http://dx.doi.org/10.5012/bkcs.2012.33.12.4231

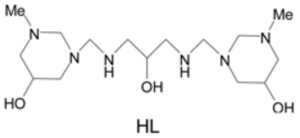
Metal-template Condensation of 1,3-Diamino-2-propanol and Formaldehyde: Synthesis, Crystal Structure, and Magnetic Properties of a New Dinuclear Copper(II) Complex

Shin-Geol Kang,* Yun-Taek Lee, Kil Sik Min,† and Jinkweon Kim‡

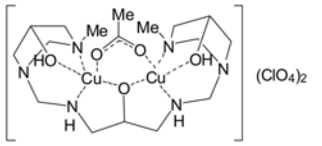
*Department of Chemistry, Daegu University, Gyeongsan 712-714, Korea. *E-mail: sgkang@daegu.ac.kr*
†Department of Chemistry Education, Kyungpook National University, Daegu 702-701, Korea
‡Department of Chemistry, Kongju National University, Kongju 314-701, Korea
Received August 25, 2012, Accepted September 17, 2012

Key Words : Dinuclear copper(II) complex, Reductive methylation, Crystal structure, Magnetic properties, Template condensation

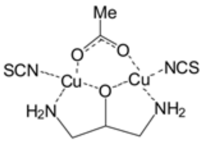
Polynuclear transition metal complexes with relatively strong intramolecular metal-metal interactions have received considerable attention because of their interesting chemical properties and/or potential applications in various fields, such as supramolecular chemistry, catalysts for organic reactions, and materials chemistry.[1-11] Especially, dinuclear copper(II) complexes are known to be useful systems for the study of long-distance metal-metal interactions, since the metal ion has only one unpaired electron.[3-11]



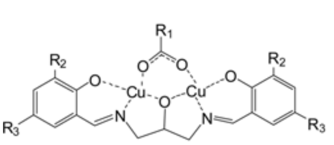
HL



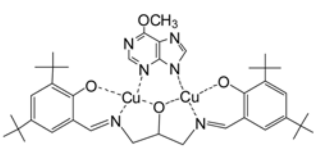
1



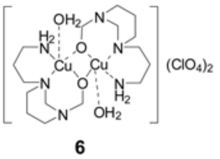
2



3: R_1 = Me; R_2 = OCH_3; R_3 =H
4: R_1 = R_2 = H; R_3 = Br



5



6

$$2Cu^{2+} + 2H_2N(CH_2)_3NH(CH_2)_3NH_2 + 4HCHO \rightarrow \mathbf{6} \quad (1)$$

$$2Cu(OOCMe)_2\cdot H_2O + 3H_2NCH_2CH(OH)CH_2NH_2 + 6HCHO \rightarrow [Cu_2(L)(OOCMe)]^{2+} \quad (2)$$

Some μ-alkoxo-μ-carboxylato or μ-alkoxo-μ-methoxypurinate double bridge dinuclear copper(II) complexes, such as **2-5** containing two N_2O_2 or NO_3 donor sets, have been prepared.[3-9] It has been revealed that their metal-metal interactions are influenced by various structural factors, such as the Cu-X-Cu (X = bridging atom) bridging angle, coordination geometry, the nature of the donor atoms, ligand structure, and Cu···Cu distance. For example, although **2-4** exhibit antiferromagnetic coupling with J = -78 – -141 cm^{-1}, **5** is ferromagnetically coupled with J = 28.1 cm^{-1}.[6-9] However, the effects of the structural factors upon the magnetic properties of such complexes are not thoroughly investigated.

Metal-template condensation reactions involving amines and formaldehyde have been utilized for the preparation of various types of polyaza macrocyclic or non-macrocyclic complexes containing $N\text{-}CH_2\text{-}N$ linkages.[10-14] Recently, such reactions have been extended to the preparation of the alkoxo-bridged dinuclear copper(II) complex **6** that exhibits unusually strong antiferromagnetic interactions between the copper(II) ions; **6** can be prepared by the reaction (Eq. (1)) of bis(3-aminopropyl)amine with formaldehyde in the presence of the metal ion. In this work, we examined the metal-directed reaction (Eq. (2)) involving 1,3-diamino-2-propanol and formaldehyde and prepared a new dinuclear copper(II) complex $[Cu_2(L)(OAc)](ClO_4)_2\cdot H_2O$ (**1**·H_2O) (HL = *N,N'*-bis(3-methyl-5-hydroxy-1,3-diazacyclohexylmethyl)-1,3-diamino-2-propanol), in which two metal centers are bridged by the alkoxo group of L and the acetate ion. Interestingly, **1**·H_2O exhibits relatively strong ferromagnetic coupling between two copper(II). Synthesis, crystal structure, and chemical properties of the complex are reported.

Experimental

Measurements. Electronic absorption spectra were obtained with an Analytik Jena Specord 200 UV-vis spectrophotometer, infrared spectra with a Genesis II FT-IR spectrometer, and conductance measurements with a Z18 Oyster conductivity/temperature meter. Microanalyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. FAB-mass analysis was performed at the Korea Basic Science Institute, Daegu, Korea.

Magnetic susceptibilities were measured in an applied field of 1000 Oe between 3 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made by using Pascal's constants.

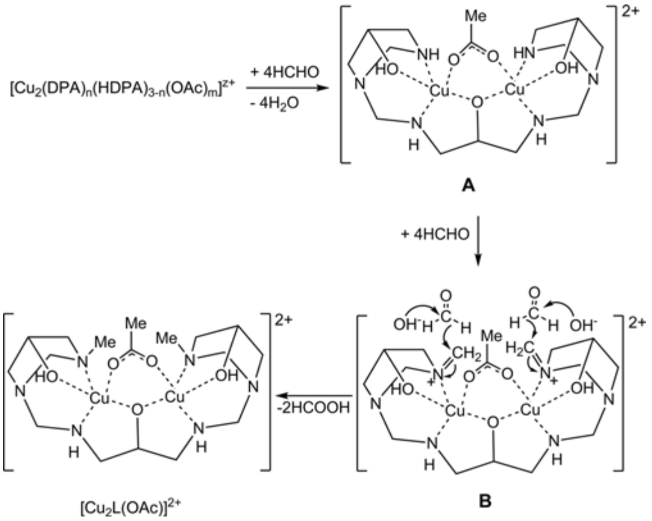
Safety Note. Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Preparation of 1·H_2O. To a methanol solution (30 mL) of $Cu(OAc)_2\cdot H_2O$ (3.0 g, 15 mmol) were added 1,3-diamino-2-propanol (2.0 g, 22 mmol) and 35% formaldehyde (4.7 mL, 60 mmol). The mixture was stirred at room temperature for *ca.* 20 h. After the addition of an excess $NaClO_4$, the solution was slowly evaporated at room temperature to yield a blue solid. The product was collected by filtration, washed with diethyl ether, and dried in air. It was recrystallized from acetonitrile-water (2:1) at room temperature. Yield: ≈ 30% based on the metal salt. *Anal.* Found: C, 26.76; H, 4.95; N, 10.97. Calc. for $C_{17}H_{38}N_6Cu_2Cl_2O_{14}$: C, 27.28; H, 5.12; N, 11.23%. IR (Nujol mull): 3500 (νO-H, H_2O), 3300 (νO-H), 3258 (νN-H), 3237 (νN-H), and 1100 (ClO_4^-) cm^{-1}. FAB mass (*m/z*): 631.7 ($[Cu_2(L^1)_2 + CH_3COO - ClO_4]^+$), 571.5 ($[Cu_2(L^1)_2\text{-}H^+\text{-}ClO_4]^+$). UV/Vis spec. ($\lambda_{max}$, nm (ε, M^{-1} cm^{-1})): 665 (138) in CH_3NO_2, 660 (137) in H_2O, 650 in Nujol mull.

Crystal Structure Determination. A single crystal of **1**·H_2O suitable for X-ray study was grown from acetonitrile-water. Intensity data were collected with an Enraf-Nonius CAD4 diffractometer using monochromated Mo *K*α radiation at 20 °C. The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97.[15] Anisotropic displacement parameters were determined for all non hydrogen atoms.

Results and Discussion

Synthesis and Characterization. The dinuclear complex **1**·H_2O can be prepared by the reaction (Eq. (2)) of 1,3-diamino-2-propanol (HDAP) with excess formaldehyde in the presence of Cu^{2+} ion. The proposed route to give the complex is shown in Scheme 1. The metal salt $Cu(OAc)_2\cdot H_2O$ binds HDAP to form the complex $[Cu_2(DAP)_n(HDAP)_{3-n}(OAc)_m]^{z+}$ (z = 4 − n − m; DAP = a deprotonated form of HDAP). The reaction of $[Cu_2(DAP)_n(HDAP)_{3-n}(OAc)_m]^{z+}$ with four equivalents of formaldehyde may produce **A** containing four N-CH_2-N linkages as an intermediate. The coordinated secondary amino groups at the 1,3-diazacyclohexane rings of **A** react with formaldehyde to form $[Cu_2L(OAc)]^{2+}$ through the intermediate **B**. A similar reductive methylation of a coordinated amino group has been reported for a cobalt(III) complex.[14,16]



Scheme 1. The proposed route to give the dinuclear complex.

The dinuclear complex **1**·H_2O is quite stable in the solid state and in various solvents, such as nitromethane, acetonitrile, and water. However, the complex is rapidly decomposed in acidic aqueous solutions (pH ≤ 4). FAB mass spectrum of the complex shows two groups of peaks corresponding to $[Cu_2(L)(CH_3COO) + ClO_4]^+$ and $[Cu_2(L) - H + ClO_4]^+$ fragments at *m/z* 631.7 and 571.5, respectively. Infrared spectrum of the complex shows $\nu_{N\text{-}H}$ of the coordinated secondary amino groups at 3237 and 3258 cm^{-1}. Peaks corresponding to $\nu_{O\text{-}H}$ of the secondary alcohol groups and lattice water molecule are also observed at 3300 and 3500 cm^{-1}, respectively. The molar conductance values of **1**·H_2O measured in water (220 $\Omega^{-1}mol^{-1}cm^2$), acetonitrile (270 $\Omega^{-1}mol^{-1}cm^2$), and nitromethane (135 $\Omega^{-1}mol^{-1}cm^2$) indicate that the complex is 1:2 electrolyte. The electronic absorption spectrum of **1**·H_2O measured in Nujol mull shows a d-d band at 650 nm. The spectra measured in water and nitromethane also show the band at 660 (ε = 137 $M^{-1}cm^{-1}$) and 665 nm (ε = 138 $M^{-1}cm^{-1}$), respectively, indicating that the coordination geometry of **1**·H_2O in the solvents is nearly the same as that in the solid state.

Crystal Structure of 1·H_2O. The crystal structure (Fig. 1) of **1**·H_2O shows that the compound is a dinuclear copper(II) complex containing the N_4O_3-donor ligand (L) and an acetato ligand. The ligand L contains two (2-*N*-methyl-4-hydroxy)-1,3-diazacyclohexane rings and one alkoxo group. The copper(II) centers are bridged by the alkoxo oxygen atom (O(3)) of L and the acetato ligand, and each mononuclear

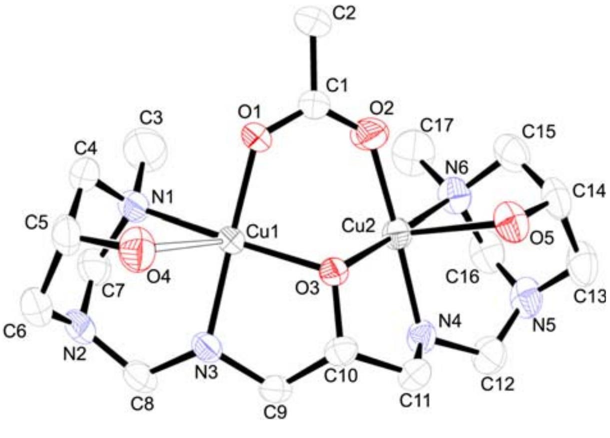


Figure 1. An ORTEP drawing of **1**·H_2O with the atomic numbering scheme.

Table 1. Crystal Data and Structure Refinement for **1**·H_2O

Empirical formula (M)	$C_{17}H_{38}Cl_2Cu_2N_6O_{14}$ (748.51)
Crystal system (space group)	monoclinic ($P2_1/n$)
a / b / c (Å)	12.745(1)/12.947(1)/18.787(2)
β (°)	100.903(7)
V (Å^3)	3044.1(5)
Z	4
D_{calc} (g cm^{-3})	1.638
μ (cm^{-1})	16.44
F(000)	1552
θ range for data collection (°)	2.13-24.98
Index ranges	$-15 \leq h \leq 14, 0 \leq k \leq 15, 0 \leq l \leq 22$
Reflections collected / unique	5495 / 5322 [R(int) = 0.0247]
Data Completeness	99.5
Data / restraints / parameters	5322 / 0 / 383
Goodness-of-fit on F^2	1.087
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.048$, $wR_2 = 0.147$
R indices (all data)	$R_1 = 0.062$, $wR_2 = 0.156$
Largest diff. peak and hole (eÅ^{-3})	1.155 and -0.611

Table 2. Selected Bond Distances (Å) and Angles (°) of **1**·H_2O

Cu(1)-O(1)	1.911(3)	Cu(1)-O(3)	1.964(3)
Cu(1)-O(4)	2.622(4)	Cu(1)-N(1)	2.034(4)
Cu(1)-N(3)	1.990(3)	Cu(2)-O(2)	1.947(4)
Cu(2)-O(3)	1.965(3)	Cu(2)-O(5)	2.329(3)
Cu(2)-N(4)	2.006(4)	Cu(2)-N(6)	2.048(4)
N(1)-C(3)	1.480(7)	N(6)-C(17)	1.498(7)
O(1)-C(1)	1.247(5)	O(2)-C(1)	1.237(6)
O(3)-C(10)	1.438(5)	O(4)-C(5)	1.421(6)
O(5)-C(14)	1.429(6)	Cu(1)---Cu(2)	3.220(1)
O(1)-Cu(1)-O(3)	91.7(2)	O(1)-Cu(1)-N(3)	166.1(2)
O(3)-Cu(1)-N(3)	84.0(2)	O(1)-Cu(1)-N(1)	87.3(2)
O(3)-Cu(1)-N(1)	171.3(2)	N(3)-Cu(1)-N(1)	98.9(2)
O(4)-Cu(1)-N(1)	76.8(2)		
O(2)-Cu(2)-O(3)	90.8(2)	O(2)-Cu(2)-N(4)	175.2(3)
O(3)-Cu(2)-N(4)	84.5(2)	O(2)-Cu(2)-N(6)	88.0(3)
O(3)-Cu(2)-N(6)	177.7(3)	N(4)-Cu(2)-N(6)	96.8(3)
O(2)-Cu(2)-O(5)	92.7(3)	O(3)-Cu(2)-O(5)	101.2(2)
N(4)-Cu(2)-O(5)	87.9(3)	N(6)-Cu(2)-O(5)	80.9(2)
Cu(1)-O(3)-Cu(2)	110.1(3)	C(1)-O(1)-Cu(1)	130.5(3)
C(1)-O(2)-Cu(2)	133.6(3)	O(2)-C(1)-O(1)	125.9(4)
C(11)-C(10)-C(9)	112.8(4)	C(10)-O(3)-Cu(1)	113.3(2)
Cu(1)-O(3)-Cu(2)	110.1(3)		

unit has N_2O_3-donor donor set and exhibits distorted square-pyramidal coordination geometry with an apical hydroxo group.

Selected bond distances and angles of the complex are listed in Table 2. The in-plane Cu(1)-O(3) (bridging oxygen) distance (1.964(3) Å) is considerably longer than the Cu(1)-O(1) (acetato) distance (1.911(3) Å), but is distinctly shorter than the Cu-N(1) and Cu-N(3) distances (2.034(4) and 1.990(3) Å, respectively). The apical Cu(1)-O(4) distance (2.622(4) Å) is much longer than the in-plane Cu(1)-O and Cu(1)-N distances. The N(1)-Cu(1)-O(3) and N(3)-Cu(1)-O(1) angles (171.3(2) and 166.1(2)°, respectively) are deviated from 180°. The N(1)-Cu(1)-O(4) angle (76.8(1)°) is smaller than the in-plane N(3)-Cu(1)-O(3) angle (84.0(2)°) involved in the five-membered chelate ring. The N(1)-Cu(1)-N(3) angle (98.9(2)°) is larger than the in-plane N-Cu(1)-O and O(1)-Cu(1)-O(3) angles (84.0(2)-91.7(2)°). The Cu(1)-O(3)-Cu(2) angle (110.1(3)°) is comparable with the Cu-O-Cu angles of **3** (107.0(2)°) and **5** (110.3(2)°), but is considerably smaller than those of **2** (130.3(3)°) and **4** (132.9(3)°). The average Cu-O(3) distance (1.695 Å) is quite similar to the Cu-O (bridging oxygen) distance of **5** (1.694 Å), but is distinctly longer than those of **2-4** (1.840-1.916 Å). The Cu(1)···Cu(2) distance (3.220(1) Å) is also similar to the distance of **5** (3.223(3) Å) and is considerably shorter than **2** (3.341(8) Å) and **4** (3.511 Å).

Magnetic Properties. Magnetic susceptibilities (χ) of **1**·H_2O were measured at 3-300 K. The effective magnetic moment (μ_{eff} [$=(8\chi_M T)^{1/2}$]) of **1**·H_2O was found to be 2.72 μ_B/Cu_2 at room temperature. The value is slightly larger than 2.45 μ_B expected for independent two copper(II) ions (S = 1/2, Cu(II), g = 2). Figure 2 shows that μ_{eff} increases monotonically with decreasing temperature and reaches the maximum value of 2.99 μ_B at *ca.* 20 K. This clearly indicates a strong intramolecular ferromagnetic interaction of the dinuclear complex. The decrease of μ_{eff} below *ca.* 20 K can be attributed to intermolecular antiferromagnetic coupling, which often occurs in ferromagnetically coupled complexes.[9] The μ_{eff} data was fit to an analytical expression for χ for a coupled $S = 1/2$ dinuclear spin model (Eq. (3)) based on the Hamiltonian $H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = 1/2$).[17] The best fit to Eq. (3) had $J = 53.5$ cm^{-1}, $g = 2.18$, $\rho = 0.03$, $\theta = -0.78$ K, and temperature independent paramagnetism (TIP) = 200 × 10^{-6} emu/mol. The J value indicates that the oxygen bridged bonding in **1**·H_2O mediates a strong ferromagnetic coupling

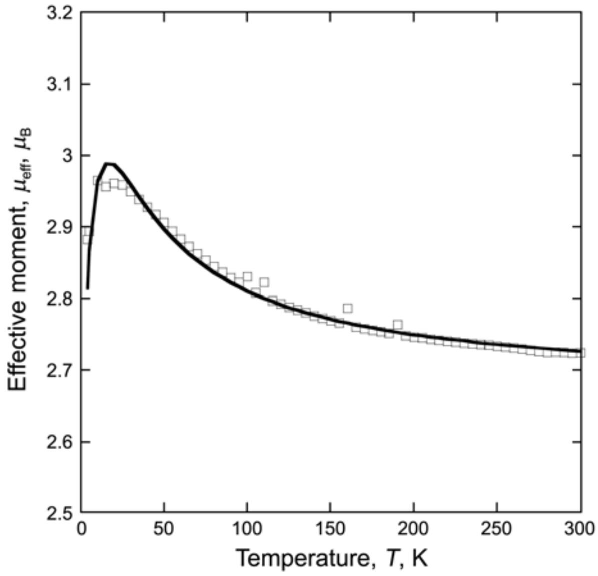


Figure 2. Fitting of effective magnetic moment versus temperature (K) data of **1**·H_2O using dimer model of $S = 1/2$ local spin. Solid line shows the best fit obtained.

Table 3. Structural Features and Magnetic Parameters of the Dinuclear Copper(II) Complexes

Complex	Cu···Cu	Cu-O[a]	Cu-O-Cu	δ[b]	g	J, cm^{-1}
1·H_2O	3.220(1)	1.965	110.1(3)	62.9	2.18	+53.5
2[c]	3.341(8)	1.840	130.3(3)		2.22	-141
3[d]	3.154(2)	1.931	107.0(2)	56.8	2.16	-92.7
4[e]	3.511	1.916	132.9(2)		2.0	-78
5[f]	3.223(3)	1.964	110.3(2)	58.2	2.0	+28.1

[a]The average distance between the copper(II) and the bridging oxygen atom. [b]Dihedral angles between coordination planes. [c]Ref. 6. [d]Ref. 7. [e]Ref. 8. [f]Ref. 9.

between two copper(II) ions separated by *ca.* 3.220 Å.

$$\chi_M = \frac{2N\beta^2 g^2}{3k(T-\theta)}[1 + \frac{1}{3}\exp(-2J/kT)]^{-1}(1-\rho) + \frac{N\beta^2 g^2}{2kT}\rho + \mathrm{TIP} \quad (3)$$

The structural features and magnetic parameters of **1**·H_2O are listed in Table 3, along with those of **2-5**, for comparison. Table 3 shows that **5** also exhibits ferromagnetic coupling, unlike **2-4**. Interestingly, the ferromagnetic coupling for **1**·H_2O is stronger than that for **5**, even though both of them exhibit similar Cu···Cu and Cu-O distances; the dihedral angles of them as well as the Cu-O-Cu angles are also similar. According to the orbital counter-complementarity phenomenon,[4] the value and sign of the J coupling is mainly dependant on the Cu-O-Cu bridge angle and/or the dihedral angle. However, unfortunately, it is very difficult to find any direct correlation between the J values and the structural features of **1** - **5** (Table 3).

Concluding Remarks

This work shows that a new μ-alkoxo-μ-acetato-bridged dinuclear copper(II) complex, **1**, can be prepared by the one-pot reaction of 1,3-diamino-2-propanol and formaldehyde in the presence of $Cu(OAc)_2 \cdot H_2O$. Each mononuclear unit has N_2O_3-donor donor set and exhibits distorted square-pyramidal coordination geometry with an apical hydroxo group. Interestingly, the complex shows relatively strong ferromagnetic coupling.

Acknowledgments. This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2010-0007251).

Supplementary Material. CCDC 897197 contains the supplementary crystallographic data for **1**·H_2O. These data can be obtained free of charge from The Cambridge Structural Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

References

1. (a) Vigato, P. A.; Peruzzo, V.; Tamburini, S. *Coord. Chem. Rev.* **2012**, *256*, 953. (b) Desbouis, D.; Troitsky, I. P.; Belousoff, M. J.; Spiccia, L. Graham, B. *Coord. Chem. Rev.* **2012**, *256*, 897. (c) Selmeczi, K.; Reglier, M.; Giorgi, M.; Speier, G. *Coord. Chem. Rev.* **2003**, *245*, 191.
2. (a) Massoud, S. S.; Mautner, F. A.; Louka, F. R.; Demeshko, S.; Dechert, S.; Meter, F. *Inorg. Chim. Acta* **2011**, *370*, 435 and references cited therein. (b) Chaudhuri, P.; Wagner, R.; Weyhermuller, T. *Inorg. Chem.* **2007**, *46*, 5134. (c) Siluval, G. S.; Vargheese, B.; Murthy, N. N. *Inorg. Chim. Acta* **2011**, *375*, 93.
3. (a) Escuer, A.; El Fallah, M. S.; Vicente, R.; Sanz, N.; Font-Bardia, M.; Solans, X.; Mautner, F. A. *Dalton Trans.* **2004**, 1867. (b) Averseng, F.; Lacroix, P. G.; Malfant, I.; Périssé, N.; Lepetit, C. *Inorg. Chem.* **2001**, *40*, 3797.
4. El Fallah, M. S.; Vicente, R.; Tercero, J.; Elpelt, C.; Rentschler, E.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **2008**, *47*, 6322 and references cited therein.
5. (a) Siluvai, G. S.; Murthy, N. N. *Polyhedron* **2009**, *28*, 2149. (b) Huang, S.-F. Chou, Y.-C.; Misra, P.; Lee, C.-J.; Mohananta, S.; Wei, H.-H. *Inorg. Chim. Acta* **2004**, *357*, 1627.
6. El Fallah, M. S.; Badyne, F.; Vicente, R.; Escuer, A.; Solans, X.; Font-Bardia, M. *Dalton Trans.* **2006**, 2934.
7. Elmaili, A.; Zeyrek, C. T.; Elerman, Y. *J. Mol. Struct.* **2004**, *693*, 225.
8. Weng, C.-H.; Cheng, S.-C.; Wei, H.-M.; Wei, H.-H.; Lee, C.-J. *Inorg. Chim. Acta* **2006**, *359*, 2029.
9. Lai, T.-C.; Chen, W.-H.; Lee, C.-J.; Wang, B.-C.; Wei, H.-H. *J. Mol. Struct.* **2009**, *935*, 97.
10. Kang, S.-G.; Lee, Y. H.; Jeong, J. H. *Inorg. Chem. Commun.* **2007**, *10*, 1429.
11. Kang, S.-G.; Nam, K.; Min, K. S.; Lee, U. *Bull. Korean Chem. Soc.* **2011**, *32*, 1037.
12. Kim, H.; Kang, S.-G.; Jeong, S.-K. *Bull. Korean Chem. Soc.* **2012**, *33*, 1329 and references cited therein.
13. Suh, M. P.; Kang, S.-G. *Inorg. Chem.* **1988**, *27*, 2544.
14. (a) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016. (b) Angus, P. M.; Elliott, A. J.; Sargeson, A. M.; Willw, A. C. *J. Chem. Soc., Dalton Trans.* **2000**, 2933.
15. (a) Sheldrick, G. M. *SHELXS-97*, Program for the solution of crystal structure, University of Göttingen, Göttingen, Germany, 1990. (b) Sheldrick, G.. M. *SHELXL-97*, Program for crystal structure refinement, University of Göttingen, Göttingen, Germany, 1997.
16. (a) Da Silva, R. A.; Bieber, L. W. *Tetrahedron Lett.* **2010**, *51*, 689. (b) Da silva, R. A.; Estevam, I. H. S.; Bieber, L. W. *Tetrahedron Lett.* **2007**, *48*, 7680.
17. Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.