

Template Syntheses, Crystal Structures and Supramolecular Assembly of Hexaaza Macrocyclic Copper(II) Complexes

Taehyung Kim, Alan J. Lough,[†] and Ju Chang Kim*

Department of Chemistry, Pukyong National University, Busan 608-737, Korea. *E-mail: kimjc@pknu.ac.kr

[†]Department of Chemistry, University of Toronto, Toronto, ONT, Canada M5S 3H6

Received March 12, 2013, Accepted March 27, 2013

Key Words : Macrocyclic copper(II) complexes, Hydrogen bonds, C-H... π interactions, π - π interactions, Supramolecule

Supramolecules constructed from metal complexes have attracted great attention due to their structures^{1,2} and potential applications such as in catalysis,³⁻⁶ magnetism,⁷⁻⁹ nonlinear optical behavior,^{10,11} gas storage,^{12,13} and molecular sensing,^{14,15} etc. The metal complexes can be further extended by secondary interactions such as hydrogen bonding,¹⁶ π - π ,¹⁷ C-H... π ,¹⁸ and C-H...O¹⁹ interactions to form supramolecules. It has been understood that the macrocyclic metal complexes can be utilized for the construction of supramolecules through self-assembly processes.²⁰ Especially, the functional pendants on the hexaaza macrocycles afford a favorable environment for the possible intermolecular interactions through pendants.^{16,21-23} In this regard, we introduced imidazoles as pendants on the hexaaza macrocyclic nickel(II) complexes and reported the importance of pendants for the construction of supramolecules in our early investigation.¹⁶ As an extension of the supramolecular chemistry of metal complexes of macrocycles, we synthesized the hexaaza macrocyclic copper(II) complex [Cu(L+2H)](ClO₄)₄ by a template method and by the reactions between [Cu(L+2H)](ClO₄)₄ and an appropriate aromatic carboxylate ligand or acetonitrile molecules, we obtained two new copper(II) complexes [Cu(L+2H)]₂(μ -tp)](ClO₄)₆·2H₂O (**1**) and [Cu(L)](CH₃CN)₂(ClO₄)₂ (**2**), where L = 3,10-bis{3-(1-imidazolyl)propyl}-1,3,5,8,10,12-hexaazacyclotetradecane, tp = terephthalate.

In this report, we describe the structures and properties of

1 and **2** in detail. The complexes **1** and **2** were self-assembled by intermolecular interactions such as hydrogen bonds, C-H... π interactions and π - π interactions, resulting in the formation of supramolecules in the solid state, respectively.

The reaction of copper(II) complex [Cu(L+2H)](ClO₄)₄ with Na₂tp in water was carried out and a five-coordinate copper(II) complex **1** was isolated. In **1**, the skeleton of the macrocyclic unit adopts the classical *trans III* (*R,R,S,S*) configuration.²⁴ Both of the imidazole pendants in the hexaaza macrocycle remain protonated. The structure of **1** exhibits a macrocyclic copper(II) dimer and the coordination environment around the copper(II) ion can be described as a square pyramid with four Cu-N and one Cu-O bonds (Figure 1). The copper atom sits ~0.11 Å away from the four secondary amine nitrogen atom plane of the macrocycle. The formation of tp bridged copper(II) dimer was not unusual in the copper(II) system although the tp bridged 1D macrocyclic nickel(II) coordination polymer was observed in the similar nickel(II) system.¹⁶ It is believed that the preference of five-coordination in the macrocyclic copper(II) complex compared to that in the nickel(II) complex allows the formation of such a five-coordinate copper(II) dimer.^{25,26} The Cu-N bond distances in **1** vary from 2.013(4) Å to 2.018(4) Å, which are typical for hexaaza macrocyclic copper(II)

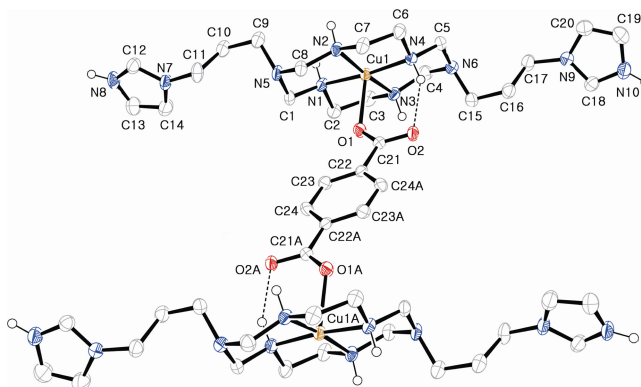
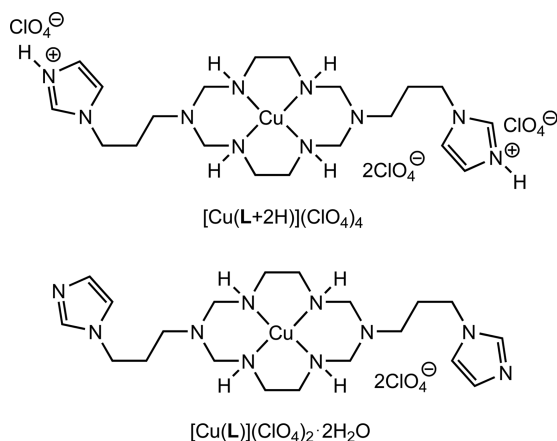


Figure 1. Molecular structure of **1** with atom-labeling scheme. Perchlorate ions and hydrogen atoms other than those on secondary amine nitrogen atoms and protonated imidazole nitrogen atoms are omitted for clarity. Symmetry code: #1 -x+1, -y+1, -z+1.

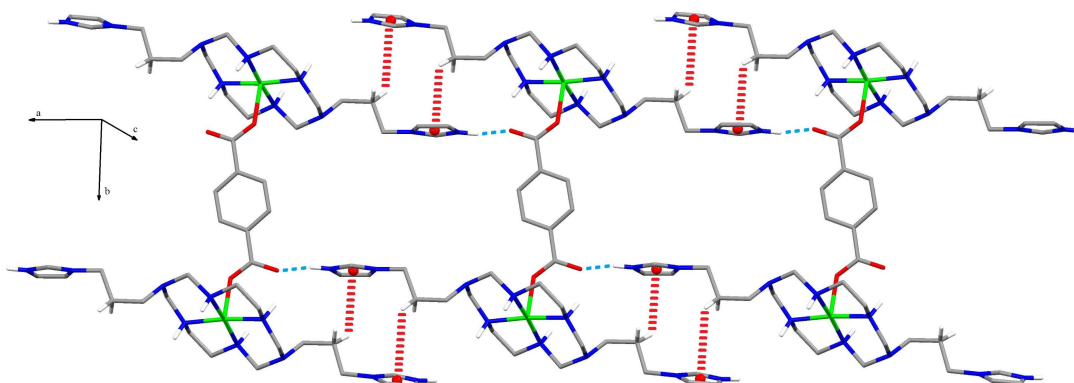


Figure 2. View of an undulated double stranded 1D supramolecular structure of **1** by hydrogen bonds (---) and C-H... π interactions (---). Hydrogen atoms are omitted for clarity other than those on nitrogen atoms and participating in C-H... π interactions.

systems.²⁵⁻²⁸ The Cu-O distance of 2.258(3) Å is a normal case in apical site coordination of O donor with four coordination N donor of the saturated tetraazamacrocyclic ligand at basal plane.²⁹ It is well comparable to those observed in macrocyclic copper(II) systems {[Cu(L1)(O₂CH)](ClO₄)·H₂O (L1 = 5,16-dimethyl-2,6,13,17-tetraazatricyclo(14,4,0)^{1,18}, 0^{7,12})docosane; Cu-O = 2.2343 Å,²⁵ [Cu(L2)(H₂O)(O₂CCH=CHCO₂)]·H₂O (L2 = 3,10-bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane; Cu-O = 2.3601(18) Å²⁶}. One of the pertinent structural features found in **1** is the formation of a macrocyclic copper(II) dimer (Figure 2), where the dimer extends its structure by intermolecular hydrogen bonds through imidazole pendants as well as C-H... π interactions to form a double stranded 1D supramolecule {C-H... π = C(16)-H(16B)...Im_{centroid}; d(H... π) = 3.128 Å, d(C... π) = 3.739 Å, \angle (CH π) = 121.24°, C-H... π = C(10)-H(10A)...Im_{centroid}; d(H... π) = 3.345 Å, d(C... π) = 3.961 Å, \angle (CH π) = 122.05°, Im = imidazole}. The imidazole pendants in the structure **1** act as a hydrogen bond donor (Figure 2).

The complex [Cu(L+2H)](ClO₄)₄ in which two imidazole pendants are protonated can be deprotonated by the addition of an excess amount of triethylamine in acetonitrile, giving the copper(II) complex **2** with fully deprotonated imidazole pendants on the macrocycle and axially coordinated acetonitrile molecules to the copper(II) ion. The structure of **2** is described in Figure 3. In **2**, the coordination environment of copper(II) ion exhibits a distorted octahedron with macrocyclic secondary amine nitrogen atoms and acetonitrile molecules. The Cu-N bond distances range from 2.012(4) Å to 2.018(4) Å, indicating a normal six-coordinated copper(II) d⁹ system.^{25-28,30,31} The Cu-N_{acetonitrile} distance of 2.534(3) Å is comparable to those found in related systems {*trans*-[Cu(L1)(CH₃CN)₂](PF₆)₂; Cu-N_{acetonitrile} = 2.594(2) Å,³¹ [Cu(L3)(CH₃CN)₂][Ni(dmit)₂]₂ (L3 = 1,4,8,11-tetraazacyclotetradecane, dmit = isotrithionedithiolate); Cu-N_{acetonitrile} = 2.491(6) Å³²}. The macrocycle in the complex **2** adopts the *trans III* configuration which is the most stable in the solid state.²⁴ The monomeric complex **2** is self-assembled by intermolecular hydrogen bonds and C-H... π interactions to form a 1D supramolecule.

The imidazole pendants play a role as hydrogen bond

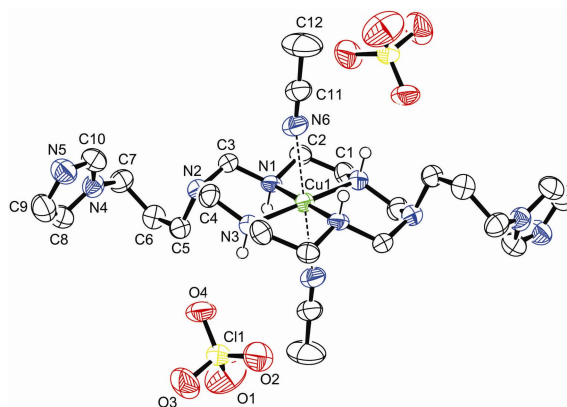


Figure 3. Molecular structure of **2** with atom-labeling scheme. Hydrogen atoms are omitted for clarity other than those on nitrogen atoms.

acceptors with one of the hydrogen atoms of secondary amines belonging to an adjacent copper(II) macrocycle, forming 1D chain. Furthermore, the C-H... π interactions between the methyl groups of the acetonitrile ligands and imidazole pendants of the adjacent macrocycle support the formation of supramolecular polymer {C-H... π = C(12)-H(12C)...Im_{centroid}; d(H... π) = 3.568 Å, d(C... π) = 4.272 Å, \angle (CH π) = 130.81°} (Figure 4). The formation of 1D chain in **2** is different from that of the nickel(II) analogue in which two 1D hydrogen bonded chains are interconnected by C-

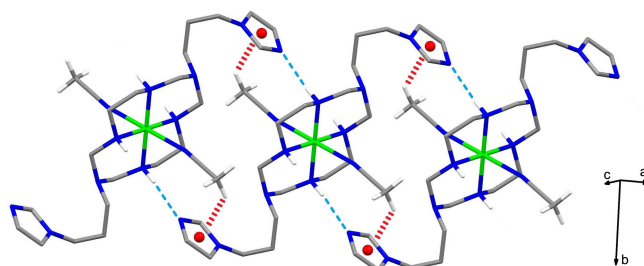


Figure 4. View of 1D supramolecular structure of **2** by hydrogen bonds (---) and C-H... π interactions (---). Hydrogen atoms are omitted for clarity other than those on nitrogen atoms and participating in C-H... π interactions.

H $\cdots\pi$ interactions between the methyl groups of the acetonitrile ligands and the imidazole pendants, forming a 2D network.¹⁶ By the coordination of acetonitrile molecules to the copper(II) ion, the complex **2** shows an axially elongated octahedron around the copper(II) ion due to the well-known Jahn-Teller effect. It has been reported that the long contact of axial ligands in [Cu(L1)(H₂O)₂](Cl)₂·2H₂O is supported by hydrogen bonds composed of dihydrate, chloride and secondary amines.³³ Although no such hydrogen bonding interactions are involved in **2**, acetonitrile molecules interact to the central copper(II) ion due to their fairly good σ -donor and π -acceptor properties. The purple octahedral copper(II) complex **2** is stable in air at ambient temperature.

The presence of perchlorate ions for complexes **1** and **2** was suggested by the very strong absorptions at 1088 (ν_{as} Cl-O) and 625 (δ O-Cl-O) cm⁻¹ in the IR spectra and these were assigned to antisymmetric and bending vibrations of perchlorate anions, respectively. The broad strong bands in **1** and **2** indicate that the perchlorates present in ionic forms. It is well-known that these bands split into two well-defined bands with maxima between 1200 and 1000 cm⁻¹ on monodentate coordination to a metal ion.³⁴ In addition, typical bands at appropriate positions for ν OH (in **1**), ν NH (in **1** and **2**) and ν COO (in **1**) due to the presence of macrocycles, lattice waters and aromatic carboxylates were observed as described in experimental section, respectively. Along with the bands assignable to the perchlorate and macrocycle in **2**, the observed sharp medium band at 2295 (ν C \equiv N) cm⁻¹ in the IR spectrum was attributed to the presence of coordinated acetonitrile ligands.³⁴ The solution electronic spectra of **1** and **2** in DMF showed characteristic d-d bands at 506 nm in both complexes, corresponding to the composite of two possible $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions. The third transition belonging to the near infrared $d_{z^2} \rightarrow d_{x^2-y^2}$ was not observed.^{27,35}

In summary, two new hexaaza macrocyclic copper(II) complexes were prepared by a template method and structurally characterized. In the solid state, they were self-assembled by intermolecular interactions to form the corresponding supramolecules **1** and **2**, respectively. In the structure of **1**, the copper(II) macrocycles are bridged by a tp ligand to form a macrocyclic copper(II) dimer. The dimer extends its structure by intermolecular forces such as hydrogen bonds and C-H $\cdots\pi$ interactions, resulting in the formation of a double stranded 1D supramolecule. In **2**, the basic structure is a monomeric copper(II) macrocycle with deprotonated imidazole pendants. An undulated 1D hydrogen bonded array is achieved through hydrogen bonds between imidazole pendants and secondary amines, where the imidazole pendants act as a hydrogen bond acceptor. The 1D hydrogen bonded supramolecular chain is supported by C-H $\cdots\pi$ interactions between the methyl groups of acetonitrile ligands and imidazole pendants of the copper(II) macrocycles. In both complexes, the introduction of imidazoles to the macrocycle as a pendant plays an important role for the formation of supramolecules, where they act as intermolecular hydrogen bond donors and/or acceptors, C-H $\cdots\pi$ and

π - π interactions.

Experimental Section

Physical Measurements. All chemicals except solvents were purchased from Aldrich, and were used without further purification. Distilled water was used for all procedures. Infrared spectra of solid samples were recorded on a Perkin-Elmer Spectrum X spectrophotometer between 4000 cm⁻¹ and 400 cm⁻¹ as Nujol mulls on KBr discs. Electronic spectra were measured on a Varian Cary 1C UV/vis spectrophotometer. The elemental analyses (C, H, N) were performed on crystalline samples using a CE Instruments EA-1110 Elemental Analyzer at KRICT, Korea. The starting material [Cu(L+2H)](ClO₄)₄ was prepared according to the literature procedures.^{16,21,23}

Caution! All the complexes dealing in this study contain perchlorates. The perchlorate salts are potentially explosive and should be handled with care in small quantities.

Synthesis of [Cu(L+2H)]₂(μ -tp)](ClO₄)₆·2H₂O (1**).** To a warm (~60 °C) aqueous (10 mL) solution of [Cu(L+2H)](ClO₄)₄ (353 mg, 0.4 mmol) was added Na₂tp (42 mg, 0.2 mmol) dissolved in water (10 mL), which was kept in a refrigerator. After two weeks, purple blocks of **1** were obtained. Suitable crystals of **1** were picked up for X-ray diffraction studies and subsequent spectroscopic measurements. The complex **1** was always the isolated product even under the excess use of Na₂tp up to 0.4 mmole. Yield: 78%. Anal. Calcd. for C₄₈H₈₈Cl₆Cu₂N₂₀O₃₀ (**1**): C, 32.63%; H, 4.99%; N, 15.86%. Found C, 32.54%; H, 5.06%; N, 16.00%. IR (Nujol mull, cm⁻¹): 3432 br (ν OH), 3251 w, 3144 w (ν NH),

Table 1. Crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	C ₄₈ H ₈₈ Cl ₆ Cu ₂ N ₂₀ O ₃₀	C ₂₄ H ₄₄ Cl ₂ CuN ₁₂ O ₈
Formula weight	1765.16	763.15
Temperature(K)	150(1)	150(1)
Wavelength(Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
<i>a</i> (Å)	14.2692(5)	7.9515(3)
<i>b</i> (Å)	16.3485(6)	22.4038(11)
<i>c</i> (Å)	16.1747(4)	9.6897(4)
β (°)	108.339(2)	102.043(2)
<i>V</i> (Å ³)	3581.6(2)	1688.17(13)
<i>Z</i>	2	2
<i>D</i> _{calcd} (Mg/m ³)	1.637	1.501
Absorption coefficient (mm ⁻¹)	0.916	0.869
Independent reflections	8078 [R(int) = 0.0801]	3836 [R(int) = 0.0786]
Goodness-of-fit on F ²	1.032	1.056
Final R indices [I > 2 σ (I)]	R ₁ =0.0642, wR ₂ =0.1556	R ₁ =0.0668, wR ₂ =0.1723
R indices (all data)	R ₁ =0.1205, wR ₂ =0.1890	R ₁ =0.1328, wR ₂ =0.2121

1621 w (δ HOH), 1569 s ($\nu_{\text{as}}\text{COO}$), 1299 m ($\nu_{\text{s}}\text{COO}$), 1089 vs ($\nu_{\text{as}}\text{Cl-O}$), 625 vs ($\delta\text{O-Cl-O}$).

Synthesis of [Cu(L)(CH₃CN)₂](ClO₄)₂ (2). To an acetonitrile solution (50 mL) of [Cu(L+2H)](ClO₄)₄ (353 mg, 0.4 mmol) was added an excess amount of triethylamine (5 mL). The solution was kept in a refrigerator for a week. The purple plates of **2** formed were collected and used for X-ray diffraction studies and subsequent spectroscopic measurements. Yield: 85%. Anal. Calcd. for C₂₄H₄₄Cl₂CuN₁₂O₈: C, 37.73%; H, 5.76%; N, 23.05%. Found C, 37.65%; H, 5.76%; N, 23.05%. IR (Nujol mull, cm⁻¹): 3246 m, 3124 m (ν_{NH}), 2295 w, 2260 s ($\nu_{\text{C}\equiv\text{N}}$), 1088 vs ($\nu_{\text{as}}\text{Cl-O}$), 625 vs ($\delta\text{O-Cl-O}$).

X-ray Crystallography. X-ray crystallographic data for **1** and **2** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo K α radiation and were measured using a combination of ϕ scans and ω scans with κ offsets. The data were processed using the Denzo-SMN package.³⁶ The structures were solved and refined using the SHELXTL/PC V6.1 package³⁷ for full-matrix least-squares refinement that was based on F^2 . Hydrogen atoms bonded to carbon atoms and secondary nitrogen atoms were included in calculated positions and treated as riding atoms. Crystallographic data for **1** and **2** are summarized in Table 1.

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. 2012010454).

Supplementary Material. CCDC 875579 and 875581 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

References

- Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810.
- Bassanetti, I.; Mezzadri, F.; Comotti, A.; Sozzani, P.; Gennari, M.; Calestani, G.; Marchiò, L. *J. Am. Chem. Soc.* **2012**, *134*, 9142.
- Brown, C. J.; Miller, G. M.; Johnson, M. W.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2011**, *133*, 11964.
- Wu, C.-D.; Hu, A.; Zhang, L.; Lin, W. *J. Am. Chem. Soc.* **2005**, *127*, 8940.
- Pramanik, A.; Abbina, S.; Das, G. *Polyhedron* **2007**, *26*, 5225.
- Yamada, Y. M. A.; Sarkar, S. M.; Uozumi, Y. *J. Am. Chem. Soc.* **2012**, *134*, 3190.
- Schwarz, G.; Bodenthin, Y.; Tomkowicz, Z.; Haase, W.; Geue, T.; Kohlbrecher, J.; Pietsch, U.; Kurth, D. G. *J. Am. Chem. Soc.* **2011**, *133*, 547.
- Hazra, S.; Mondal, S.; Fleck, M.; Sasmal, S.; Sañudo, E. C.; Mohanta, S. *Polyhedron* **2011**, *30*, 1906.
- Ma, Y.; Zhou, N.; Chen, X.-P.; Cao, D.; Liao, D.-Z.; Yan, S.-P. *J. Coord. Chem.* **2009**, *62*, 3913.
- Le Bozec, H.; Le Bouder, T.; Maury, O.; Bondon, A.; Ledoux, I.; Deveau, S.; Zyss, J. *Adv. Mater.* **2001**, *13*, 1677.
- Le Bozec, H.; Le Bouder, T.; Maury, O.; Zyss, J. *J. Opt. A: Pure Appl. Opt.* **2002**, *4*, S189.
- Duriska, M. B.; Neville, S. M.; Lu, J.; Iremonger, S. S.; Boas, J. F.; Kepert, C. J.; Batten, S. R. *Angew. Chem.* **2009**, *121*, 9081.
- Yang, W.; Greenaway, A.; Lin, X.; Matsuda, R.; Blake, A. J.; Wilson, C.; Lewis, W.; Hubberstey, P.; Kitagawa, S.; Champness, N. R.; Schröder, M. *J. Am. Chem. Soc.* **2010**, *132*, 14457.
- Kumar, A.; Sun, S.-S.; Lees, A. J. *Coord. Chem. Rev.* **2008**, *252*, 922.
- Iki, N.; Ohta, M.; Tanaka, T.; Horiuchi, T.; Hoshino, H. *New J. Chem.* **2009**, *33*, 23.
- Han, S.; Kim, T.; Lough, A. J.; Kim, J. C. *Inorg. Chim. Acta* **2011**, *370*, 170.
- Wan, C.-Q.; Mak, T. C. W. *Cryst. Growth Des.* **2011**, *11*, 832.
- Biradha, K.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 6431.
- Moon, J. R.; Lough, A. J.; Yoon, Y. T.; Kim, Y. I.; Kim, J. C. *Bull. Korean Chem. Soc.* **2011**, *32*, 325.
- Suh, M. P.; Cheon, Y. E.; Lee, E. Y. *Coord. Chem. Rev.* **2008**, *252*, 1007.
- Min, K. S.; Suh, M. P. *Eur. J. Inorg. Chem.* **2001**, 449.
- Han, S.; Lough, A. J.; Kim, J. C. *J. Coord. Chem.* **2010**, *63*, 2069.
- Han, S.; Lough, A. J.; Kim, J. C. *Bull. Korean Chem. Soc.* **2012**, *33*, 2381.
- Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.
- Kim, J. C.; Roh, J.; Lough, A. J. *J. Chem. Cryst.* **2007**, *37*, 615.
- Kim, J. C.; Lough, A. J. *J. Chem. Cryst.* **2005**, *35*, 535.
- Azcondo, M. T.; Ballester, L.; Gutiérrez, A.; Perpiñán, M. F.; Amador, U.; Ruiz-Valero, C.; Bellitto, C. *J. Chem. Soc., Dalton Trans.* **1996**, 3015.
- Cho, J.; Lough, A. J.; Kim, J. C. *Inorg. Chim. Acta* **2003**, *342*, 305.
- Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R., *J. Chem. Soc., Dalton Trans.* **1989**, S1.
- Shin, J. W.; Yeo, S. M.; Min, K. S. *Inorg. Chem. Commun.* **2012**, *22*, 162.
- Kim, J. C.; Fettingner, J. C.; Kim, Y. I. *Inorg. Chim. Acta* **1999**, *286*, 67.
- Oshio, H. *Inorg. Chem.* **1993**, *32*, 4123.
- Choi, K.-Y.; Kim, J. C.; Jensen, W. P.; Suh, I.-L.; Choi, S.-S. *Acta Cryst.* **1996**, *C52*, 2166.
- Wickenden, A. E.; Krause, R. A. *Inorg. Chem.* **1965**, *4*, 404.
- Donlevy, T. M.; Gahan, L. R.; Hambley, T. W.; Hanson, G. R.; McMahon, K. L.; Stranger, R. *Inorg. Chem.* **1994**, *33*, 5131.
- Otwinowski, Z.; Minor, W. In *Methods in Enzymology, Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: London, 1997; Vol. 276, pp 307-326.
- Sheldrick, G. M. SHELXTL/PC V6.1, Bruker Analytical X-ray Systems, Madison, WI, 2001.