Mercury(II) Halide and Copper(I) Iodide Complexes of Double-Tweezer Ligand with Thiocyclohexyl End-Group

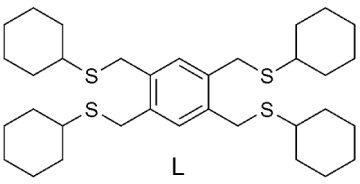
Jai Young Lee, Sanjina Lee, Minhye Jo, Hayan Lee, Ki-Min Park, and Shim Sung Lee*

*Department of Chemistry (BK21) and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea. *E-mail: sslee@gnu.ac.kr*

Received February 6, 2009, Accepted February 26, 2009

Key Words: Double-tweezer ligand, Mercury(II) halide, Copper(I) iodide, Complex, Crystal structure

Research on the multi-dentate ligand system for binuclear compounds is in great demand due to the prospect that such species may serve as models of electron transfer, charge transfer and allosteric behaviors observed in biochemical system.[1-3] The structural topologies of the binucleating frameworks are often determined by arguments of donor system and organic linkers. Our group[4] and others[5] have reported a series of dinuclear complexes of macrocyclic ligands with discrete and continuous forms. Parallel to this, noncyclic podal ligand system often give the dinuclear complexes. A further possibility to prepare the dinuclear complexes with soft metals could be given by applying the multipodal ligands with sulfur donors in each arm. Recently, Hanton *et al.*[6] and our group[7] have reported a double tweezer-type ligand with four thiopyridyl arms, [1,2,4,5-tetrakis(2-pyridylmethylsufanylmethyl)benzene] which forms dinuclear complexes with Cu(II) and Cd(II) instead of a polymeric array due to the three-layered π-stacking motif. In this regard, we are interested in using a ligand-directed approach to construct new discrete dinuclear complexes as well as to achieve the construction of infinite coordination polymers. Thus, the double tweezer-type ligands with non-aromatic end-groups are of particular interest. The proposed quadru-armed ligand **L** employs one sulfur donor as a binding site and cyclohexane end-group in each arm which, in turn, will serve to minimize the inter- and/or intramolecular interactions. In this paper, we report dimercury(II) halide complexes $[Hg_2(\mathbf{L})X_4]$ (X = Cl: **1a**, X = Br: **1b**, X = I: **1c**) and copper(I) iodide coordination polymer $[Cu_2(\mathbf{L})I_2]_n$ of **L** which were structurally characterized by single-crystal X-ray analysis. The thermal properties and comparative NMR study of the complexes were also accomplished.



L

Experimental Section

Materials and Instruments. All chemicals used in synthesis were of reagent grade without purification. The IR spectrum was recorded as KBr pellet on a Shimadzu FT-IR 8400S spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Advance-300 (300 MHz) NMR spectrometer. Chemical shifts for samples were expressed in ppm and calibrated against TMS as a reference. The ESI mass spectrum was measured with a QTARP 3200 spectrometer. The EI mass spectrum was measured with a JEOL GC Mate II spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer. Thermogravimetric analysis (TGA) was performed under N_2 at a scan rate of 10 ^oC min^{-1} using a Scinco TGA 1000 thermal analyzer at the Central Instrument Facility of Gyeongsang National University.

Synthesis of Ligand. 1,2,4,5-Tetrakis(bromomethyl)benzene (1.01 g, 2.22 mmol) in THF (15 mL) was slowly added to a stirred solution of cyclohexanethiol (1.03 g, 8.88 mmol) in THF (10 mL) in the presence of NaOH (0.36 g, 8.88 mmol) in water (5 mL). The solution was refluxed for 2 h. After being cooled to room temperature the reaction mixture was filtered and evaporated. 10% HCl was added, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate and evaporated. The product **L** was obtained by recrystallization from dichloromethane/*n*-haxane (1/30) as colorless solid (1.12 g, 84%). M.p.: 111-112 ^oC, IR (KBr, pellet): 2923, 2848, 1446, 1199, 999, 738 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.15 (s, 2 H, Ar), 3.86 (s, 8 H, ArC***H***$_2$), 2.67-2.60 (m, 4 H, S-C***H***), 2.00-1.75 (mm, 16 H, CHC***H***$_2$CH$_2$CH$_2$), 1.60 (m, 4 H, CHCH$_2$CH$_2$C***H***$_2$), 1.56-1.25 (m, 20 H, CHCH$_2$C***H***$_2$C***H***$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): 135.51, 132.44, 43.81, 33.53, 31.60, 31.54, 26.03, 25.87, 22.67, 14.14. Anal. Calc. for $C_{34}H_{54}S_4$: C, 69.09; H, 9.21; S, 21.70. Found: C, 69.47; H, 9.34; S, 21.92. MS (ESI): *m*/*z* = 590 [$(M)^+$, $(C_{34}H_{54}S_4)^+$].

Preparation of $[Hg_2(L)Cl_4]$ (1a). Colorless crystalline product was obtained from dichloromethane solution of **L** (9.99 mg, 16.9 mmol) layered with methanol solution of $HgCl_2$ (10.1 mg, 37.2 mmol). Yields: 75%. M.p. 203-206 ^oC (decomp). IR (KBr, pellet): 2840, 2362, 2347, 1448, 1265, 997 cm^{-1}. Anal. Calc. for $C_{34}H_{54}Cl_4Hg_2S_4$: C, 36.01; H, 4.80; S, 11.31. Found: C, 36.22; H, 4.84; S, 11.52. MS (ESI): *m*/*z* = 1133.1 [$(M)^+$, $(C_{34}H_{54}S_4Hg_2Cl_4)^+$].

Preparation of $[Hg_2(L)Br_4]$ (1b). General procedures are same as for **1a**. Yields: 68%. M.p. 196-197 ^oC (decomp). IR (KBr, pellet): 2850, 2364, 2343, 1444, 1263, 999 cm^{-1}. Anal. Calc. for $C_{34}H_{54}Br_4Hg_2S_4$: C, 31.13; H, 4.15; S, 9.78. Found: C, 31.35; H, 4.34; S, 9.84. MS (ESI): *m*/*z* = 1311.8 [$(M)^+$,

$(C_{34}H_{54}S_4Hg_2Br_4)^+$].

Preparation of $[Hg_2(L)I_4]$ (1c). General procedures are same as for **1a**. Yields: 63%. M.p. 175-177 °C (decomp). IR (KBr, pellet): 2854, 2369, 2341, 1442, 1269, 995 cm^{-1}. Anal. Calc. for $C_{34}H_{54}I_4Hg_2S_4$: C, 27.23; H, 3.63; S, 9.78. Found: C, 27.40; H, 3.74; S, 9.86. MS (ESI): *m/z* = 1498.8 [$(M)^+$, $(C_{34}H_{54}S_4Hg_2I_4)^+$].

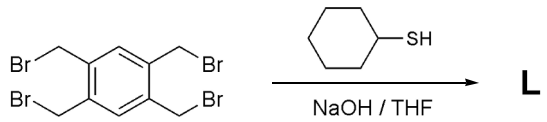
Preparation of $[Cu_2(L)I_2]_n$ (2). Pale-yellow crystalline product was obtained from dichloromethane solution of **L** (10.0 mg, 16.9 mmol) layered with acetonitrile solution of CuI (7.08 mg, 37.2 mmol). Yields: 67%. M.p. 245-246 °C (decomp). IR (KBr, pellet): 2927, 2850, 1448, 1263, 999 cm^{-1}. Anal. Calc. for $C_{34}H_{54}Cu_2I_2S_4$: C, 42.10; H, 5.40; S, 13.22. Found: C, 42.25; H, 5.52; S, 13.57.

Crystal Structure Determination and Refinement: All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated Mo*Kα* (λ = 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The two-dimensional diffraction images were collected, each of which was measured at -100 °C (**1a**, **1b** and **2**) and room temperature (**1c**). The frame data were processed to give structure factors using the program SAINT.[8] The structure was solved by a direct method and refined by full matrix least square against F^2 for all data using SHELXTL software.[9] All hydrogen atoms were included in calculated position with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 1.

Results and Discussion

A typical approach to the preparation of thiaethers invokes C-S bond formation in a halide-thiol based bimolecular reaction. Thus **L** was synthesized by reaction between 1,2,4,5-tetrakis(bromomethyl)benzene and cyclohexanethiol in the presence of NaOH in good yield (84%)[10] (Scheme 1). The ^1H and ^{13}C NMR spectra together with elemental analysis and mass spectrum are in agreement with the proposed structure.

Reactions of **L** with two molar equivalents of $HgCl_2$, $HgBr_2$, and HgI_2 afforded colorless X-ray quality crystalline products **1a**, **1b** and **1c**, respectively, and their crystal structures were characterized (Figure 1). The three mercury(II) halides (X) complexes **1a**, **1b** and **1c** are almost isostructural with a 2:1 (metal:ligand) stoichiometry as expected. Selected geometric parameters are presented in Table 2. Since each complex molecule shows an imposed inversion at the center of its aromatic group, the asymmetric unit of the complex contains a half molecule of **L**, one mercury and two halide atoms. Each mercury atom is in a tetrahedral geometry with two coordination sites occupied by two sulfur atoms from **L** in



Scheme 1. Synthesis of **L**.

Table 1. Crystal data and structure refinement for **1a**, **1b**, **1c** and **2**

	1a	1b	1c	2
Empirical formula	$C_{34}H_{54}Cl_4Hg_2S_4$	$C_{34}H_{54}Br_4Hg_2S_4$	$C_{34}H_{54}I_4Hg_2S_4$	$C_{34}H_{54}Cu_2I_2S_4$
Formula weight	1133.99	1311.83	1499.79	969.88
Temperature (K)	173(2)	173(2)	298(2)	173(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	$P2_1/n$	$P2_1/n$	*P*-1
a (Å)	8.619(1)	13.585(1)	9.031(1)	9.411(2)
b (Å)	10.109 (1)	10.615 (1)	15.686(2)	9.833(2)
c (Å)	12.630(1)	14.6781(7)	16.527(2)	10.502 (2)
α	94.690(1)	90	90	86.828(3)
β	90.316(1)	103.348(1)	104.938(3)	84.343(3)
γ	110.300(1)	90	90	80.472(3)
Volume ($Å^3$)	1027.9 (1)	2059.5(2)	2262.1(5)	953.0(3)
Z	1	2	2	1
Calculated density (g/cm^3)	1.832	2.115	2.202	1.690
Absorption coefficient (mm^{-1})	7.945	11.552	9.714	2.977
θ range for data collection (deg)	1.62 -27.00	1.84 -27.00	1.82 -27.00	2.79 -26.00
Reflections collected	8779/4399	12177/4487	13670/4907	5463/3680
Completeness to θ_{max}	θ = 27.0°, 98.3%	θ = 27.0°, 99.7%	θ = 27.0°, 99.4%	θ = 26.0°, 98.3%
Absorption method	Empirical SADABS	Empirical SADABS	None	Empirical SADABS
Data / restraints / parameters	4399 / 0 / 199	4487 / 0 / 199	4907 / 0 / 199	3680 / 0 / 190
Goodness-of-fit on F^2	1.154	1.104	1.031	1.097
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0290, *wR*2 = 0.0741	*R*1 = 0.0437, *wR*2 = 0.1085	*R*1 = 0.0447, *wR*2 = 0.0964	*R*1 = 0.0516, *wR*2 = 0.0912
R indices (all data)	*R*1 = 0.0325, *wR*2 = 0.0860	*R*1 = 0.0672, *wR*2 = 0.1315	*R*1 = 0.1050, *wR*2 = 0.1330	*R*1 = 0.0734, *wR*2 = 0.0986
Largest diff. peak and hole (e $Å^{-3}$)	1.138 and -1.665	2.777 and -3.032	1.211 and -1.319	0.883 and -0.966

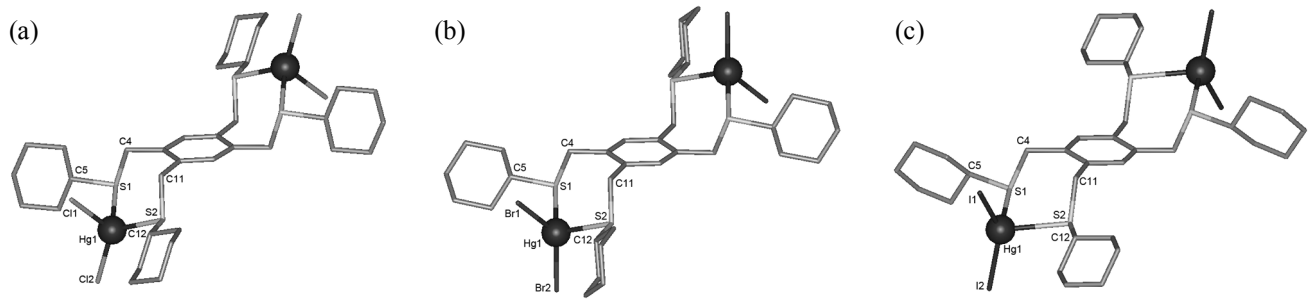


Figure 1. Molecular structures of (a) **1a** (b) **1b** and (c) **1c**, $[Hg_2(\mathbf{L})X_4]$ (**1a**: X = Cl, **1b**: X = Br and **1c**: X = I). Hydrogen atoms are omitted.

Table 2. Selected bond lengths [Å] and angles [°] for **1a-c**, $[Hg_2(\mathbf{L})X_4]$

	1a (X = Cl)	**1b** (X = Br)	**1c** (X = I)
Hg1···Hg1A	9.746(2)	9.676(1)	10.830(2)
S1···S2	4.136(2)	4.225(1)	3.762(2)
Hg1-S1	2.563(1)	2.625(2)	2.749(3)
Hg1-S2	2.657(1)	2.677(1)	2.787(3)
Hg1-X1	2.471(1)	2.572(1)	2.660(1)
Hg1-X2	2.383(1)	2.494(1)	2.655(1)
S1-Hg1-S2	104.79(3)	105.66(6)	85.63(7)
X1-Hg1-S1	97.71(4)	95.79(5)	109.75(6)
X1-Hg1-S2	95.40(4)	95.66(4)	98.78(5)
X2-Hg1-S1	124.72(4)	115.49(5)	101.82(6)
X2-Hg1-S2	109.27(4)	107.98(5)	107.54(5)
X1-Hg1-X2	120.33(5)	132.50(3)	140.10(4)

a bent arrangement. Two halide atoms occupy two coordination sites on the mercury atom. The coordination sphere of the mercury is considerably distorted from regular tetrahedral; the bond angles range 95.40-124.72° for **1a**, 95.66-132.50° for **1b** and 85.68-140.10° for **1c**. The bond angles for X1-Hg-X2 are observed 120.33° (X=Cl; **1a**), 132.50° (X = Br; **1b**) and 140.10° (X = I; **1c**). These distortion may reflect that the bulk atoms like I atom in **1c** are sterically hindered by each other. Considering the larger size of I atom than the Cl and Br atoms, the smaller bite angle (< S1-Hg-S2) for **1c** (85.63°) than those of **1a** (104.79°) and **1b** (105.66°) can be explained. The Hg···Hg separations in **1a**, **1b**, and **1c** are 9.746, 9.676 and 10.830 Å, respectively. The difference of crystal system for **1a** (triclinic) from that of **1b** and **1c** (monoclinic), to some extent, is due to the difference of their packing modes.

Having obtained mercury(II) halides complexes of **L**, we proceeded to the preparation of **L** complex with copper(I) iodide system. Slow diffusion of dichloromethane solution of **L** into an acetonitrile solution of CuI afforded pale-yellow crystalline product **2**. Unlike the dinuclear structures **1a-c**, the complex **2** features a 1D polymer with formula $[Cu_2(\mathbf{L})I_2]_n$ (Figure 2). In **2**, each **L** is linked with the Cu–(μ-I)$_2$–Cu rhomboid unit via Cu–S bonds, showing an alternating linear arrangement of the ligand and the dinuclear iodo-bridged copper(I) unit. The copper(I) coordination sphere is a

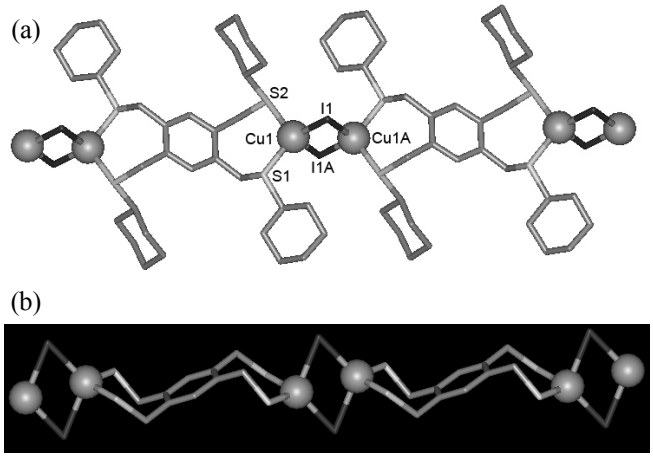


Figure 2. Molecular structure of **2**, $[Cu_2(\mathbf{L})I_2]_n$: (a) top view and (b) side view (cyclohexyl end-groups were deleted).

Table 3. Selected bond lengths [Å] and angles [°] for **2**

Cu1-S2	2.318(2)	Cu1-I1	2.587(1)
Cu1-S1	2.346(2)	Cu1-I1A	2.745(1)
Cu1···Cu1A	2.856(2)		
S2-Cu1-S1	109.80(6)	S1-Cu1-I1	115.67(5)
S2-Cu1-I1	116.02(5)	S1-Cu1-I1A	94.35(5)
S2-Cu1-I1A	103.04(5)	I1-Cu1-I1A	115.31(3)

distorted tetrahedral shape, with the tetrahedral angles falling in the range 94.34(5)-116.02(5)°. The Cu···Cu distance (2.856 Å) is longer than the van der Waals radii (2.8 Å), indicating no cuprophilic interaction.

Thermogravimetric analysis (TGA) of the complexes are conducted (Figure 3). In case of the mercury(II) halides complexes **1a-c**, there is no significant difference in the thermal properties. Therefore, the discussion was made only for the bromide form **1b**. The TG curve for **1b** exhibits a sharp weight loss of 45.0% from 180 to 208 °C, due to the release of the ligand molecule (calcd: 45.1%). For **2**, the TG curve exhibits three steps of weight losses; the total weight loss of 61.6% by two step decompositions, which are a significant weight loss of 46% from 178-259 °C and a gradual weight loss of 15.6% between 259-293 °C is attributable to the concomitant release of the ligand molecule, with a calculated value of 60.9%.

To obtain further information on the mercury(II) ion

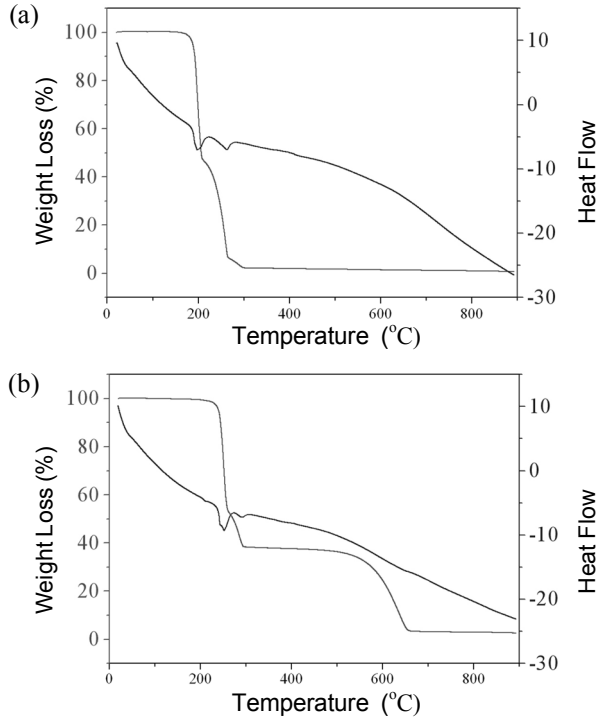


Figure 3. TGA and DSC for (a) **1b** and (b) **2**.

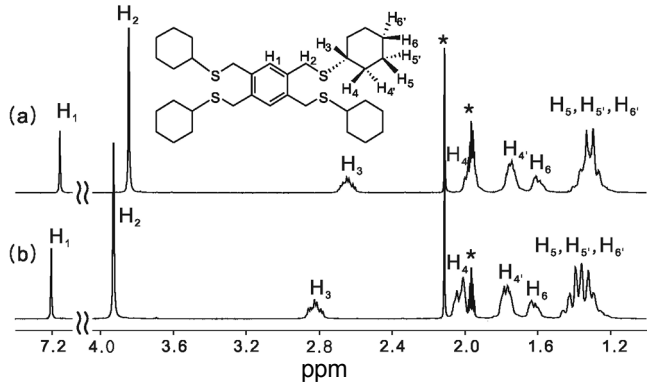


Figure 4. ^{1}H NMR spectra of (a) **L** and (b) **L**+$HgBr_2$ (0.5 equiv) in $CD_3CN/CDCl_3$ (v/v 1:1).

binding behavior of the ligand, comparative NMR studies were performed. ^{1}H NMR spectra of free **L** and **L**-$HgBr_2$ system are shown in Figure 4. However, due to the precipitation no satisfying NMR spectra could be obtained above the addition of 0.5 equiv $HgBr_2$. Upon addition of $HgBr_2$ to the solution of **L**, most protons display downfield shifts, indicating that **L** forms stable complex with mercury(II) with a fast-exchange rate between ligand and cation on NMR time scale. The order of magnitude of the chemical shift variation is H_3 ($\Delta\delta$ = 0.18 ppm) > H_2 ($\Delta\delta$ = 0.08 ppm) > H_1, H_4 ($\Delta\delta$ = ~0.05 ppm) > $H_{4'}$, H_5, H_6 ($\Delta\delta$ = ~0.02 ppm). The largest chemical shift change shown by the H_3 adjacent to the sulfur donor can be explained that the mercury(II) is strongly coordinated by S atoms. The results above described indicate the formation of the complex which is also similar to the case in the solid state.

In summary, a new double-tweezer type ligand **L** with four cyclohexanethiol moieties was employed in the assembly reactions with some d^{10} metal halides and its discrete type isostructural dimercury(II) halides complexes (**1a-c**) and 1D copper(I) iodide coordination polymer (**2**) in crystalline state were isolated. A comparative NMR study suggested the similar mercury(II) complex also exist in solution. The structural characteristics revealed here could be useful in the design of new dinuclear ligand system for the soft metal species.

Supplementary Material. Supplementary crystallographic data associated to compounds **1a-c** and **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 714758 (**1a**), 714759 (**1b**), 714760 (**1c**) and 714761 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments. We thank the Korea Research Foundation (2008-313-C00432) for financial support and acknowledge.

References

1. Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, 199.
2. Lehn, J.-M. *Pure Appl. Chem.* **1980**, *52*, 2441.
3. 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.
4. (a) Jin, Y.; Yoon, I.; Seo, J.; Lee, J.-E.; Moon, S.-T.; Kim, J.; Han, S. W.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Dalton Trans*. **2005**, *4*, 788. (b) Yoon, I.; Seo, J.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Choi, K. S.; Jung, O.-S.; Park, K.-M.; Lee, S. S. *Dalton Trans*. **2005**, *14*, 2352. (c) Kim, H. J.; Jin, Y.; Seo, J.; Lee, J.-E.; Lee, J. Y.; Lee, S. S. *Inorg. Chem. Commun*. **2006**, *9*, 1040. (d) Seo, J.; Song, M. R.; Lee, J.-E.; Lee, S. Y.; Yoon, I.; Park, K.-M.; Kim, J.; Jung, J. H.; Park, S. B.; Lee, S. S. *Inorg. Chem*. **2006**, *45*, 952. (e) Lee, J.-E.; Kim, H. J.; Lee, S. Y.; Lee, J. Y.; Jin, Y.; Lee, S. S. *Bull. Korean Chem. Soc.* **2007**, *28*, 2041.
5. (a) Vetrichelvan, M.; Lai, Y.-H.; Mok, K. F. *Eur. J. Inorg. Chem*. **2004**, 2086. (b) Vasilescu, I. M.; Bray, D. J.: Clegg, J. K.; Lindoy, L. F.; Meehan, G. V.; Wei, G. *Dalton Trans*. **2006**, 5115. (c) Kickham, J. E.; Loeb, S. J.; Murphy, S. L. *J. Am. Chem. Soc*. **1993**, *115*, 7031. (d) Habata, Y.; Seo, J.; Otawa, S.; Osaka, F.; Noto, K.; Lee, S. S. *Dolton Trans*. **2006**, 2202.
6. Cordes, D. B.; Hanton, L. R. *Inorg. Chem. Commun.* **2005**, *8*, 967.
7. Kang, D.; Kim, Y.; Choi, K. S.; Lee, H.; Kim, H. J.; Lee, S. S. *Bull. Korean Chem. Soc.* **2008**, *29*, 1253.
8. Bruker, *SMART and SAINT: Area Detector Control and Integration Software*, Ver. 6.22; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 2001.
9. Bruker, *SHELXTL: Structure Determination Programs*, Ver. 6.10; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 2000.
10. Kim, T. H.; Seo, J.; Park, K.-M.; Lee, S. S.; Kim, J. *Inorg. Chem. Commun*. **2007**, *10*, 313.