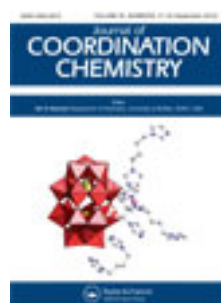


This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:38

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>

A new linear trinuclear cobalt complex bearing oximate and azido ligands: synthesis, structure, and magnetic characterization

Xiu-Min Qiu^a, Su-Na Wang^a, Jing Lu^a, Ling-Qian Kong^b, Da-Cheng Li^a & Jian-Min Dou^a

^a Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China

^b Department of Chemistry and Biology, Dongchang College Liaocheng University, Liaocheng 252059, China

Accepted author version posted online: 18 Jun 2012. Published online: 10 Aug 2012.

To cite this article: Xiu-Min Qiu, Su-Na Wang, Jing Lu, Ling-Qian Kong, Da-Cheng Li & Jian-Min Dou (2012) A new linear trinuclear cobalt complex bearing oximate and azido ligands: synthesis, structure, and magnetic characterization, Journal of Coordination Chemistry, 65:18, 3308-3315, DOI: [10.1080/00958972.2012.703779](https://doi.org/10.1080/00958972.2012.703779)

To link to this article: <http://dx.doi.org/10.1080/00958972.2012.703779>

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>

A new linear trinuclear cobalt complex bearing oximate and azido ligands: synthesis, structure, and magnetic characterization

XIU-MIN QIU[†], SU-NA WANG[†], JING LU[†], LING-QIAN KONG[‡],
DA-CHENG LI[†] and JIAN-MIN DOU^{†*}

[†]Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, China

[‡]Department of Chemistry and Biology, Dongchang College Liaocheng University, Liaocheng 252059, China

(Received 19 January 2012; in final form 7 May 2012)

The reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, mpkoH (methyl 2-pyridyl ketone oxime), NEt_3 , and NaN_3 in a 1:1:2:1 molar ratio affords a linear trinuclear complex, $[\text{Co}_2^{\text{III}}\text{Co}^{\text{II}}(\text{mpko})_4(\text{N}_3)_4(\text{H}_2\text{O})_2]$ (**1**). Complex **1** has been characterized by single-crystal X-ray diffraction, elemental analysis, and infrared spectrum. Three cobalt ions are in the center of distorted octahedra, which are connected by two μ -1,1 azides and two oxime oxygen atoms to form a linear trinuclear structure. Discrete units of **1** are connected to form a stable 3-D supramolecular network by C–H \cdots O and C–H \cdots N weak interactions. Variable temperature magnetic susceptibility measurements reveal that **1** exhibits antiferromagnetic behavior.

Keywords: Oxime; Cobalt complex; Crystal structure; Magnetic properties

1. Introduction

The preparation of molecule-based magnets has been of considerable interest to obtain high- T_c compounds. The usual synthetic approach is to build high-dimensional polynuclear derivatives by mixing paramagnetic centers with suitable bridging and terminal ligands. Ferromagnetic couplers in such reactions have been successful for the synthesis of molecular species with high-spin ground states [1], one of the requirements for single-molecule magnets (SMMs). Azide is an excellent ligand for constructing diverse structural topologies from discrete molecules to 3-D networks and predicting the magnetic nature based on a binding mode [2]. In general, an end-on mode gives a ferromagnetic interaction and the end-to-end mode produces an antiferromagnetic coupling [3]. Meanwhile, 2-pyridyloximates (paoH/mpkoH/ppkoH/phpaoH in figure 1)

*Corresponding author. Email: dougroup@163.com

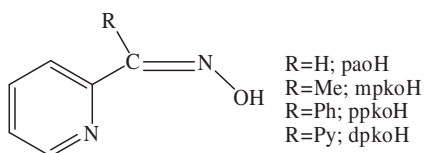


Figure 1. General structural formula and abbreviations of 2-pyridyl oximes.

have proved useful in the synthesis of new magnetic materials [1b, 4] because of their coordination modes. The 2-pyridyloximates and azides (N_3^-) in Mn chemistry have afforded new Mn clusters, which displayed SMM behavior [1, 5].

Co, as a large anisotropic ion, is an attractive alternative to the isotropic Mn to obtain SMM compounds with 2-pyridyloximate and azide. Some groups have had a longstanding interest in the use of different chelating ligands in cobalt cluster chemistry, including hydroxymethylpyridine (hmpH) [6], 2-hydroxy-[1,2-di(pyridin-2-yl)]ethane-1-one (Hhdeo) [7], 1,1,1-trifluoro-7-hydroxy-4methyl-5-aza-hept-3-en-2-one [8], and 2-benzoyl pyridine (bzip) [9], which play a key role in the synthesis of cobalt SMMs. No azide cobalt compounds with 2-pyridyloximate have been described yet. Herein we report the synthesis, crystal structure, and magnetic behavior of a new linear complex, $[Co_3(mpko)_4(N_3)_4(H_2O)_2]$, containing methyl 2-pyridyl ketoxime and azide.

2. Experimental

2.1. Materials and physical measurements

All reagents were purchased commercially and used as received. Methyl 2-pyridyl ketone oxime was prepared according to the literature [10]. Infrared (IR) spectra were obtained from KBr pellets on a Nicolet 460 FT-IR spectrophotometer. Elemental analysis (C, H, and N) was performed with a Perkin-Elmer 2400 II elemental analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer pyris-1 TG/DTA instrument. Ultraviolet and visible spectra were measured in a DMF solution on a HP8453A UV-Vis/NIR spectrophotometer. Direct current magnetic susceptibility studies were performed on polycrystalline samples of **1** from 2 to 300 K using a Quantum Design MPMS-XL7 SQUID magnetometer in an applied field of 0.1 T.

Caution! Azide compounds are potentially explosive! Only a small amount of material should be prepared, and it should be handled with care.

2.2. Preparation of $[Co_2^{III}Co^{II}(mpko)_4(N_3)_4(H_2O)_2]$ (**1**)

$CoCl_2 \cdot 6H_2O$ (0.1190 g, 0.5 mmol) was added to a stirred solution of mpkoH (0.0680 g, 0.5 mmol) and NEt_3 (0.14 mL, 1.0 mmol) in MeOH (20 mL). After stirring for 30 min, NaN_3 (0.0325 g, 0.5 mmol) was added slowly. After 6 h, a dark red mixture was filtered. Red crystals were obtained after 3 weeks with $(CH_3)_2CO$ layered on the filtrate. Yield: 35 mg, 30% (based on mpkoH). Anal. Calcd for $C_{28}H_{32}Co_3N_{20}O_6$ (%): C, 36.46; H, 3.47; N, 30.38. Found (%): C, 36.38; H, 3.42; N, 30.45. IR (KBr pellet: cm^{-1}): 3450 (br), 2060(s), 2030(s), 1630(w), 1601(s), 1475(m), 1384(m), 1294(w), 1270(w), 1181(s), 1110(m), 1086(s), 1045(m), 776(m), 749(w), 696(s), 660(m), 570(w), 516(m), 489(m), 496(m).

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

CCDC	838490
Empirical formula	C ₂₈ H ₃₂ Co ₃ N ₂₀ O ₆
Formula weight	921.53
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P2(1)/c</i>
Unit cell dimensions (Å, °)	
<i>a</i>	10.8469(8)
<i>b</i>	9.3647(11)
<i>c</i>	20.0588(17)
α	90
β	95.3570(10)
γ	90
Volume (Å ³), <i>Z</i>	2028.6(3), 2
Calculated density (mg m ⁻³)	1.509
<i>F</i> (000)	942
Crystal size (mm ³)	0.31 × 0.22 × 0.10
Crystal color	Dark-red
θ range for data collection (°)	2.88–25.02
Absorption coefficient (mm ⁻¹)	1.278
Limiting indices	–11 ≤ <i>h</i> ≤ 12; –8 ≤ <i>k</i> ≤ 11; –23 ≤ <i>l</i> ≤ 23
Reflections collected	9505
Independent reflection	3537 [<i>R</i> (int) = 0.0594]
Max/min transmission	0.8829/0.6928
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3537/0/262
Goodness-of-fit on <i>F</i> ²	1.002
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0486, <i>wR</i> ₂ = 0.1188
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0949, <i>wR</i> ₂ = 0.1557
Largest difference peak and hole (e Å ⁻³)	0.542 and –0.353

2.3. X-ray crystallography

Collection of intensity data was carried out on a Bruker Smart-1000 CCD diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by direct methods and expanded using Fourier difference techniques with the SHELXTL-97 program package [11]. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on *F*². Positions of hydrogen atoms attached to carbons were geometrically placed and refined isotropically as a riding mode. Crystallographic data and refinement parameters for **1** are presented in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. X-ray structural characterization

Single-crystal X-ray structural analysis reveals that **1** has a linear trinuclear structure (figure 2). The asymmetric unit is composed of one and a half crystallographically independent cobalt atoms, two mpko⁻, two azides, and one water molecule.

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

Bond lengths			
Co(1)–N(1)	1.920(4)	Co(2)–O(2)	2.004(3)
Co(1)–N(3)	1.917(4)	Co(2)–O(3)	2.123(4)
Co(1)–N(4)	1.934(4)	Co(2)–N(8)	2.141(4)
Co(1)–N(2)	1.948(4)	Co(1)–N(5)	1.975(5)
Co(1)–N(8)	1.952(4)	N(5)–N(6)	1.178(4)
N(6)–N(7)	1.164(5)	N(8)–N(9)	1.210(4)
N(9)–N(10)	1.136(5)		
Bond angles			
N(1)–Co(1)–N(3)	96.48(18)	N(2)–Co(1)–N(8)	92.45(17)
N(1)–Co(1)–N(4)	90.24(18)	N(1)–Co(1)–N(5)	172.79(18)
N(3)–Co(1)–N(4)	82.40(17)	N(3)–Co(1)–N(5)	90.70(18)
N(1)–Co(1)–N(2)	82.28(18)	N(4)–Co(1)–N(5)	90.00(19)
N(3)–Co(1)–N(2)	177.46(17)	N(2)–Co(1)–N(5)	90.52(19)
N(4)–Co(1)–N(2)	95.38(18)	N(8)–Co(1)–N(5)	91.81(19)
N(1)–Co(1)–N(8)	88.92(18)	O(2)–Co(2)–N(8)	94.55(14)
N(3)–Co(1)–N(8)	89.76(17)	O(2)–Co(2)–O(3)	92.14(16)
N(4)–Co(1)–N(8)	171.96(18)	O(3)–Co(2)–N(8)	91.91(16)

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

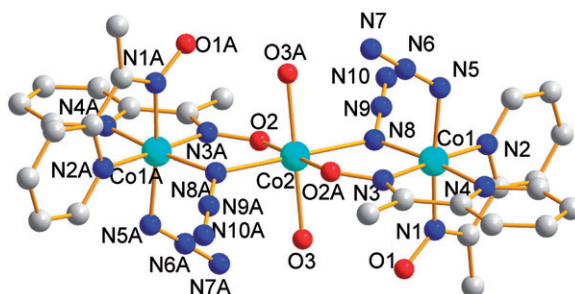


Figure 2. X-ray crystal structure of **1** (all hydrogen atoms and solvent water molecules are omitted for clarity).

The coordination geometry of Co1 and Co2 could be described as distorted octahedral. For Co(1), the six sites are occupied by six nitrogen atoms (N(1)–N(5) and N(8)), four of which belong to two chelated mpko^- ligands, and the other two to μ -1,1 and terminal azides. The central Co(2), which is located on a crystallographic inversion center, is octahedrally coordinated by two coordination water molecules, O(3) and O(3A), two nitrogen atoms, N(8) and N(8A), from two μ -1,1 azides and two oxime oxygen atoms of mpko^- , O(2) and O(2A).

As a result, Co(2) is connected with Co(1) and its symmetry-related Co(1A) by two μ -1,1 azides to form a linear trinuclear structure. Co(1) is clearly low-spin Co^{III} based on Co–N bond lengths, which are similar to Co^{III} –N bond lengths in other structurally characterized complexes [12]. The central Co(2) has Co–O distances from 2.004(3) to 2.123(3) Å and Co–N distance of 2.141 Å, indicating that this is a Co^{II} ion [12]. The oxidation states of Co(1) and Co(2) have also been confirmed by BVS calculations [13], which give the values of 3.05 and 2.16 for Co(1) and Co(2), respectively.

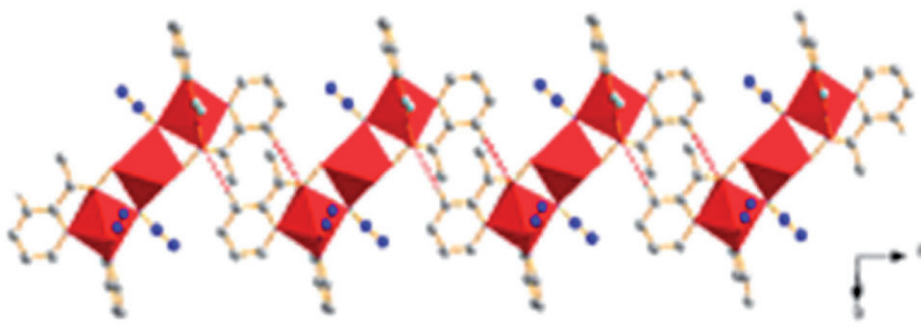


Figure 3. View of the 1-D chain structure of **1**.

Two kinds of weak interactions, C–H···O and C–H···N, exist in this complex. As shown in figures 3 and 4, single molecules are linked by C11–H11···O1 (C11···O1 = 3.184 Å) [14] weak interactions to give a 1-D chain along the *a*-axis, which are further connected by C7–H7···N7 (C7···N7 = 3.330 Å) [15] weak interactions to form a 2-D layer parallel to the *ab* plane. These 2-D layers are extended to a 3-D supramolecular network by C4–H4···N7 (C4···N7 = 3.329 Å) [15] weak interactions. The C···X distances and C–H···N angles (X = O, N) are 3.184–3.330 Å and 126.93–152.13°, respectively, consistent with the previously reported values [14, 15]. These supramolecular interactions, together with the coordinate–covalent interactions between metal ions and organic ligands, strengthen the stability of the network structure.

3.2. Spectroscopic properties

The IR spectrum of **1** exhibits a broad band characteristic of a coordinated water molecule at 3400–3490 cm⁻¹. The IR spectrum of the complex reveals coordinated azide with very strong bands at 2060 cm⁻¹ for antisymmetric vibrations and at 1181 cm⁻¹ for symmetric vibrations [16]. A strong absorption at 1601 cm⁻¹ and a weak absorption at 1294 cm⁻¹ are assigned to the (C=N) and (N–O oximate) stretching vibrations, respectively, of mpko⁻ [17].

The electronic spectrum of **1** in DMF from 190 to 800 nm has λ_{\max} (ϵ , L mol⁻¹ cm⁻¹) of 285(6500) and tails into the visible region. The absorption at 285 nm may be assigned to π – π^* transitions in the oximate and oxime oxygen atom. The absorption at 364 nm may be assigned to ligand-to-metal charge transfer (LMCT) [18].

3.3. Thermogravimetric analyses

TGA was performed on **1** to investigate the thermal stability (Supplementary material). The TGA curve of **1** displays steady weight loss from 100 to 150°C (found: 3.4%), corresponding to the loss of H₂O (Calcd 3.9%). The decomposition of the whole structure corresponds to a rapid weight loss from 150 to 300°C. No further weight loss occurred until 550°C, indicating decomposition of the whole structure.

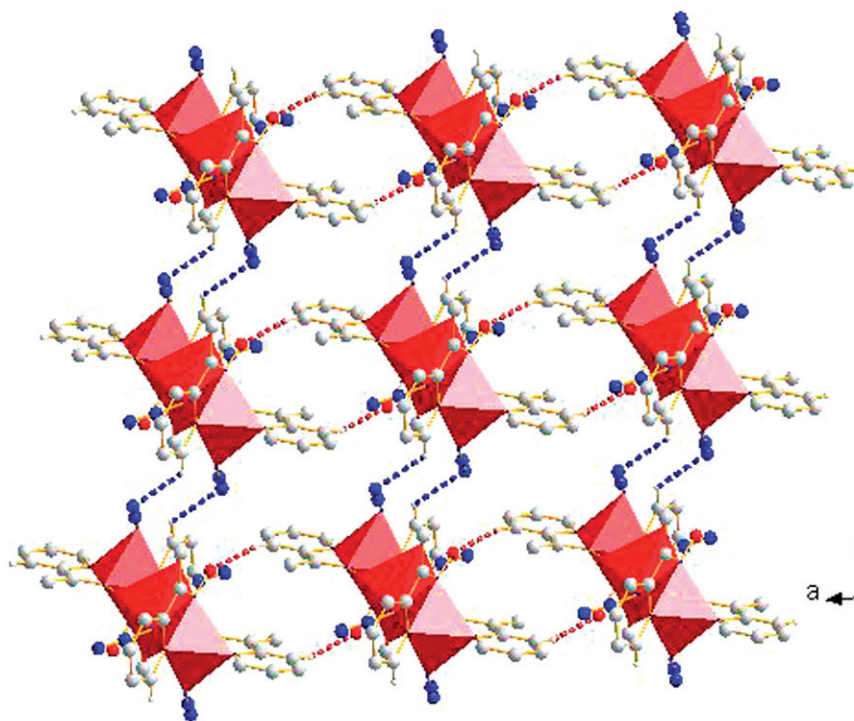


Figure 4. View of the 2-D supramolecular structure of **1**.

3.4. Magnetic susceptibility measurements

Direct current magnetic susceptibility measurements were performed on polycrystalline samples of **1** from 2 to 300 K in an applied field of 0.1 T. The results are plotted as $\chi_M T$ and χ_M^{-1} versus T in figure 5. The $\chi_M T$ at 300 K is $2.607 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, higher than the spin-only Co(II) ion ($1.875 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with $S=3/2$ and $g=2$), but much smaller than that of three uncoupled high-spin Co(II) ions. This confirms that **1** is a mixed valence with Co(III)($S=0$)–Co(II)($S=3/2$)–Co(III)($S=0$), consistent with the structure determined by X-ray diffraction and similar to other reported mixed valence linear trinuclear cobalt compounds [19]. The higher value at room temperature may be due to the first-order orbital contribution to the magnetic moment, typical of the $^4T_{1g}$ ground state [20]. Upon lowering the temperature, the value of $\chi_M T$ gradually decreases, reaching $1.63 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.0 K, which may be mainly caused by depopulation of the higher energy Kramers doublets of Co(II) centers or zero-field-splitting effects [18].

An attempt to fit the experimental data using the one-ion approximation for Co(II), similar to that of a similar compound, was unsuccessful [19a]. Instead, the data were fitted well by an expression for $S=3/2$ systems with zero-field-splitting effects, D [21]. The best-fit parameters of the experimental data are $g=2.34$ and $D=50.2 \text{ cm}^{-1}$, with an agreement factor of 1.31×10^{-3} ($R = \sum(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2 / \sum\chi_{\text{obsd}}^2$) and close to that of the high-spin Co(II) complexes [21].

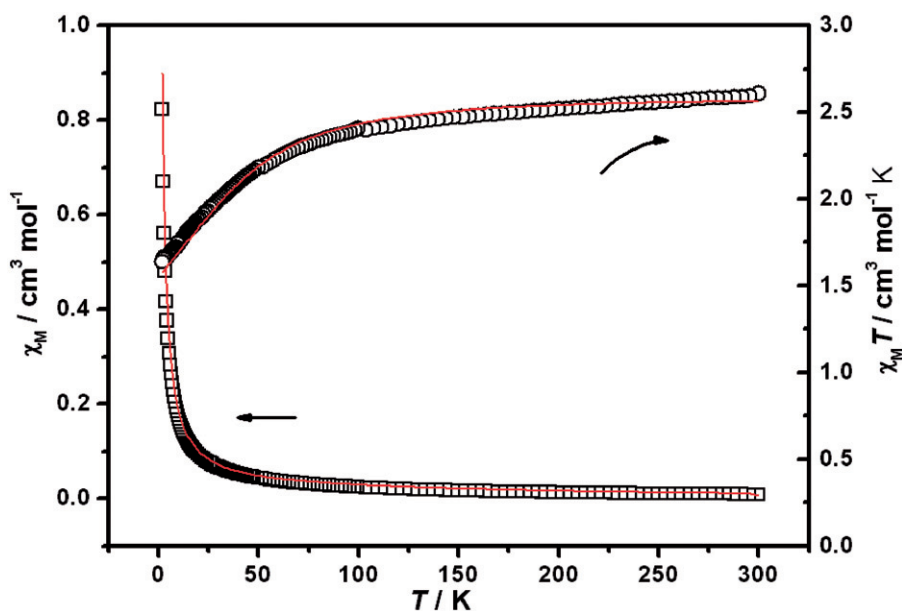


Figure 5. Plots of $\chi_M T$ and χ_M^{-1} vs. T for **1**.

4. Conclusion

We have synthesized and characterized a new azido-bridged linear trinuclear cobalt complex with mpkoH, in which azides coordinate $\mu_{1,1}$ (end-on, EO). Molecules are linked by C–H \cdots O and C–H \cdots N weak interactions to form a 2-D layer paralleled to the *ab* plane. Then 2-D layers along the *c*-axis form a 3-D supramolecular architecture with weak interactions important for the stability of the structure. The magnetic behavior of **1** was determined.

Supplementary material

CCDC 838490 contains the supplementary crystallographic data for this article. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB 21EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work was supported by the National Natural Science Foundation of P.R. China (No. 21141003 and 20671048).

References

- [1] (a) C. Lampropoulos, T.C. Stamatatos, M.J. Manos, A.J. Tasiopoulos, K.A. Abboud, C. George. *Eur. J. Inorg. Chem.*, 2244 (2010); (b) H.S. Wang, Z.C. Zhang, X.J. Song, J.W. Zhang, H.B. Zhou, J. Wang, Y. Song, X.Z. You. *Dalton Trans.*, **40**, 2703 (2011).
- [2] H.R. Wen, C.F. Wang, Y. Song, J.L. Zuo, X.Z. You. *Inorg. Chem.*, **44**, 9039 (2005).
- [3] (a) A. Escuer, A. Gromi. *Eur. J. Inorg. Chem.*, 4721 (2006); (b) C.S. Hong, J. Koo, S.K. Son, Y.S. Lee, Y.S. Kim, Y. Do. *Chem. Eur. J.*, **7**, 4243 (2001); (c) C.S. Hong, Y. Do. *Angew. Chem. Int. Ed.*, **38**, 193 (1999); (d) Y.S. You, C.S. Hong, K.M. Kim. *Polyhedron*, **24**, 249 (2005).
- [4] C.C. Stoumpos, R. Inglis, O. Roubeau, H. Sartz, A.A. Kito. *Inorg. Chem.*, **49**, 4388 (2010).
- [5] T.C. Stamatatos, A. Bell, P. Cooper. *Inorg. Chem. Commun.*, **8**, 533 (2005).
- [6] E.C. Yang, D.N. Hendrickson. *J. Appl. Phys.*, **91**, 7382 (2002).
- [7] X.T. Wang, B.W. Wang, Z.M. Wang, W. Zhang, S. Gao. *Inorg. Chim. Acta*, **361**, 3895 (2008).
- [8] L.F. Chibotaru, L. Ungur, C. Aronica, H. Elmol. *J. Am. Chem. Soc.*, **130**, 12445 (2008).
- [9] Y.Z. Zhang, W. Wernsdorfer, F. Pan. *Chem. Commun.*, 3302 (2006).
- [10] C.D. Samara, M. Alexiou, C.M. Zaleski, J.W. Kampf, M.L. Kirk, D.P. Kessissoglou, V.L. Pecoraro. *Angew. Chem. Int. Ed.*, **42**, 63 (2003).
- [11] G.M. Sheldrick, *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Madison, WI (1997).
- [12] Y.A. Milway, L.K. Thompson, D.O. Miller. *Chem. Commun.*, 1790 (2004).
- [13] H.H. Thorpe. *Inorg. Chem.*, **31**, 85 (1992).
- [14] L. Walz, H. Paulus, W. Haasem. *Dalton Trans.*, 657 (1983).
- [15] D.L. Reger, J.R. Jardinier, R.F. Semeniuc. *Dalton Trans.*, 1712 (2003).
- [16] M.A.M. Abu-Youssef, F.A. Mautner, R. Vicente. *Inorg. Chem.*, **46**, 4654 (2007).
- [17] D. Burdinski, F. Birkelbach, T. Weyhermüller, U. Florke, H.J. Haupt, M. Lengen, A.X. Trautwein, E. Bill, K. Wieghardt, P. Chaudhuri. *Inorg. Chem.*, **37**, 1009 (1998).
- [18] M. Herrera, A. Bleuzen, Y. Dromzee, M. Julve, F. Lloret, M. Verdager. *Inorg. Chem.*, **42**, 7052 (2003).
- [19] (a) C. Yang, Q.L. Wang, G.T. Tang, C. Wang, S.P. Yan, D.Z. Liao. *J. Coord. Chem.*, **63**, 505 (2010); (b) X. He, C.Z. Lu, C.D. Wu. *J. Coord. Chem.*, **59**, 977 (2010).
- [20] (a) B. Zurowska, A. Brzuskiewicz. *Polyhedron*, **27**, 1623 (2008); (b) F. Dumestre, B. Soula, A.M. Galibert, P.L. Fabre, G. Bernardinelli, B. Donnadiou, P. Castan. *J. Chem. Soc., Dalton Trans.*, 4131 (1998).
- [21] S.R. Marshall, A.L. Rheingold, L.N. Dawe, W.W. Shum, C. Kitamura, J.S. Miller. *Inorg. Chem.*, **41**, 3599 (2002).