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Synthesis, Crystal Structure, and Magnetic Characterization of Two Manganese Schiff-Base-Containing Complexes[1]

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Abstract—The reactions of $[Mn^{III}(3\text{-}MeOSalen)(H_2O)_2]^+$ (Salen = *N*,*N*-ethylenebis(salicylideneaminato) dianion) with $(Et_4N)_4[M(CN)_8]$ (M = Mo, W) have been investigated and one mononuclear manganese(II) complex $[Mn^{II}(Salen)(H_2O)]$ (**I**) and one bimetallic ion-pair complex $[Mn^{III}(3\text{-}MeOSalen)(H_2O)_2]_4[W(CN)_8] \cdot DMSO \cdot 4H_2O$ (**II**) were obtained unexpectedly and characterized by element and single crystal structure analysis. Single crystal X-ray diffraction (CIF files CCDC nos. 1456365 (**I**) and 1456366 (**II**)) showed that the Mn^{2+} ion in complex **I** is five-coordinated involving in a distorted square pyramid. Furthermore, with the help of the intermolecular hydrogen bond interactions, this complex can be constructed into interesting one-dimensional zig-zag chain structure. For complex **II**, the coordination sphere of Mn^{3+} ion is an elongated octahedron. Additional, the four mononuclear manganese(III) units are self-complementary through the coordinated aqua ligand from one molecule and the free O(4) compartment from the neighboring molecule, giving supramolecular dimmers structure. Investigation of the magnetic susceptibility of the two complexes reveals the overall weak antiferromagnetic interactions between the adjacent manganese centers caused by H-bond interactions.

Keywords: manganese(II/III) Schiff-base, crystal structure, magnetic properties

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INTRODUCTION

During the past several decades, there has been great interest in cyanide-bridged bimetallic assemblies due not only to their divers structure types from 0D clusters to three-dimensional network but also to their interesting magnetic properties [1–8]. Among the polycyanidemetalate members used to construct cyanide-bridged magnetic complexes, the octacyanometalates $[M(CN)_8]^{3-/4-}$ (M = Mo or W) have been widely used to prepare supranolecular assembles with potential utility for functional materials for the following reasons. The octacyanometalates of molybdenum and tungsten, containing the maximum numbers of cyanide groups in the polycyanidemetalate family, display three idealized basic geometries: square antiprism (SAPR-8, *D*4*d*), dodecahedron (DD-8, *D*2d) or bicapped trigonal prism (TPRS-8, *C*2*v*), and the rearrangements between them have been found to be almost barrierless [9–11]. Obviously, the existence of the three closely related geometries and the facile interconversion between them endow these two cyanide-containing precursors with high flexibility, thereby generating cyanide-bridged heterobimetallic systems displaying all possible dimensionalities [12, 13].

Among the counterpart paramagnetic segments used to synthesize cyanide-bridged magnetic systems, manganese(III)-Salen complexes $[Mn^{III}(Salen)(H_2O)]^+$ or $[Mn^{III}(BS)]^+$ (BS = the Salen-substituted ligand) containing N_2O_2 equatorial Salen-type ligands play an important role because of their facile preparation and large spin state ($S = 2$) as well as the usually negative magnetic anisotropy of the central Mn^{3+} ions [14]. Up to now, some cyanide-bridge bimetallic magnetic complexes with various structures based-on manganese(III)-salen type compounds and $K_3[M(CN)_8]$ (M = Mo or W) have been reported [15–22]. Here, we investigated the reactions of $[Mn^{III}(3\text{-}MeOSalen)(H_2O)]^+$ with $(Et_4N)_4[M(CN)_8]$, for the latter which have been given much attention in recent years due to their interesting photomagnetic properties [23] and the potential application of their compounds as porous materials [12, 13]. Unexpectedly, one mononuclear manganese(II) complex and one bimetallic ion-pair complex and with the formula $[Mn^{II}(Salen)(H_2O)]$ (**I**) and $[Mn^{III}(3\text{-}MeOSalen)(H_2O)_2]_4[W(CN)_8]$ · DMSO ·

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$4H_2O$ (**II**) were obtained. The synthesis, crystal structure and magnetic property for these two complexes will be described in this paper.

EXPERIMENTAL

General procedures, materials and physical measurements. The preparation reactions for these two complexes were carried out under an air atmosphere and all chemicals and solvents used were reagent grade without further purification. The cyanide precursor $(Et_4N)_4[M(CN)_8]$ was prepared by the simple metathesis reaction of $K_4[M(CN)_8]$ with Et_4NCl in water, while the $[Mn^{III}(3\text{-MeOSalen})(H_2O)_2]ClO_4$ was synthesized according to the literature method [24].

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El. Variable-temperature magnetic susceptibility was performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with care.

Synthesis of complex I. $(Et_4N)_4[Mo(CN)_8]$ (82.5 mg, 0.1 mol) dissolved in 5 mL methanol was added into a solution of $[Mn^{III}(3\text{-MeOSalen})(H_2O)_2]ClO_4$ (0.4 mmol, 207 mg) in methanol (20 mL), and the mixture was stirred for 5 min at room temperature. The suspension was filtered to remove a small amount of insolvable material, and the filtrate was allowed to slow evaporate in air. The brown-yellow single crystals suitable for X-ray diffraction obtained after about two weeks were collected by filtration, washed with ether and dried in air. The yield was ~35%.

For $C_{18}H_{20}N_2O_5Mn$ (**I**)

anal. calcd., %:	C, 54.14;	H, 5.05;	N, 7.02.
Found, %:	C, 54.01;	H, 5.08;	N, 7.10.

Synthesis of complex II. $(Et_4N)_4[W(CN)_8]$ (91.2 mg, 0.1 mol) dissolved in 5 mL methanol was added into a solution of $[Mn^{III}(3\text{-MeOSalen})(H_2O)_2]ClO_4$ (0.4 mmol, 207 mg) in methanol (20 mL), and the mixture was stirred for 5 min at room temperature accompanying the formation of comparatively large amount of the dark-brown precipitate. The solid was filtered out and dissolved in as less as DMSO. The dark-brown single crystals suitable for X-ray diffraction obtained from the DMSO solution after about two months were collected by filtration, washed with ether and dried in air. The yield was ~40%.

For $C_{82}H_{102}N_{16}O_{29}SMn_4W$ (**II**)

anal. calcd., %:	C, 44.54;	H, 4.65;	N, 10.13.
Found, %:	C, 44.41;	H, 4.48;	N, 10.39.

X-ray structure determination. Data were collected on a Oxford Diffraction Gemini E diffractometer with MoK_α radiation (λ = 0.71073 Å) at 293 K. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientation matrix. CrysAlisPro Agilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction, The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-97) on F^2 [25]. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced as fixed contributors. All the nonhydrogen atoms except the disordered ones were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C)$ and their coordinates were allowed to ride on their respective carbons using SHELXL-97 except some of the H atoms of the solvent molecules. For these H atoms, they were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Some selected structural parameters for complexes **I** and **II** are given in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1456365 (**I**) and 1456366 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The perspective view of the molecular structure and the supramolecular structure formed by the intermolecular hydrogen bond interactions are shown in Figs. 1, 2, respectively.

As tabulated in Table 2, complex **I** contains four independent units in the unit cell. The coordination sphere of the Mn^{2+} ion is a distorted square-pyramid, in which four basal sites are occupied by two N atoms and two O atoms of the Schiff-base ligand, and the additional apical site is occupied by the O atom of the

Table 1. Crystallographic data and structure refinement summary for the compounds **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	399.30	2211.47
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$	$C2/c$
a, Å	7.8787(7)	27.549(3)
b, Å	8.8348(8)	25.163(2)
c, Å	25.247(2)	14.5636(12)
β, deg	90	109.187(2)
V, Å^3	1757.4(3)	9534.8(15)
Z	4	4
ρ_{calcd}, g/cm^{-1}	1.509	1.541
F(000)	828	4512
μ, mm^{-1}	0.783	1.824
θ Range	2.44–25.01	1.57–25.01
Index range hkl	$-9 \le h \le 9$, $-10 \le k \le 6$, $-30 \le l \le 27$	$-32 \le h \le 23$, $-29 \le k \le 26$, $-13 \le l \le 17$
Reflections collected/unique	7998/2918	22777/8382
R_{ink}	0.0191	0.0846
Reflections with $I > 2\sigma(I)$	2431	5312
Data/restraints/parameters	2918/1/157	8382/0/615
Goodness-of-fit on F^2	1.094	1.017
Final R indices ($I > 2\sigma(I)$)	0.0498	0.0749
R indices (all data)	0.0615	0.1164
Largest diff. peak and hole, e/Å^3	1.155 and 0.622	1.600 and −1.803

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

Bond	*d*, Å	Bond	*d*, Å
	I		
Mn(1)–N(1)	2.147(7)	Mn(1)–N(2)	2.211(8)
Mn(1)–O(1)	1.944(5)	Mn(1)–O(3)	1.946(5)
Mn(1)–O(5)	2.277(3)		
Angle	ω, deg	Angle	ω, deg
O(1)Mn(1)O(2)	101.34(11)	N(1)Mn(1)N(2)	75.34(17)
O(1)Mn(1)N(1)	80.4(3)	O(1)Mn(1)O(5)	107.6(2)
O(2)Mn(1)N(1)	139.1(3)	O(2)Mn(1)O(5)	106.8(2)
O(1)Mn(1)N(2)	139.3(4)	N(1)Mn(1)O(5)	111.6(3)
O(2)Mn(1)N(2)	77.9(2)	N(2)Mn(1)O(5)	111.6(3)
	II		
Mn(1)–O(1)	1.854(5)	Mn(1)–O(2)	1.855(7)
Mn(1)–N(5)	1.990(10)	Mn(1)–N(6)	1.935(7)
Mn(1)–O(11)	2.359(7)	Mn(1)–O(12)	2.226(6)
Mn(2)–O(5)	1.869(7)	Mn(2)–O(6)	1.851(5)
Mn(2)–N(7)	1.943(7)	Mn(2)–N(8)	1.930(9)
Mn(2)–O(9)	2.227(6)	Mn(2)–O(10)	2.287(8)
Angle	ω, deg	Angle	ω, deg
O(11)Mn(1)O(12)	171.0(2)	O(2)Mn(1)O(12)	92.7(3)
O(1)Mn(1)O(2)	92.5(3)	N(6)Mn(1)O(12)	85.7(3)
O(1)Mn(1)N(6)	175.6(4)	N(5)Mn(1)O(12)	90.8(3)
O(2)Mn(1)N(6)	91.8(3)	O(1)Mn(1)O(11)	94.9(3)
O(1)Mn(1)N(5)	92.1(4)	O(2)Mn(1)O(11)	90.8(3)
O(2)Mn(1)N(5)	174.0(3)	N(6)Mn(1)O(11)	85.8(3)
N(6)Mn(1)N(5)	83.6(4)	N(5)Mn(1)O(11)	85.1(3)
O(1)Mn(1)O(12)	93.3(2)		

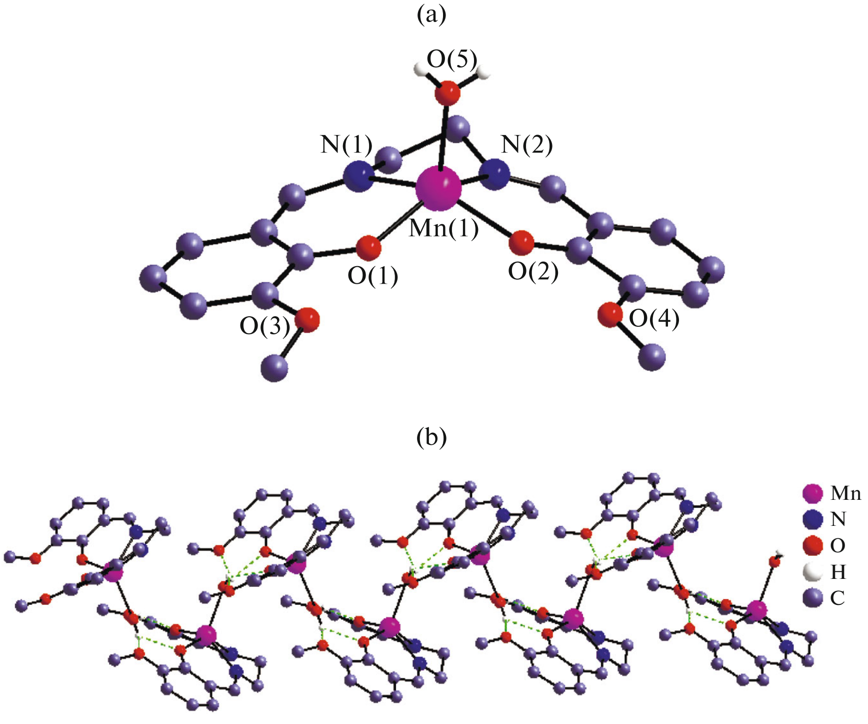

Fig. 1. Perspective view of the molecular structure of **I** (a) and one-dimensional supramolecular structure formed by H-bond interactions (b). All the H atoms except those used to form H bond interactions have been omitted for clarity.

coordinated solvent water molecule. The Mn^{2+} ion is displaced towards the Mn–O(H_2O) bond from the plane formed by the two N atoms and two O atoms by 0.723(2) Å. As can be found, the bond length of Mn–O(H_2O) 2.277(3) Å is obvious longer than the averaged $Mn–O_{Schiff\text{-}base}$ 1.945 Å and $Mn–N_{Schiff\text{-}base}$ 2.175 Å. All the bond parameters around the Mn^{2+} ion are basically consistent with the corresponding distances found in another reported Mn(II) Schiff-base complex $[Mn(Acacen)]_2$ (Acacen = *N*,*N*'-ethylenebis(acetylacetonylideneaminato) [26]. Under the help of the intermolecular hydrogen bond interactions, this complex can be constructed into interesting one-dimensional zig-zag chain supramolecular structure (Fig. 1).

Complex **II**, which is comprised by four mononuclear $[Mn^{III}(3\text{-}MeOSalen)(H_2O)_2]^+$ cations, $[W(CN)_8]^{4-}$ anion, one DMSO and four water molecules. The coordination sphere of the Mn^{2+} ions is an octahedron, in which the four equatorial positions are occupied by two N atoms and two O atoms from the Schiff-base ligand, and the other two axial ones come from the O atoms of the coordinated solvent water molecules. The Mn–N and $Mn–O_{Schiff\text{-}base}$ bond lengths (with Mn(1) as representative) are 1.935(7), 1.990(10), 1.854(5) and 1.855(7) Å, respectively, markedly shorter than the distances between the manganese ion and the oxygen atom of the coordinated water molecules with the values of 2.226(6) and 2.355(7) Å, which provides further information about the elongated octahedron around the Mn^{2+} ion, typically accounting for the well known Jahn–Teller effect. The $O_{H_2O}MnO_{H_2O}$ bond angles are 171.0(2)° and 173.4(3)°, respectively, indicating that the three atoms are in a good linear configuration. It should be pointed out, because of the excellent encapsulating ability of the O(4) unit from the Schiff-base ligand, the mononuclear manganese Schiff-base cations are assembled into supramolecular dimer structure with the help of the intermolecular O–H···O hydrogen bond interactions between the coordinated aqua ligand from one molecule and the phenolic oxygen atoms from the neighboring one (Fig. 2).

The temperature dependence of magnetic susceptibility for these two complexes measured in the temperature range of 2–300 K under the applied field of 2000 Oe is shown in Fig. 3. The χ_mT value at room temperature of is about 8.61 and 5.91 emu K mol^{-1}, respectively, which is consistent with the spin-only value 8.75 for two manganese(II) ions ($S = 5/2$) and 6.0 emu K mol^{-1} for two manganese(III) ions ($S = 2$). Within the temperature range of 300–50 K, the χ_mT

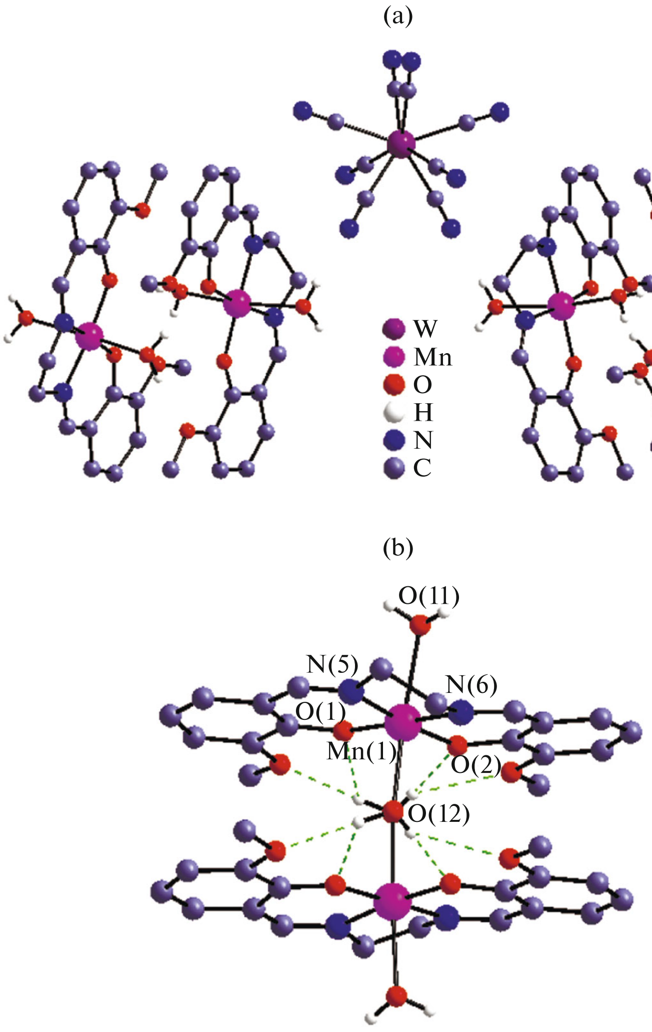

Fig. 2. The molecular structure of complex **II** (a) and the manganese Schiff-base supramolecular dimer structure formed by the intermolecular H-bond interactions in complex **II** (b). All the H atoms except those used to form H bond interactions and the solvent molecules have been omitted for clarity.

remains almost constant. After that, the $\chi_m T$ value begins to decrease and reaches its lowest value about 4.47 and 4.34 emu K mol^{-1} at 2 K.

As has been proven, the intermolecular hydrogen bond could result in obvious antiferromagnetic interactions between the paramagnetic mental centers [27–30]. Therefore, the magnetic behavior of these two complexes might be due to antiferromagnetic interaction between the manganese ions within the supramolecular dimer mediated by hydrogen bonds. Additional, for complex **II**, it should be noted that the zero-field splitting (D) of the ground state of Mn^{2+} ion may also have some contribution to the decrease of the magnetic susceptibility at low temperature. The magnetic susceptibility data for complex **I** was simultaneously fitted by the binuclear manganese(II) model based-on Hamiltonian $H = -2JS_1S_2$, while that for complex **II** the full-matrix diagonalization of the following spin Hamiltonian [31] was used:

$$H = -2JS_1S_2 + D_1[S_{1z}^2 - 1/3S_1(S_1 + 1)] \\ + D_2[S_{1z}^2 - 1/3S_2(S_2 + 1)].$$

The J represents the exchange interaction between the manganese(III) ions within the supramolecular dimer. For complex **II**, the D represents the zero-field splitting (ZFS) effects for the two manganese ions ($D_1 = D_2$). In view of the axially elongated structure around Mn(III) and the previous results [32], D was constrained to negative values in our calculations. The best set of parameters which match the experimental data were found to be $J = -0.67$ cm^{-1}, $g = 2.02$ for complex **I** and $J = -1.05$ cm^{-1}, $D = -1.98$ cm^{-1}, $g = 2.01$ for complex **II**, respectively.

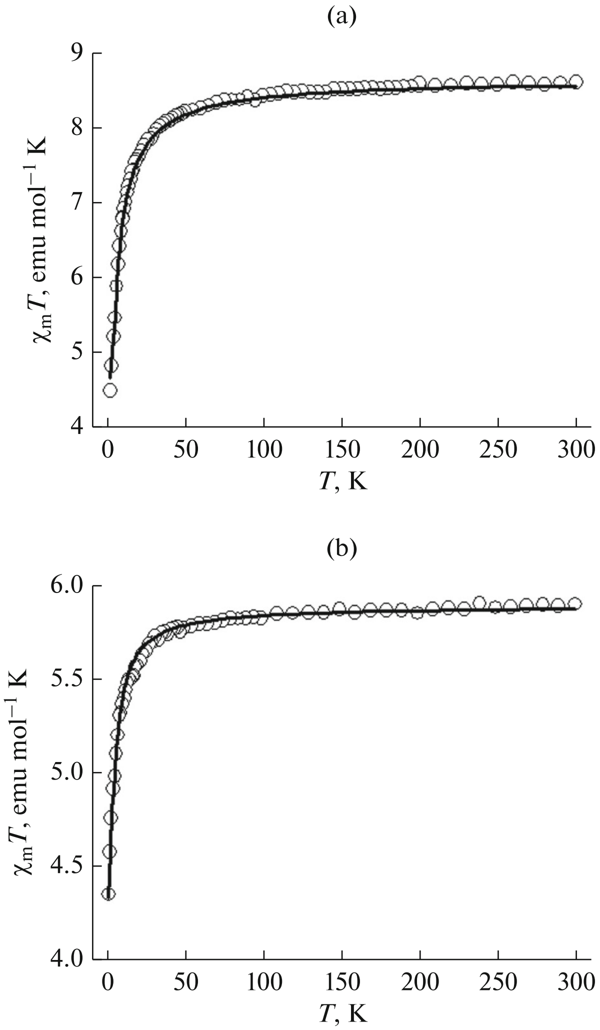

Fig. 3. χ_m and $\chi_m T$ vs. T curves for complexes **I** (a) and **II** (b).

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REFERENCES

1. Dunbar, K.R. and Heintz, R.A., *Prog. Inorg. Chem.*, 1997, vol. 45, p. 283.
2. Verdaguer, M., Bleuzen, A., Marvaud, V., et al., *Coord. Chem. Rev.*, 1999, vols. 190–192, p. 1023.
3. Ohba, M. and Okawa, H., *Coord. Chem. Rev.*, 2000, vol. 198, no. 1, p. 313.
4. Cernák, J., Ōrendác, M., Potocnák, I., et al., *Coord. Chem. Rev.*, 2002, vol. 224, nos. 1–2, p. 51.
5. Shatruk, M., Avendano, C., and Dunbar, K.R., *Prog. Inorg. Chem.*, 2009, vol. 56, p. 155.
6. Wang, S., Ding, X.H., Zuo, J.L., et al., *Coord. Chem. Rev.*, 2011, vol. 255, nos. 15–16, p. 1713.
7. Wang, S., Ding, X.H., Li, Y.H., and Huang, W., *Coord. Chem. Rev.*, 2012, vol. 256, nos. 3–4, p. 439.
8. Li, Y.H., He, W.R., Ding, X.H., et al., *Coord. Chem. Rev.*, 2012, vol. 256, nos. 23–24, p. 2795.
9. Pribush, R.A. and Archer, R.D., *Inorg. Chem.,* 1974, vol. 13, no. 11, p. 2556.
10. Kiernan, P.M., *Inorg. Chim. Acta*, 1976, vol. 20, p. 89.
11. Burdett, J.K., Hoffmann, R., and Fay, R.C., *Inorg. Chem.*, 1978, vol. 17, no. 9, p. 2553.
12. Przychodzén, P., Korzeniak, T., Podgajny, R., and Sieklucka, B., *Coord. Chem. Rev.*, 2006, vol. 250, nos. 17–18, p. 2234.
13. Sieklucka, B., Podgajny, R., Przychodzen, P., and Korzeniak, T., *Coord. Chem. Rev.*, 2005, vol. 249, nos. 21–22, p. 2203.
14. Miyasaka, H., Saitoh, A., and Abe, S., *Coord. Chem. Rev.*, 2007, vol. 251, nos. 21–24, p. 2622.
15. Przychodzén, P., Lewiński, K., Bałanda, M., et al., *Inorg. Chem.*, 2004, vol. 43, no. 9, p. 2967.
16. Przychodzen, P., Rams, M., Guyard-Duhayon, C., and Sieklucka, B., *Inorg. Chem. Commun.*, 2005, vol. 8, no. 4, p. 350.
17. Kou, H.Z., Ni, Z.H., Zhou, B.C., and Wang, R.J., *Inorg. Chem. Commun.*, 2004, vol. 7, no. 10, p. 1150.
18. Yoo, H.S., Ko, H.H., Ryu, D.W., et al., *Inorg. Chem.*, 2009, vol. 48, no. 13, p. 5617.
19. Ko, H.H., Lim, J.H., Yoo, H.S., et al., *Dis. Faraday Soc.*, 2007, no. 20, p. 2070.
20. Yoon, J.H., Ryu, D.W., Choi, S.Y., et al., *Chem. Commun.*, 2011, vol. 47, no. 37, p. 10416.
21. Long, J., Chamoreau, L.M., and Marvaud, V., *Eur. J. Inorg. Chem.*, 2011, vol. 2011, no. 29, p. 4545.
22. Yoon, J.H., Lee, J.K., Ryu, D.W., et al., *Inorg. Chem.*, 2011, vol. 50, no. 22, p. 11306.
23. Herrera, J.M., Marvaud, V., Verdaguer, M., et al., *Angew. Chem. Int. Ed.*, 2004, vol. 43, no. 41, p. 5468.
24. Miyasaka, H., Matsumoto, N., Okawa, H., et al., *J. Am. Chem. Soc.*, 1996, vol. 118, no. 5, p. 981.
25. Sheldrick, G.M., *SHELXTL-97, Program for the Refinement of Crystal Structure*, Göttingen: Univ. of Göttingen, 1997.
26. Gallo, E., Solari, E., Floriani, C., et al., *Inorg. Chem.*, 1997, vol. 36, no. 10, p. 2178.
27. Plass, W., Pahlmann, A., and Rautengarten, J., *Angew. Chem. Int. Ed.*, 2001, vol. 40, no. 22, p. 4207.
28. Desplanches, C., Ruiz, E., Rodrgíuez-Fortea, A., and Alvarez, S., *J. Am. Chem. Soc.*, 2002, vol. 124, no. 18, p. 5197.
29. Tang, J.K., Coster, J.S., Golobi, A., et al., *Inorg. Chem.*, 2009, vol. 48, no. 12, p. 5473.
30. Zhang, D.P., Wang, H.L., Chen, Y.T., et al., *Inorg. Chem.*, 2009, vol. 48, no. 23, p. 11215.
31. Kahn, O., *Molecular Magnetism*, Weinheim: VCH, 1993.
32. Kennedy, B.J. and Murray, K.S., *Inorg. Chem.*, 1985, vol. 24, no. 10, p. 1552.