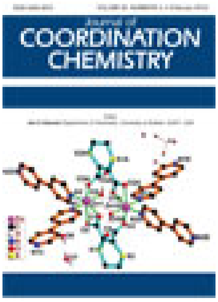
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:43
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Synthesis, structure, and magnetic property of Co(II)-based metal-organic framework with 4,4′-oxy bis(benzoate) ligand

Genhua Wu [a], Yanxiao Han [a], Dayu Wu [a], Wei Huang [a] & Xiaohong Zhou [a]

[a] School of Chemistry & Chemical Engineering, Anqing Normal College, Anqing 246011, P.R. China

Published online: 14 Feb 2012.

To cite this article: Genhua Wu, Yanxiao Han, Dayu Wu, Wei Huang & Xiaohong Zhou (2012) Synthesis, structure, and magnetic property of Co(II)-based metal-organic framework with 4,4′-oxy bis(benzoate) ligand, Journal of Coordination Chemistry, 65:4, 681-687, DOI: 10.1080/00958972.2012.658779

To link to this article: http://dx.doi.org/10.1080/00958972.2012.658779

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 &

Journal of Coordination Chemistry
Vol. 65, No. 4, 20 February 2012, 681–687

Synthesis, structure, and magnetic property of Co(II)-based metal–organic framework with 4,4′-oxy bis(benzoate) ligand

GENHUA WU, YANXIAO HAN, DAYU WU*,
WEI HUANG and XIAOHONG ZHOU*

School of Chemistry & Chemical Engineering, Anqing Normal College,
Anqing 246011, P.R. China

(*Received 9 October 2011; in final form 22 November 2011*)

A 2-D coordination polymer, $[Co(OBA)_2]_\infty$ (OBA = 4,4′-oxy bis(benzoate)), where OBA ligands bridge cobalt in a terminal fashion to build up a 2-D layer structure with strong hydrogen-bonding interaction was isolated and structurally characterized from the reaction of OBA with $Co(OAc)_2 \cdot 4H_2O$. Magnetic data indicate the Co(II) centers in **1** are negligibly magnetically coupled to each other and the single-ion magnetic behavior of Co(II) in octahedral environment is dominated at low temperature to give an effective $S' = 1/2$ ground state from $S = 3/2$ state due to spin–orbit coupling.

Keywords: Coordination framework; Cobalt; 4,4′-Oxy bis(benzoate); Spin–orbit coupling

1. Introduction

The construction of coordination polymers plays a prominent role in materials science [1–4]. The construction of supramolecular networks containing divalent cobalt as connectors is attractive because of electronic and magnetic properties, which have been effective in exotic magnetic characteristics of single-molecule magnets [5], single-chain magnets [6], and photomagnets [7]. In particular, the molecular approaches to combining building units with essential properties *via* self-assembly processes can offer models to better understand fundamental phenomena and correlation, such as ferromagnetic, antiferromagnetic, and magnetic complexes with blended properties (spin canting/metamagnetism, spin canting/spin flop, etc.) [8].

One synthetic strategy in the coordination polymer field involves the use of carboxylates, which show versatile coordination characteristics and/or bridging modes to prepare target compounds [9, 10]. Aromatic dicarboxylate ligands such as benzenedicarboxylates and biphenylcarboxylates have been widely used to link metal ions in construction of coordination polymers [11]. Despite successes, the structural prediction and rational design of coordination polymers remains a challenge, arising from combined influences of coordination flexibility, versatility of metal ions and ligands, and subtle influences of weak interactions (e.g., hydrogen bonds), as well as

---

*Corresponding authors. Email: wudayu_nju@yahoo.com.cn; zhouxh@aqtc.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2012.658779

synthetic conditions. Magnetic interactions can also be very different owing to the change of the bridging mode and environments of the metal centers [12–16]. For example, Salifoglou *et al.* [17] reported structurally diverse array of polynuclear complexes from the reaction of 6-methylpyridine-2-methanol with a range of cobalt(II) salts under a variety of reaction conditions. Recently, Zeng *et al.* [18] reported a new pillared-layer coordination polymer, $[Co_3(pybz)_2(pico)_2]_n$ (pybz = 4-(pyridin-4-yl) benzoate, pico = 3-hydroxypicolinate), which contained rare 2-D $[Co_3(pico)_2]_n^{2n+}$ layers formed by linear cobalt(II) trimers and exhibited ferrimagnetic long-range ordering below 2.6 K [18].

Herein, we report the synthesis, crystal structure, and magnetic properties of a new coordination polymer of cobalt 4,4′-oxy bis(benzoate) (OBA) prepared by the reaction of $Co(OAc)_2 \cdot 4H_2O$ and 4,4′-oxy bis(benzoate) (OBA) [19, 20]. Single-crystal X-ray analysis showed that the complex exhibits a 2-D structure interlinked *via* strong hydrogen bonds on the terminal of free carboxylate groups. The magnetic property of the title compound is also discussed.

2. Experimental

2.1. *General*

All reagents were commercially available and used as received. IR (KBr pellet) spectra were recorded on a Vector 22 Bruker spectrophotometer from 400 to 4000 cm^{-1}. C, N, and H analyses were performed with a Perkin-Elmer 240 analyzer. Variable temperature magnetic susceptibility data on **1** were measured using an MPMS Quantum Design SQUID magnetometer at a constant magnetic field of 5000 G.

2.2. *Synthesis of title compound*

A mixture of $Co(OAc)_2 \cdot 4H_2O$ (0.0245 g, 0.1 mmol) and 4,4′-oxy bis(benzoic acid) (0.021 g, 0.1 mmol) was dissolved in 8 mL of water and placed in a 30 mL Teflon-lined stainless steel autoclave and heated at 150°C for 1 day, then slowly cooled to room temperature after 1 day. Red colored block-shaped crystals of **1** were obtained in 67% yield. Anal. Calcd (%) for $C_{28}H_{22}CoO_{12}$: H, 3.64; C, 55.19. Found: H, 3.72; C, 55.32.

2.3. *X-ray crystallography*

Diffraction data of **1** were collected on a Bruker Apex II CCD area-detector diffractometer (Mo-Kα, $\lambda = 0.71073$ Å) [21]. Absorption correction was applied by using multiscan program SADABS. The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package [22]. Anisotropic thermal parameters were applied to all non-hydrogen atoms of **1**. The positions of hydrogen atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbons before the final cycle of refinement. The crystal data are given in table 1 and selected bond distances and angles are listed in table 2.

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{28}H_{22}O_{12}Co$
Formula weight	609.39
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions (Å, °)	
a	6.6354(3)
b	7.3611(3)
c	25.5389(13
α	91.708(4)
β	91.207(4)
γ	90.251(4)
Volume ($Å^3$), Z	1246.57(10), 2
Calculated density ($Mg\,m^{-3}$)	1.624
$F(000)$	626
Absorption coefficient (mm^{-1})	0.760
θ range for data collection (°)	2.86–25.00
Limiting indices	$-7 \le h \le 7$; $-8 \le k \le 8$; $-30 \le l \le 29$
Reflections collected	11,221
Unique reflections	4384 [$R_{\text{int}} = 0.0406$]
Data/restraints/parameters	4384/0/373
S	1.107
R_1, wR_2 [$I \ge 2\sigma(I)$]	$R_1 = 0.0684$, $wR_2 = 0.2012$
R_1, wR_2 (all data)	$R_1 = 0.0825$, $wR_2 = 0.2141$

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

Co1–O11W	2.069(3)	Co2–O12W	2.071(3)
Co1–O2	2.104(3)	Co2–O8	2.107(3)
Co1–O9	2.130(3)	Co2–O1	2.126(3)
O11W(A)–Co1–O2	89.06(11)	O12W–Co2–O8(C)	89.72(11)
O11W–Co1–O2	90.94(11)	O12W–Co2–O1(B)	90.69(11)
O11W(A)–Co1–O9	91.16(11)	O12W– Co2–O1	89.31(11)
O11W–Co1–O9	88.84(11)	O8(C)–Co2–O1	87.51(11)
O2–Co1–O9	92.93(11)	O8(D)–Co2–O1	92.49(11)
O2–Co1–O9(A)	87.07(11)		

Symmetry code: (A): $-x, 2-y, -z$; (B): $-1-x, 3-y, -z$; (C): $-1-x, 2-y, -z$; (D): $x, y+1, z$.

3. Results and discussion

Complex **1** was synthesized under hydrothermal conditions. X-ray diffraction analysis revealed that **1** crystallizes in triclinic crystal system, space group *P*-1. As depicted in figure 1(a), the asymmetric unit of **1** contains two half Co(II) cations, two terminal coordinated OBA ligands, and two ligated water molecules. The cobalts sit on centers of inversion. The fully deprotonated terminal OBA^- exhibits an η^1–η^1 coordination mode and one carboxylate adopts bis-monodentate bridging to two Co(II) cations. The central Co(II) cation is six-coordinate in octahedral geometry, with four oxygen atoms from the carboxylate defining the equatorial positions, and the axial positions occupied by two oxygen atoms from crystallographically related water molecules. The Co–O distance in the equatorial plane falls within the range 2.104–2.130 Å, while the distance on the apical position is 2.069 Å, indicating a compressed octahedral environment.

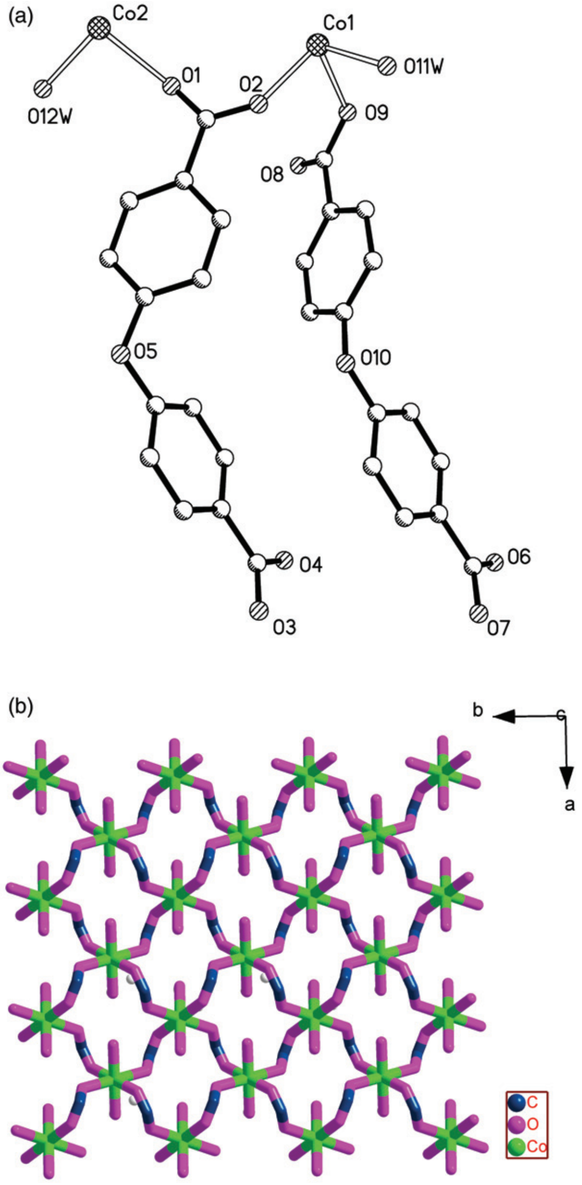


Figure 1. (a) Structure of $[Co(OBA)_2(H_2O)_2]$ with atom-labeling scheme. Thermal ellipsoids are drawn with 50% probability surfaces. (b) The 2-D cobalt carboxylate-bridged structure in the crystallographic *ab* plane.

The Co(II) cations are linked by 1,3-coordinated carboxylates in the crystallographic *ab* plane to form a 2-D layer (figure 1b). The layers are connected to each other by two sets of free carboxylic acid groups on another terminal along the crystallographic *c*-axis to generate a 3-D supramolecular framework (figure 2). The connection is evidenced by short $O \cdots O$ contact distances of 2.614 and 2.621 Å between free carboxylic acid groups of two adjacent layers, which suggests that the layers are strongly hydrogen-bonded to each other.

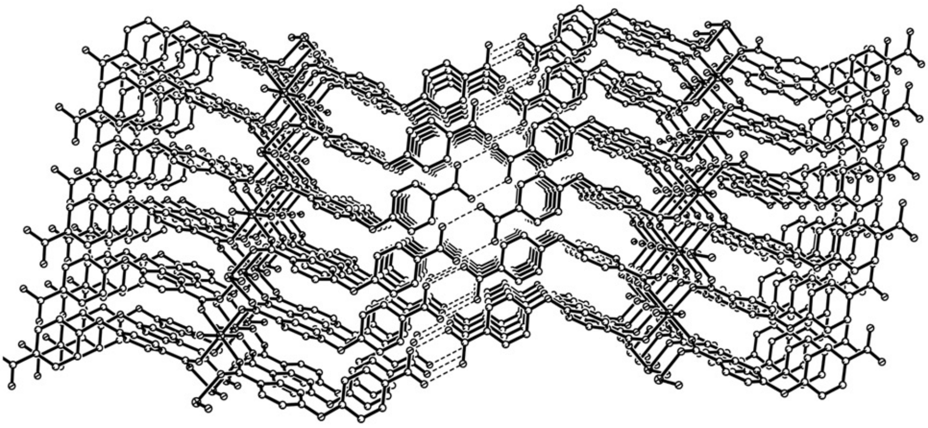


Figure 2. Hydrogen-bonding connectivity between layers of cobalt planes in **1**.

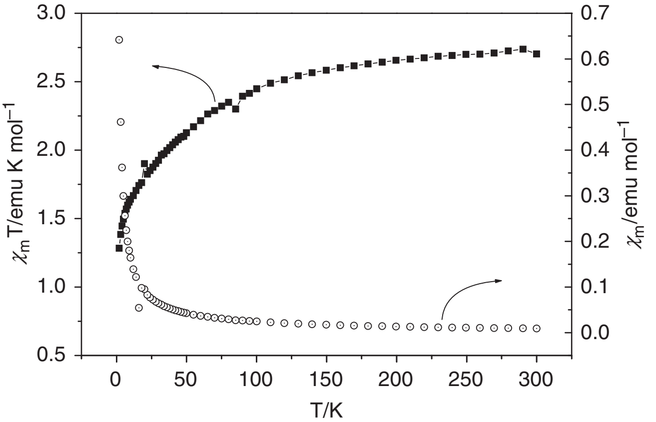


Figure 3. Temperature dependence of the magnetic susceptibility in the form of χ_mT *vs.* T from 1.8 to 300 K.

The temperature dependence of the molar magnetic susceptibility (χ_m) of the Co(II)–(OBA)$_2$ polymer was studied from 300 to 1.8 K. The magnetic susceptibility (χ_m) and product of the susceptibility with temperature (χ_mT) are shown in figure 3. The χ_mT value, 2.70 emu K mol^{-1}, at 300 K is larger than the value for a spin-only $S = 3/2$ system (1.875 emu K mol^{-1}), due to a large first-order orbital contribution to the magnetic moment as expected for octahedral high-spin cobalt(II) [23]. The fitting according to Curie–Weiss laws, $\chi_m = C/(T-\theta)$, down to 30 K gave $\theta = -12.4$ T and $C = 2.81$ cm^3 mol^{-1} K. As the temperature decreases, χ_mT decreases and reaches a value of 1.28 emu K mol^{-1} at 1.8 K. The decrease in χ_mT can be ascribed to weak antiferromagnetic interactions, as well as the single-ion effects of the cobalt(II) center. However, if we keep in mind that the Co(II) ions are singly bridged by carboxylate, clearly a poor mediator of magnetic exchange in **1**, the antiferromagnetic interactions between the cobalt(II) centers are very weak. Despite the large drop in χ_mT, there is no maximum χ_mT observed down to 1.8 K in the temperature dependence of χ_m *versus* T; thus, single-ion effects dominate the magnetic behavior. Thus, the decrease in χ_mT can

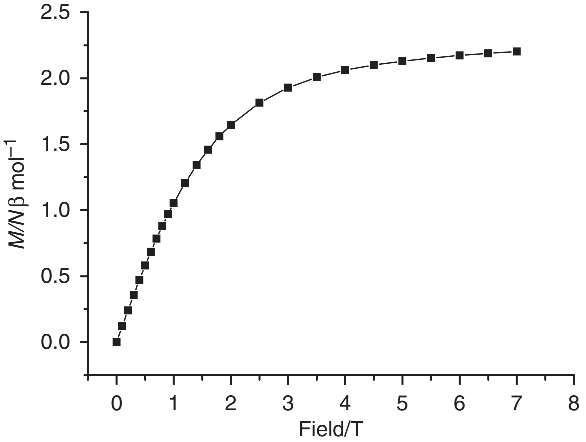


Figure 4. Magnetization measurements in the field range 0–7 T.

be ascribed to the effect of spin–orbit coupling of Co^{II}, resulting in an effective $S' = 1/2$ at low temperature from an $S = 3/2$ state at high temperature [24].

To further support the above proposal, magnetization measurements on **1** were run at 1.8 K and in the field range 0–7 T. The derived data are shown in the form of M/N [$\mu\beta$] *versus* $H\,[T]$ in figure 4. The value of the saturated M of *ca* 2 μB at 1.8 K per Co(II) is consistent with a very small interaction between Co(II) magnetic centers, assuming independent spins in the coordination polymers with $S' = 1/2$ with effective g value of *ca* 4.0. They clearly reveal the negligible antiferromagnetic exchange interaction between cobalt(II) ions and, indeed, the behavior of Co(II) single ion is responsible for the magnetic behavior.

4. Conclusion

We have synthesized a cobalt-based layered coordination polymer with strong layer···layer hydrogen-bonding interactions and interesting magnetic properties. Further research on design and construction of a series of tunable magnetic metal–organic frameworks for interesting magnetic chemistry is underway.

Supplementary material

CCDC 836791 contains the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html

Acknowledgments

The authors gratefully acknowledge the financial support from NSFC (Grant Nos 21001007, 21001008, and 21171008) and State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University).

References

[1] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **34**, 319 (2001), and references therein.

[2] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem.*, **116**, 2388 (2004); *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).

[3] G. Férey. *Chem. Soc. Rev.*, **37**, 191 (2008).

[4] A.U. Czaja, N. Trukhan, U. Müller. *Chem. Soc. Rev.*, **38**, 1284 (2009).

[5] (a) M.-H. Zeng, M.-X. Yao, H. Liang, W.-X. Zhang, X.-M. Chen. *Angew. Chem., Int. Ed.*, **46**, 1832 (2007); (b) Q. Chen, M.-H. Zeng, Y.-L. Zhou, H.-H. Zou, M. Kurmoo. *Chem. Mater.*, **22**, 2114 (2010); (c) Y.-L. Zhou, M.-H. Zeng, L.-Q. Wei, B.-W. Li, M. Kurmoo. *Chem. Mater.*, **22**, 4295 (2010); (d) M. Murrie, S.J. Teat, H. Stoeckli-Evans, H.U. Güdel. *Angew. Chem. Int. Ed.*, **42**, 4653 (2003); (e) Y. Zheng, M. Tong, W. Zhang, X. Chen. *Angew. Chem. Int. Ed.*, **45**, 6310 (2006).

[6] E. Coronado, J.R. Galán-Mascaros, C. Martí-Gastaldo. *J. Am. Chem. Soc.*, **130**, 14987 (2008).

[7] O. Sato, A. Cui, R. Matsuda, J. Tao, S. Hayami. *Acc. Chem. Res.*, **40**, 361 (2007).

[8] (a) O. Kahn. *Molecular Magnetism*, VCH Publishers, New York (1993); (b) J.S. Miller, M. Drillon. *Magnetism: Molecules to Materials I–V*, Wiley-VCH Publishers, Weinheim, Germany (2001); (c) V. Laget, C. Hornick, P. Rabu, M. Drillon, R. Ziessel. *Coord. Chem. Rev.*, **178–180**, 1533 (1998) and references cited therein; (d) Y.-L. Zhou, M.-C. Wu, M.-H. Zeng, H. Liang. *Inorg. Chem.*, **48**, 10146 (2009); (e) M.-H. Zeng, H.-H. Zou, S. Hu, Y.-L. Zhou, M. Du, H.-L. Sun. *Cryst. Growth Des.*, **9**, 4239 (2009).

[9] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 1504 (2005).

[10] F. Luo, Y. Che, J. Zheng. *Cryst. Growth Des.*, **9**, 1066 (2009).

[11] (a) S. Horike, S. Hasegawa, D. Tanaka, M. Higuchi, S. Kitagawa. *Chem. Commun.*, 4436 (2008); (b) T.K. Maji, M. Ohba, S. Kitagawa. *Inorg. Chem.*, **44**, 9225 (2005); (c) F. Luo, Y.-X. Che, J.-M. Zheng. *Cryst. Growth Des.*, **9**, 1066 (2009).

[12] K.L. Gurunatha, K. Uemura, T.K. Maji. *Inorg. Chem.*, **47**, 6578 (2008).

[13] W. Liu, T. Jiao, Y. Li, Q. Liu, M. Tan, H. Wang, L. Wang. *J. Am. Chem. Soc.*, **126**, 2280 (2004).

[14] F. Liu, Y. Zeng, J. Jiao, X. Bu, J. Ribas, S.R. Batten. *Inorg. Chem.*, **45**, 2776 (2006).

[15] J. Yang, Q. Yue, G. Li, J. Cao, G. Li, J. Chen. *Inorg. Chem.*, **45**, 2857 (2006).

[16] Z. Wang, B. Zhang, K. Inoue, H. Fujiwara, T. Otsuka, H. Kobayashi, M. Kurmoo. *Inorg. Chem.*, **46**, 437 (2007).

[17] N. Kotsakis, C.P. Raptopoulou, V. Tangoulis, A. Terzis, J. Giapintzakis, T. Jakusch, T. Kiss, A. Salifoglou. *Inorg. Chem.*, **42**, 22 (2003).

[18] M. Zeng, Y. Zhou, M. Wu, H. Sun, M. Du. *Inorg. Chem.*, **49**, 6436 (2010).

[19] P. Mahata, A. Sundaresan, S. Natarajan. *Chem. Commun.*, **00**, 4471 (2007).

[20] P. Mahata, M. Prabu, S. Natarajan. *Inorg. Chem.*, **47**, 8451 (2008).

[21] *SMART/SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA (2004).

[22] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).

[23] (a) R. Boča. *Coord. Chem. Rev.*, **248**, 757 (2004); (b) R. Boča. *Theoretical Foundations of Molecular Magnetism*, Elsevier, Amsterdam (1999).

[24] (a) R.L. Carlin. *Magnetochemistry*, Springer, New York (1983); (b) B.N. Figgis, M.A. Hitchman. *Ligand Field Theory and its Applications*, Wiley-VCH, New York (2000). (c) J.S. Wood. *Inorg. Chem.*, **7**, 852 (1968).