(8)	O(5)#3–Co(2)–O(5)#4	180.00(13)
O(3)#1–Co(1)–O(2)	87.17(8)	O(6)–Co(2)–O(4)	89.17(8)
Co(2)–O(4)	2.125(2)	O(6)#2–Co(2)–O(4)	90.83(8)
Co(1)–O(3)	2.102(2)	O(5)#3–Co(2)–O(4)	87.47(8)
O(1)–Co(1)–O(1)#1	180.00(11)	O(4)–Co(2)–O(4)#2	180.00(10)
O(1)–Co(1)–O(3)	89.68(9)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y, -z$; #2 $-x+1, -y+1, -z$; #3 $-x+1, -y, -z$; #4 $x, y+1, z$.

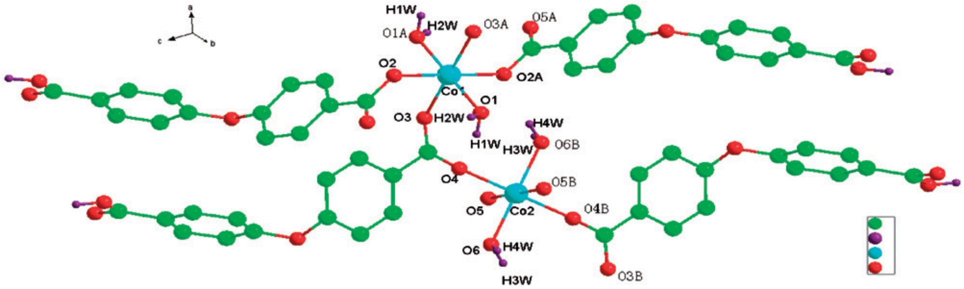


Figure 2. The coordination environment of Co(II) ion in **1**. Hydrogen atoms except on coordinated water are omitted for clarity.

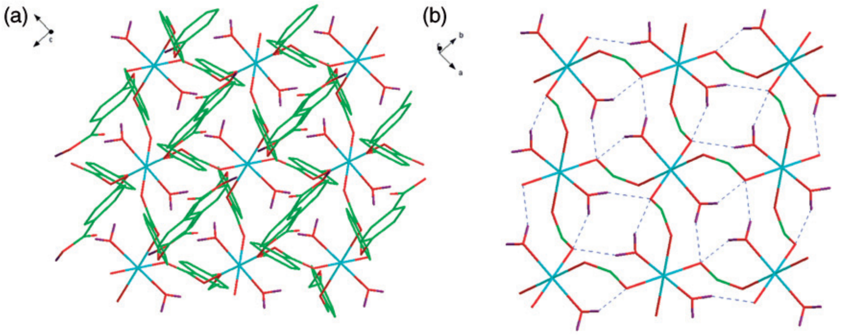


Figure 3. View of 2-D grid net of **1** and the intramolecular hydrogen bonds.

Both Co1 and Co2 sites are six-coordinate by four oxygen atoms (O2, O3, O2A, and O3A for Co1 and O4, O5, O4B, and O5B for Co2, A = 2−*x*, −*y*, −*z*, B = 1−*x*, −*y*, −*z*) from four Hoba^- ligands that build the local equatorial plane and two oxygen atoms from coordinated water (O1 and O1A for Co1, and O6 and O6A for Co2) located on the axis, thus creating a CoO_6 octahedron. The coordination bond lengths between Co(II) and Hoba^- oxygen atoms are in the range of 2.102(2)–2.125(2) Å, slightly longer than that of 2.068(2)–2.074(2) Å between Co(II) and terminal coordinated water, indicating slightly axially-condensed octahedral geometry for Co1 and Co2. The O1–Co1–O1A and O6–Co2–O6A angle is 180°, expected for octahedral geometry, implying that no distortion exists in this geometry. H_2oba in **1** is partly deprotonated and the deprotonated carboxylate is bidentate. The dihedral angle for two phenyl planes of Hoba^- is *ca* 76° and the angle for the V-shaped configuration is 118–119°.

Through Hoba^- carboxylates, Co(II) ions are associated to give the 2-D 4^4 net, where each Co(II) is a four-connecting node. The closest metal-to-metal distance is 4.9 Å. Hoba^- ligands locate at the 2-D net up and down. Coordinated water forms strong intramolecular hydrogen bonds: O1–H1W···O4/2.73 Å, O1–H2W···O4A/2.78 Å, O6–H3W···O2/2.79 Å, and O1–H2W···O2A/2.72 Å (figure 3). Further, *via* intermolecular hydrogen bonds between Hoba^- ligands (O10–H2A···O11/2.62 Å and O12–H1A···O9/2.62 Å) these 2-D layers are linked, resulting in the overall 3-D supramolecular net (figure 4).

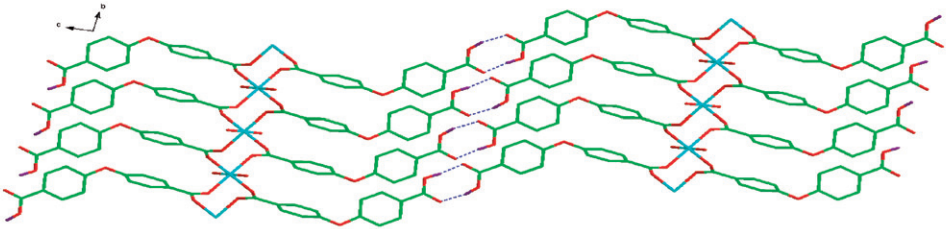


Figure 4. The 3-D network assembled by hydrogen bond interactions.

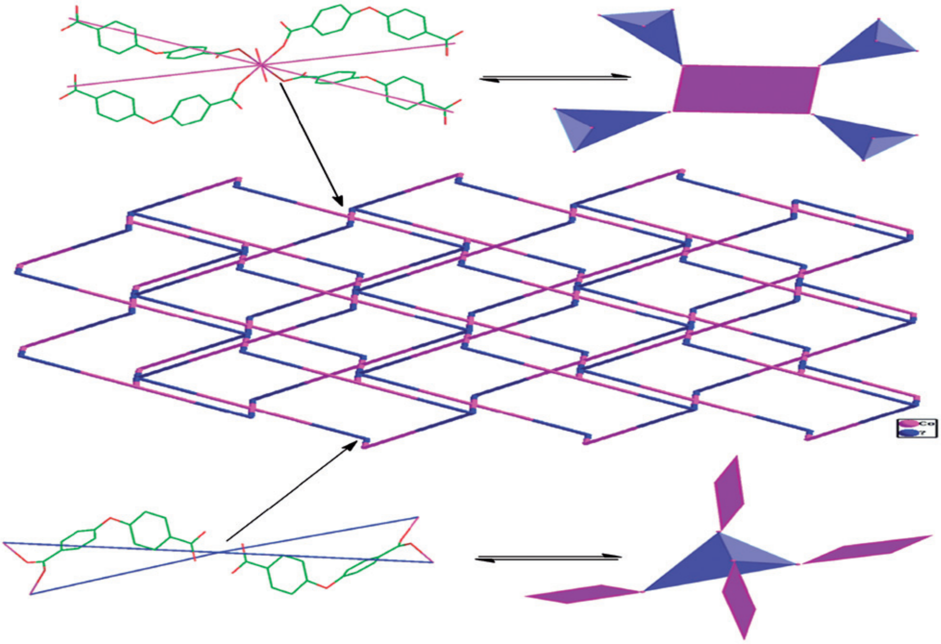


Figure 5. View of the PtS net, the square metal node and tetrahedral ligand node, and the connections.

In order to fully understand the 3-D supramolecular framework of **1**, topological analysis is applied (figure 5). If each Co(II) and the combination of two Hoba$^-$ by hydrogen bonds are a four-connecting node, then a four-connecting matrix is generated, where metal nodes and ligand nodes adopt planar square and tetrahedral geometries, respectively. Topology analysis *via* Topos program suggests a PtS net with $4^2 \cdot 8^4$ topology [16].

3.2. *Thermal analysis and magnetic properties*

Polymer **1** was heated to 600°C in N_2. The first weight loss at 30–195°C is 5.7%, consistent with the expected value for the loss of coordinated water (5.9%). The resulting phase is stable to 240°C, and then chemical decomposition begins (figure 6).

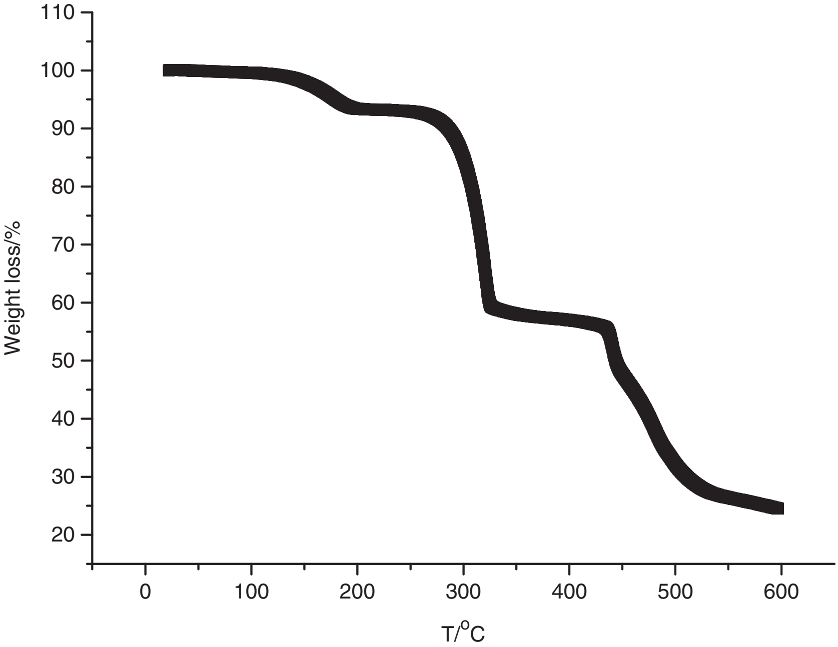


Figure 6. The TG studies of polymer **1**.

Magnetic susceptibility data for **1** were obtained in the temperature range 2–300 K at 1000 Oe (figure 7). The $\chi_M T$ value at 300 K is 4.70 $cm^3 mol^{-1} K$, larger than the expected value, 3.75 $cm^3 mol^{-1} K$ for two uncoupled Co(II) ions with $S = 3/2$, $g = 2.0$, due to spin–orbit coupling. On cooling, $\chi_M T$ decreases slowly and then sharply at low temperatures. As observed in other Co(II) compounds, the decrease of $\chi_M T$ is derived from thermal depopulation of spin–orbit coupling or antiferromagnetic interaction, or both [17, 18].

To evaluate the order of magnitude of spin–orbit coupling and antiferromagnetic interaction, a recently developed non-critical scaling theory [19] with equation $\chi_M T = C_1 * \exp(E_1/T) + C_2 * \exp(E_2/T)$ is utilized to analyze the magnetic susceptibility data, resulting in $C_1 = 2.69\,cm^3 mol^{-1} K$, $E_1 = -0.83\,K$, $C_2 = 2.48\,cm^3 mol^{-1} K$, $E_2 = -70.5\,K$, where $C_1 + C_2$ is the high-temperature extrapolated Curie constant and E_1 and E_2 denote the magnitude of the magnetic interactions and spin–orbit coupling. This shows that in **1** spin–orbit coupling dominates.

4. Conclusions

A new 2-D cobalt (II) polymer was obtained by hydrothermal synthesis and its structure, TG and magnetic properties were studied. Through supramolecular interactions, polymer **1** presents a 3-D supramolecular PtS net built on square metal node and tetrahedral ligand node. The magnetic study reveals dominating spin–orbit coupling and weak antiferromagnetic interactions, further interpreted by non-critical

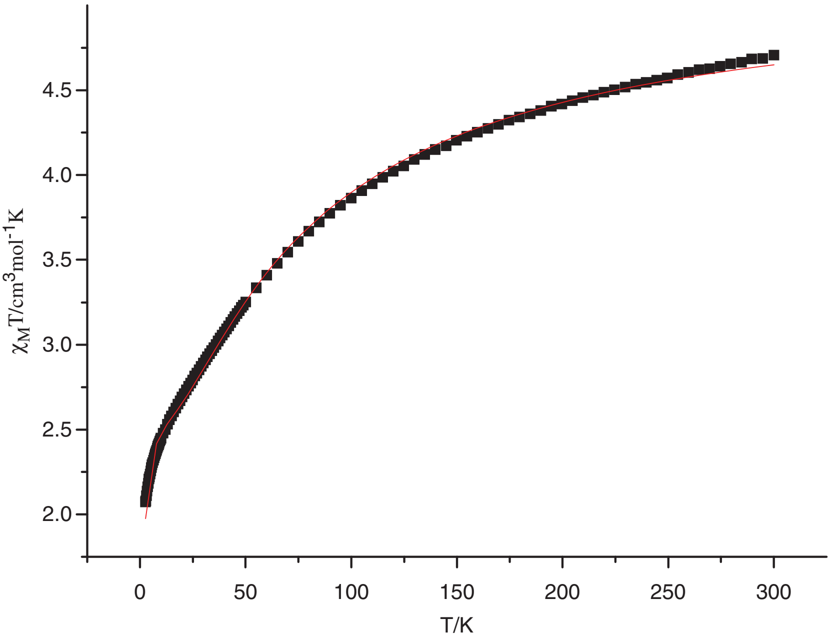


Figure 7. The experimental and simulated $\chi_M T$ *vs.* T plots marked in black and red, respectively.

scaling theory. This work presents the first Co(II) compound constructed by only H_2oba ligands and extends interest in magnetic property for H_2oba.

Acknowledgments

This work was supported by the Doctoral Start-up Fund of East China Institute of Technology, the Foundation of Jiangxi Educational Committee (No. GJJ11153), the Natural Science Foundation of Jiangxi Province of China (No. 2010GQH0005), the China Postdoctoral Science Foundation (No. 20100480725), and the Foundation of Key Laboratory of Radioactive Geology and Exploration Technology Fundamental Science for National Defense (2010RGET07).

References

[1] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Rev.*, **38**, 176 (2005).
[2] D. Bradshaw, J.B. Claridge, E.J. Cussen, T.J. Prior, M.J. Rosseinsky. *Acc. Chem. Rev.*, **38**, 273 (2005).
[3] L. Pan, H.M. Liu, X.G. Lei, X.Y. Huang, D.H. Olson, N.J. Turro, J. Li. *Angew. Chem. Int. Ed.*, **42**, 542 (2003).
[4] V. Laget, C. Hornick, P. Rabu, M. Drillon, R. Ziessel. *Coord. Chem. Rev.*, **178**, 1533 (1998).
[5] L.M. Fan, D.C. Li, P.H. Wei, P.Q. Tang, M.G. Li, D. Yuan, G.Z. Liu, X.T. Zhang, J.M. Dou. *J. Coord. Chem.*, **64**, 3031 (2011).
[6] H.L. Wu, J.K. Yuan, Y. Bai, G.L. Pan, H. Wang, X.B. Shu, G.Q. Yu. *J. Coord. Chem.*, **65**, 616 (2012).
[7] H.L. Wu, K.T. Wang, F. Kou, F. Jia, B. Liu, J.K. Yuan, Y. Bai. *J. Coord. Chem.*, **64**, 2676 (2011).

[8] (a) X.M. Chen, G.F. Liu. *J. Eur. Chem.*, **8**, 4811 (2002); (b) E. Yang, J. Zhang, Z.J. Li, S. Gao, Y. Kang, Y.B. Chen, Y.H. Wen, Y.G. Yao. *Inorg. Chem.*, **43**, 6525 (2004).

[9] (a) C.Y. Sun, X.J. Zhang, S. Gao, L.C. Li, L.P. Jin. *Eur. J. Inorg. Chem.*, 4150 (2005); (b) C.Y. Sun, L.P. Jin. *J. Mol. Struct.*, **782**, 171 (2006).

[10] Z. Jin, H.Y. Zhao, X.J. Zhao, Q.R. Fang, J.R. Long, G.S. Zhu. *Chem. Commun.*, **46**, 8612 (2010).

[11] S. Dalai, M. Bera, A. Rana, D.S. Chowdhuri, E. Zangrando. *Inorg. Chim. Acta*, **363**, 3407 (2010).

[12] J.D. Lin, X.F. Long, P. Lin, S.W. Du. *Cryst. Growth Des.*, **10**, 146 (2010).

[13] Y. Yang, Q. Li, S.W. Ng. *Acta Crystallogr. Sect. E*, **64**, m1119 (2008).

[14] J. Zhang, S.M. Chen, X.H. Bu. *Angew. Chem. Int. Ed. Engl.*, **47**, 5434 (2008).

[15] G.M. Sheldrick. *Acta Crystallogr. Sect. A*, **46**, 467 (1990).

[16] (a) V.A. Blatov, http://www.topos.ssu.samara.ru/ (2006); (b) V.A. Blatov, A.P. Shevchenko, V.N. Serezhkin. *J. Appl. Crystallogr.*, **33**, 1193 (2000).

[17] (a) M. Kurmoo. *Chem. Soc. Rev.*, **38**, 1353 (2009); (b) M. Kurmoo, H. Kumagai, K.W. Chapman, C.J. Kepert. *Chem. Commun.*, 3012 (2005); (c) N. Snejko, E. Gutierrez-Puebla, J.L. Martinez, M.A. Monge, C. Ruiz-Valero. *Chem. Mater.*, **14**, 1879 (2002); (d) C. Biswas, P. Mukherjee, M.G.B. Drew, C.J. Gomez-García, J.M. Clemente-Juan, A. Ghosh. *Inorg. Chem.*, **46**, 10771 (2007).

[18] V. Laget, C. Hornick, P. Rabu, M. Drillon, R. Ziessel. *Coord. Chem. Rev.*, **178**, 1533 (1998).

[19] (a) J. Souletie, P. Rabu, M. Drillon. In *Magnetism: Molecules to Materials*, J.S. Miller, M. Drillon (Eds), Vol. V, pp. 347–377, Wiley-VCH, Weinheim (2005); (b) J. Souletie, P. Rabu, M. Drillon. *Phys. Rev. B*, **72**, 214427 (2005); (c) M. Drillon, P. Panissod, P. Rabu, J. Souletie, V. Ksenofontov, P. Gtlich. *Phys. Rev. B*, **65**, 104404 (2002).