

## Synthesis and Characterization of Compartmental Macrocyclic Binuclear Copper(II) Complex with Bidentate Perchlorato Ligand

Jong Chul Byun,<sup>\*</sup> Dae Hun Mun,<sup>†</sup> and Ki-Min Park<sup>‡,\*</sup>

Department of Chemistry, College of Natural Sciences, Jeju National University, Jeju 690-756, Korea

<sup>\*</sup>E-mail: jchbyun@cheju.ac.kr

<sup>†</sup>Research Institute for Basic Sciences, Jeju National University, Jeju 690-756, Korea

<sup>‡</sup>Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea

<sup>\*</sup>E-mail: kmpark@gnu.ac.kr

Received October 2, 2013, Accepted October 10, 2013

**Key Words :** Compartmental Schiff base ligand, Dinuclear complex, Bridging perchlorate anion, Macrocyclic copper(II) complex, Crystal structure

In recent years, there has been immense interest in studying binuclear metal complexes using macrocyclic compartmental ligands derived from 2,6-diformyl-4-methylphenol and diamines.<sup>1-6</sup> The motivation for this is not only to understand the function of fundamental interactions in both coordination chemistry and biological mimics,<sup>2</sup> but also to explore their potential for technological applications in a number of areas of material science, including use as magnetic and non-linear optical materials.<sup>3</sup> Especially, compartmental Schiff base ligands, containing adjacent coordination sites, are capable of accommodating similar or dissimilar metal ions, resulting in the formation of homo- and heterodinuclear complexes. These complexes cause a mutual influence between the two metal ions giving rise to systems with new physicochemical properties which have been used in the design of molecular magnetic or optical devices, molecular probes for the selective recognition of charged and/or neutral molecules, and polynuclear catalytic systems.<sup>1g,3c,4</sup>

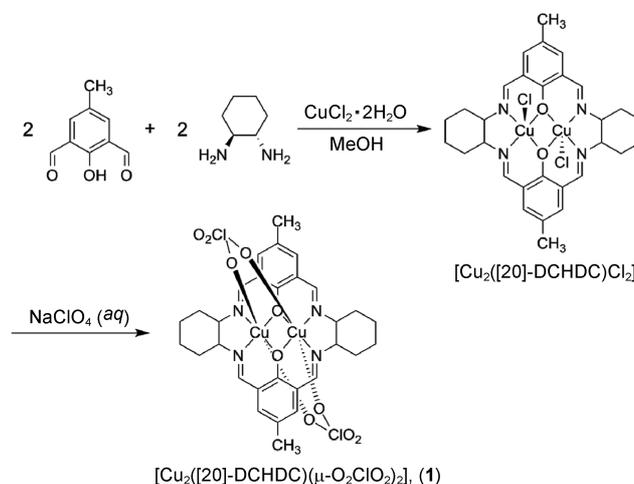
2,6-Diformyl-*p*-cresol (DFPC) is a potential precursor to synthesize the compartmental Schiff base macrocyclic ligands containing two bridging phenol groups. The [2 + 2] condensation of DFPC with a variety of diamines in the presence of template 3d transition metal ions generates predominantly oxo-bridged dinuclear complexes.<sup>1-6</sup> Generally, these macrocyclic compartmental complexes have been derived from the template condensation of achiral diamines such as ethylenediamine and propylenediamine. However, the use of chiral diamines such as 1*R*,2*R*-diaminocyclohexane, in the construction of chiral macrocycles has received only limited study.<sup>5</sup> Applications of chiral and optically active *trans*-1,2-diaminocyclohexane derivatives and their macrocyclic complexes as stereoselective catalysts<sup>6</sup> for organic reactions prompted the choice of this diamine in the preparation of the oxo-bridged dinuclear complexes.

In various compartmental macrocyclic dinuclear complexes, the metal ions can interact through their axial position with various anions such as thiosulfate, cyanide, thiocyanate, perchlorate, nitrate, and nitrite. Especially thiosulfate, nitrate, and nitrite anions can also be used to bridge two metal

centers accommodated inside the compartmental macrocyclic ligands, giving rise to the formation of complexes with anomalous supramolecular architectures and interesting physicochemical properties.<sup>7</sup>

However, the study about the behavior of perchlorate anion ClO<sub>4</sub><sup>-</sup> in the compartmental macrocyclic complexes is very rare although it can link a pair of metal centers in either an end-on (μ-1,1-O-ClO<sub>4</sub>) or end-to-end (μ-1,3-O<sub>2</sub>-ClO<sub>2</sub>) configuration.

In order to better understand some aspects of molecular topologies in compartmental binuclear complexes with bridging perchlorate anion, we explore a novel macrocyclic, phenoxide- and perchlorate-bridged dicopper(II) complex, [Cu<sub>2</sub>([20]-DCHDC)(μ-O<sub>2</sub>ClO<sub>2</sub>)<sub>2</sub>].1.6CH<sub>3</sub>CN·0.4CH<sub>3</sub>OH (**1**), where H<sub>2</sub>[20]-DCHDC = 14,29-dimethyl-3,10,18,25-tetraazapentacyclo-[25,3,1,04,9,112,16,019,24] ditriacontane-2,10,12,14,16(32),17,27(31),28,30-decane-31,32-diol. The compartmental dinuclear Cu(II) complex **1** was prepared by the anion exchange of the dinuclear Cu(II)-chloro complex,<sup>5a</sup> [Cu<sub>2</sub>([20]-DCHDC)Cl<sub>2</sub>].6H<sub>2</sub>O with ClO<sub>4</sub><sup>-</sup> in aqueous media, as depicted in Scheme 1. Herein, we report the crystal struc-



**Scheme 1.** Synthetic route of the dinuclear macrocyclic copper(II) complex.

ture and physicochemical properties of complex **1**.

### Results and Discussion

**General Properties.** The pale green perchlorato complex **1** is insoluble in cold solvents like methanol, acetone, and dimethylformamide, but has poor solubility in acetonitrile, dimethylsulfoxide, hot dimethylformamide, hot methanol, and hot acetone. In hot methanol, the air-stable moisture-insensitive complex **1** has lower value than molar conductance for 1:1 electrolytes. Thus, it seems that an anion coordination might exist in hot methanol.<sup>8</sup> Such result is in general agreement with the expectation from the spectral data and the crystal structure of complex **1**.

The electronic absorption spectrum of complex **1** shows different absorption bands of the dinuclear Cu(II)-chloro complex,<sup>5a</sup> indicating the different coordination environments for Cu(II) centers. The broad absorption band near 546 nm can be assigned to the spin-allowed d-d electronic transition of Cu(II) ( $3d^9$ ). This shows the band arising from  ${}^2E_g \rightarrow {}^2T_{2g}$  ( $O_h$ ) transition, which exhibits the characteristic feature of Jahn-Teller effects of Cu(II) ions.<sup>9</sup> The formation of dinuclear Cu(II) complex was inferable from elemental analysis, molar conductance and electronic absorption spectrum of the complex **1** as well as is evidenced by characteristic IR absorption bands and FAB mass spectrum. The IR spectrum of the perchlorato complex **1** displays the characteristic bands of coordinated perchlorate anion at 1150, 1110, 1085, and 641  $\text{cm}^{-1}$ .<sup>10</sup> The significant ions observed in the FAB mass spectrum of complex **1** include  $[\text{Cu}(\text{H}[20\text{-DCHDC}])^+]$  and  $[\text{Cu}_2(\text{[20-DCHDC]}(\text{ClO}_4))^+]$  at  $m/z$  546 and 707, respectively.

**Description of Crystal Structures.** Pale green crystals of the complex **1**,  $[\text{Cu}_2(\text{[20-DCHDC]}(\mu\text{-O}_2\text{ClO}_2)_2] \cdot 1.6\text{CH}_3\text{CN} \cdot 0.4\text{CH}_3\text{OH}$  suitable for X-ray diffraction study were obtained by recrystallization from warm acetonitrile: $\text{CH}_3\text{OH}$  (1:1) solution. The structure of complex **1** with the atomic numbering scheme is shown in Figure 1. The summary of the crystal data, experimental details and refinement results for complex **1** is listed in Table 1. Selected bond lengths and angles relevant to the coordination geometry for crystals of complex **1** are listed in Table 2.

The X-ray analysis reveals that **1** is compartmental macrocyclic dinuclear copper(II) complex bridged by two bidentate perchlorato ligand, which is located on a crystallographic inversion center (Figure 1(a)). Therefore, the asymmetric unit of **1** consists of one copper(II) ion, a half of  $[\text{20-DCHDC}]^{2-}$  macrocyclic ligand, one perchlorato ligand, four-fifths of an acetonitrile molecule and one-fifth of a methanol molecule.

In crystal structure of **1**, each copper(II) ion is six-coordinate, being bound to two oxygen and two imine nitrogen donors from each of the two  $\text{N}_2\text{O}_2$  compartments of macrocyclic  $[\text{20-DCHDC}]^{2-}$  ligand. The coordination sphere is completed by two oxygen atoms from two different perchlorato ligands. The copper(II) coordination in **1** can be described as a distorted octahedral geometry, where each of the two  $\text{N}_2\text{O}_2$  compartments of macrocyclic  $[\text{20-DCHDC}]^{2-}$  ligand

**Table 1.** Crystallographic Data and Structure Refinement for Complex **1**

Identification code	<b>1</b>
Empirical formula	$\text{C}_{33.6}\text{H}_{40.4}\text{Cl}_2\text{Cu}_2\text{N}_{5.6}\text{O}_{10.4}$
Formula weight	887.10
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ (Å)	8.0773(6)
$b$ (Å)	16.7494(13)
$c$ (Å)	14.0614(11)
$\beta$ (°)	100.447(2)
Volume (Å <sup>3</sup> )	1870.8(2)
$Z$	2
Absorption coefficient ( $\text{mm}^{-1}$ )	1.344
Theta range for data collection	1.91 to 26.50°
Reflections collected	10967
Data / restraints / parameters	3856 / 12 / 298
Goodness-of-fit on $F^2$	1.083
Final $R1$ and $wR2$ [ $I > 2\sigma(I)$ ]	0.0466, 0.1040
$R1$ and $wR2$ indices (all data)	0.0859, 0.1210

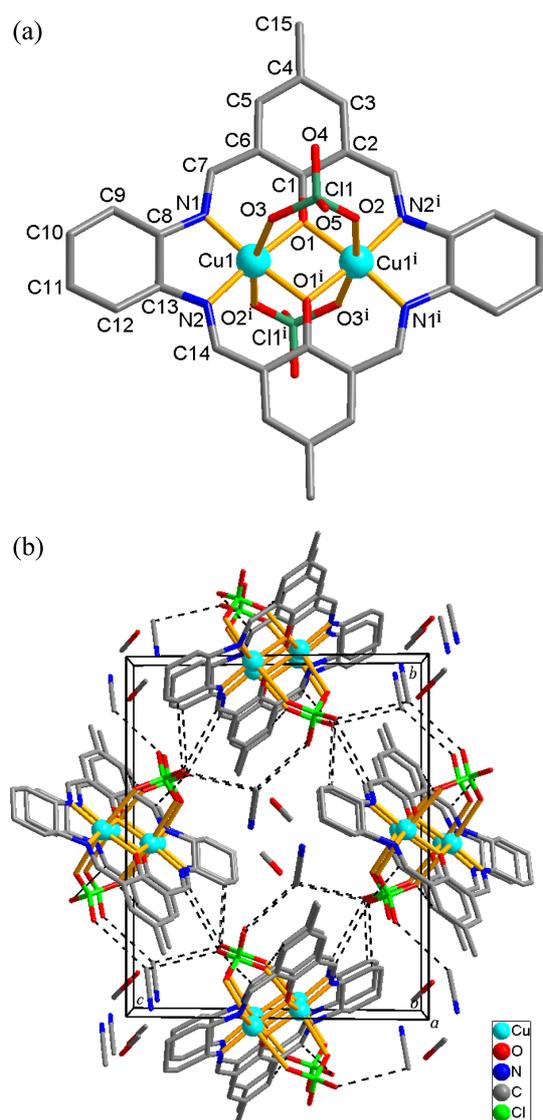
**Table 2.** Selected Bond Lengths (Å) and Angles (°) for complex **1**

Cu1-N1	1.890(3)	Cu1-N2	1.886(3)
Cu1-O1	1.899(2)	Cu1-O2 <sup>i</sup>	2.585(3)
Cu1-O3	2.660(3)	Cu1...Cu1 <sup>i</sup>	2.8785(9)
N1-Cu1-N2	90.11(13)	N1-Cu1-O1	94.14(12)
N1-Cu1-O1 <sup>a</sup>	173.84(13)	N1-Cu1-O3	88.83(14)
N1-Cu1-O2 <sup>a</sup>	100.68(13)	N2-Cu1-O1 <sup>i</sup>	94.54(12)
N2-Cu1-O1	174.47(13)	N2-Cu1-O3	97.89(13)
N2-Cu1-O2 <sup>a</sup>	89.21(13)	O1-Cu1-O1 <sup>i</sup>	81.49(11)
O1-Cu1-O3	85.75(11)	O1-Cu1-O2 <sup>i</sup>	86.52(12)
O3-Cu1-O2 <sup>i</sup>	168.15(10)		

Symmetry code: <sup>a</sup> $-x, 1-y, -z$ .

satisfies four basal positions. The basal Cu-ligand bond distances are very close falling in the range 1.886(3)-1.900(2) Å, which are similar with those of chloro cupric complex with the  $[\text{20-DCHDC}]$  macrocyclic ligand.<sup>5a</sup> The remaining apical positions of the copper(II) center are occupied by two perchlorato ligands with somewhat longer contacts [Cu1-O2 2.586(2) Å and Cu1A-O3 2.660(2) Å] owing to the Jahn-Teller effect in  $d^9$  electronic configuration. The largest distortion from the regular octahedral geometry is occurred in the angle of O3-Cu1-O2<sup>i</sup> of 168.15(10) Å (Figure 1(a)), which may be due to the fact that the perchlorato ligands bridge between two neighboring Cu(II) ions in the end-to-end ( $\mu\text{-1,3-O}_2\text{-ClO}_2$ ) configuration

Two Cu(II) centers in **1** are bridged by the two phenoxo oxygen atoms of  $[\text{20-DCHDC}]^{2-}$  and two  $\mu_{1,3}$ -perchlorato ligands with the separation distance of 2.8786(9) Å, slightly longer than the sum of van der Waals radius of Cu atoms (2.86 Å).<sup>11</sup> Thus, two Cu(II) ions accommodated within compartmental macrocyclic ligand are quadruply bridged by a bis( $\mu$ -phenoxo)-bis( $\mu$ -perchlorato) moiety, in which two



**Figure 1.** (a) Crystal structure of complex **1** with the asymmetric atom-labeling scheme. (b) Perspective views of the unit cell with hydrogen bonds shown as dashed lines along the *a*-axis. All hydrogens, disordered atoms and solvent molecules are omitted for clarity. [Symmetry codes: *i*)  $-x, 1-y, -z$ .]

perchlorato ligands exhibit the classical *syn-syn* bridging mode. To the best of our knowledge, complex **1** represents the first structurally characterized example of a macrocyclic dinuclear perchlorato Cu(II) complex containing two bridging perchlorate ligands.

As shown in Figure 1(b) and Table 3, there are many non-classic intermolecular C-H $\cdots$ O hydrogen bonds [average distance of H $\cdots$ O = 3.427(7) Å] in crystal packing structure of complex **1**. The compartmental macrocyclic dinuclear copper(II) complexes, [Cu<sub>2</sub>([20]-DCHDC)( $\mu$ -O<sub>2</sub>ClO<sub>2</sub>)<sub>2</sub>], are cross-linked by intermolecular hydrogen bonds, resulting in the pseudo 3D framework with channel cavity. Disordered solvent molecules (acetonitrile and methanol) are accommodated in the channel cavity

In summary, the compartmental macrocyclic dinuclear Cu(II)-perchlorato complex was prepared by the anion ex-

**Table 3.** Non-classic Intermolecular C-H $\cdots$ O Hydrogen Bonds (Å and °) for Complex **1**

D-H $\cdots$ A	d(D-H)	d(H $\cdots$ A)	d(D $\cdots$ A)	<(DHA)
C5-H5 $\cdots$ O2 <sup>a</sup>	0.95	2.58	3.280(5)	130.6
C7-H7A $\cdots$ O5 <sup>a</sup>	0.95	2.59	3.523(5)	165.9
C12-H12A $\cdots$ O5 <sup>b</sup>	0.99	2.54	3.511(5)	166.0
C17-H17B $\cdots$ O5 <sup>a</sup>	0.98	2.51	3.470(7)	165.8
C14-H14 $\cdots$ O5 <sup>b</sup>	0.95	2.58	3.422(5)	147.9
C17-H17A $\cdots$ O4 <sup>c</sup>	0.98	2.47	3.354(7)	150.3

Symmetry codes: <sup>a</sup> $x+1, y, z$ ; <sup>b</sup> $-x, y+1/2, -z+1/2$ ; <sup>c</sup> $x+1, -y+1/2, z+1/2$ .

change of its chloride salt and fully characterized by element analysis, conductance, electronic and IR spectra as well as FAB-MS method. Its crystal structure determined by X-ray crystallography reveals the two distorted octahedral copper(II) centers are quadruply bridged by the two phenoxide oxygen atoms of [20]-DCHDC macrocyclic ligand as well as two  $\mu_{1,3}$ -perchlorato ligands. Furthermore, complex **1** exhibits the pseudo-3D supramolecular network generated by the C-H $\cdots$ O hydrogen bonds.

## Experimental

**General Methods.** All chemicals were commercial analytical reagents and were used without further purification. Solvents used for electrochemical and spectroscopic studies were purified by standard procedures. 2,6-Diformyl-*p*-cresol (DFPC) was prepared with high yields by an improved oxidation method using active manganese(IV) dioxide. The two square pyramidal copper complex bridged by the two phenoxide oxygen atoms, [Cu<sub>2</sub>([20]-DCHDC)Cl<sub>2</sub>] $\cdot$ 6H<sub>2</sub>O was synthesized in our laboratory as described earlier.<sup>5a</sup>

**Measurements.** Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurements of the complexes were performed in CH<sub>3</sub>OH at 25  $\pm$  1 °C using an ORION 162 conductivity temperature meter. IR spectra were recorded with a Bruker FSS66 FT-IR spectrometer. FAB-MS spectra were obtained on a JEOL JMS-700 Mass Spectrometer using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectra were calibrated by Alkali-CsI positive.

**Synthesis of [Cu<sub>2</sub>([20]-DCHDC)( $\mu$ -O<sub>2</sub>ClO<sub>2</sub>)<sub>2</sub>] $\cdot$ 1.6CH<sub>3</sub>CN $\cdot$ 0.4CH<sub>3</sub>OH (**1**).** To an aqueous solution (50 mL) of [Cu<sub>2</sub>([20]-DCHDC)Cl<sub>2</sub>] $\cdot$ 6H<sub>2</sub>O (0.6986 g, 1 mmol), a saturated aqueous sodium perchlorate solution (15 mL) was added dropwise with stirring. The resulting mixture was refluxed for 2 h, and then pale green precipitate that formed was collected by filtration, thoroughly washed with water, and dried *in vacuo*. Yield 72%. Pale green crystals of the complex **1** suitable for X-ray diffraction study were obtained by recrystallization of from warm acetonitrile:CH<sub>3</sub>OH (1:1) solution. Anal. Calcd (Found) % for Cu<sub>2</sub>(C<sub>30</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>)(ClO<sub>4</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>1.6</sub>(CH<sub>3</sub>OH)<sub>0.4</sub>: C, 45.49 (45.59); H, 4.59 (4.37); N, 8.84 (8.51). IR (KBr pellet, cm<sup>-1</sup>) 3310, 3024, 2927, 2859,

1627, 1550, 1448, 1382, 1313, 1240, 1150, 1110, 1085, 862, 769, 641, 502.  $\lambda_M$  (methanol): 108  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ .

**X-ray Crystallography of Complex.** The single crystal was attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with a graphite-monochromated Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation, and a CCD detector; 50 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at 173 K. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The program SAINTPLUS<sup>12</sup> was used for integration of the diffraction profiles. All of the calculations for the structure determination were carried out using the SHELXTL package.<sup>13</sup> All nonhydrogen atoms were refined anisotropically and all hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with the their respective parent atoms. In complex **1**, four carbon atoms (C8, C10, C11, and C13) of cyclohexane moiety were disordered over two sites with site occupancy factor of 0.50. Moreover, lattice solvent molecules (acetonitrile and methanol molecules) were found to occupy two independent positions, which are too close to each other to be fully occupied at the same time. Accordingly, the SOFs of both molecules were refined with their sum fixed at 1, which resulted in the site occupancy factors of 0.80 for acetonitrile and 0.20 for methanol. The summary of the crystal data, experimental details and refinement results for complex **1** is listed in Table 1.

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-295088 for **1**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk (or FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de).

**Acknowledgments.** This research was supported by the 2013 scientific promotion program funded by Jeju National University. This work was also supported from NRF (2012R1A4A1027750).

## References

- (a) Jana, A.; Aliaga-Alcalde, N.; Ruiz, E.; Mohanta, S. *Inorg. Chem.* **2013**, *52*, 7732. (b) Miyazato, Y.; Asato, E.; Ohba, M.; Wada, T. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 895. (c) Marinescu, G.; Marin, G.; Madalan, A. M.; Vezeanu, A.; Tiseanu, C.; Andruh, M. *Cryst. Growth Des.* **2010**, *10*, 2096. (d) Byun, J. C.; Kim, K. J. *Inorg. Chem. Commun.* **2006**, *9*, 171. (e) Byun, J. C.; Han, C. H.; Kim, D. S.; Park, K.-M. *Bull. Korean Chem. Soc.* **2006**, *27*, 435. (f) Pascu, M.; Andruh, M.; Müller, A.; Schmidtman, M. *Polyhedron* **2004**, *23*, 673. (g) Kong, D.; Reibenspies, J.; Mao, J.; Clearfield, A.; Martell, A. E. *Inorg. Chim. Acta* **2003**, *342*, 158. (h) Thompson, L. K.; Mandal, S. K.; Tandon, S. S.; Bridson, J. N.; Park, M. K. *Inorg. Chem.* **1996**, *35*, 3117.
- (a) Karlin, K. D.; Tyeklár, Z. *Bioinorganic Chemistry of Copper*, Chapman and Hall: New York, U.S.A., 1993. (b) Chan, S. I.; Yu, S. S. F. *Acc. Chem. Res.* **2008**, *20*, 357. (c) Whittaker, J. W. *Copper-containing Proteins* **2002**, *60*, 1. (d) Cuff, M. E.; Miller, K. I.; van Holde, J. F.; Hendrickson, W. A. *J. Mol. Biol.* **1998**, *278*, 855.
- (a) Zarei, S. A.; Khandar, A. A.; Khatamian, M.; Hosseini-Yazdi, S. A.; Dechamps, I.; Guillon, E.; Piltan, M. *Inorg. Chim. Acta* **2013**, *394*, 348. (b) Vigato, P. A.; Tamburini, S.; Bertolo, L. *Coord. Chem. Rev.* **2007**, *251*, 1311. (c) Casellato, U.; Tamburini, P.; Tomasin, P.; Vigato, T. A. *Inorg. Chim. Acta* **2004**, *357*, 4191. (d) Bunzli, J. C. G.; Piguat, C. *Chem. Rev.* **2002**, *102*, 1987. (e) Martel, A.; Penitka, D. K. *Chem. Rev.* **2001**, *216*, 55. (f) Kaminskaia, N. B.; He, C.; Lippard, S. J. *Inorg. Chem.* **2000**, *39*, 3365.
- Guerriero, P.; Tamburini, S.; Vigato, P. A. *Coord. Chem. Rev.* **1995**, *139*, 17.
- (a) Byun, J. C.; Mun, D. H.; Park, K. M. *Bull. Korean Chem. Soc.* **2013**, *34*, 255. (b) Byun, J. C.; Lee, N. H.; Mun, D. H.; Park, K.-M. *Inorg. Chem. Commun.* **2010**, *13*, 1156. (c) Byun, J. C.; Kim, K. J. *Inorg. Chem. Commun.* **2007**, *10*, 502. (d) Kim, K. J.; Jung, D. S.; Kim, D. S.; Choi, C. K.; Park, K.-M.; Byun, J. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1747.
- (a) Gao, J.; Reibenspies, J. H.; Zingaro, R. A.; Woolley, F. R.; Martell, A. E.; Clearfield, A. *Inorg. Chem.* **2005**, *44*, 232. (b) Kuhnert, N.; Strabnig, C.; Lopez-Periago, A. M. *Tetrahedron: Asymmetry* **2002**, *13*, 123. (c) Korupoju, S. R.; Mangayarkarasi, N.; Ameerunisha, S.; Valente, E. J.; Zacharias, P. S. *J. Chem. Soc., Dalton Trans.* **2000**, 2845.
- (a) Foher, M. A. S.; Mautner, F. A.; Hafez, A. K.; Abu-Youssef, M. A. M.; Gspan, C.; Badr, A. M. A. *Polyhedron* **2003**, *22*, 975. (b) Zhang, H.; Wang, X.; Zhang, K.; Gao, B. K. *Coord. Chem. Rev.* **1999**, *183*, 157. (c) Ruiz, E.; Cano, J.; Alvaewz, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122.
- (a) Asadi, H.; Golchoubia, H.; Welter, R. J. *J. Mol. Struct.* **2005**, *779*, 30. (b) Bose, D.; Rahaman, S. H.; Mostafa, G.; Walsh, R. D. B.; Zaworotko, M. J.; Ghosh, B. K. *Polyhedron* **2004**, *23*, 545.
- (a) Hathaway, B. J. *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 5, p. 533. (b) Mukhopadhyay, U.; Bernal, I.; Massoun, S. S.; Mautner, F. A. *Inorg. Chim. Acta* **2004**, *357*, 3673.
- (a) Socrates, G. *Infrared and Raman Characteristic Group Frequencies*, 3rd ed.; Wiley: New York, 2001. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
- Jones, P. I.; Jeffery, J. C.; Maher, J. P.; McCleverty, J. A.; Rieger, P. H.; Ward, M. D. *Inorg. Chem.* **1997**, *326*, 3088.
- Bruker, SAINTPLUS NT Version 6.22. *Software Reference Manual*; Bruker AXS: Madison, Wisconsin, 2000.
- Bruker, SHELXTL-PC Version 6.22 Program for Solution and Refinement of Crystal Structures; Bruker AXS Inc., Madison, Wisconsin, U.S.A. 2001.