

Synthesis and Characterization of Oxa-azamacrocyclic Dinuclear Cu(II) Complex Containing Aqua Ligands

Jong Chul Byun,* Chung Hun Han, Duk Soo Kim, and Ki Min Park[†]

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

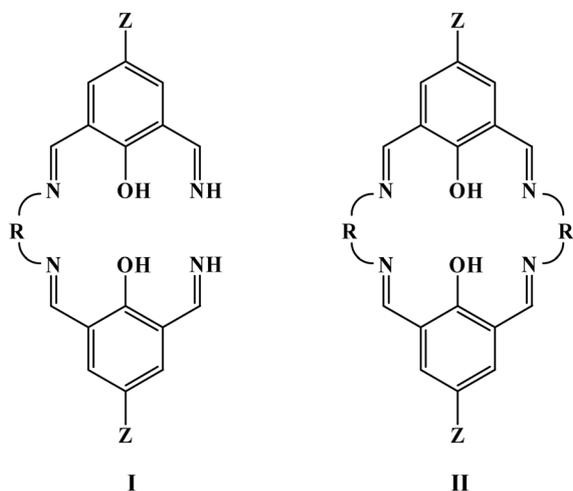
*E-mail: jchbyun@cheju.ac.kr

[†]Department of Chemistry, Research Institute of Natural Sciences, Gyeongsang National University, Jinju 660-701, Korea

Received August 16, 2005

Key Words : Macrocyclic ligand, Compartmental ligand, Dinuclear complex, Crystal structure

The rich chemistry of complexes of dicompartmental ligands binding identical metals and to a lesser extent different metals has been applied to the investigation of magnetic exchange interactions between the two metal ions, the stabilization of mixed-valent species, and the activation of small molecules.^{1,2} Particularly, significant examples (I and II) of this type are planar ligands with imine or amine donors and bridging phenolic oxygens, which are usually referred to as Robson-type ligands.³ The complexes formed from these macrocyclic ligands are also used as models for protein-metal binding sites in biological systems, as synthetic ionophores, as therapeutic reagents in chelate therapy for treatment of metal toxication, in catalysis and to investigate the mutual influence of two metal centers on their physicochemical properties.^{4,5}



The best way for their preparation is to carry out the condensation reaction of appropriate formyl and amine precursors in the presence of a templating agent. Nevertheless, the possibility to obtain these compounds by self-condensation of appropriate precursors has been successfully experienced in the past. They are identical to the compounds obtained by demetallation of the related Schiff bases complexes. Their cyclic nature was inferred especially by mass spectrometry and definitively demonstrated by single crystal structural determinations.^{6,7} So far many efforts have been devoted to the design of compartmental

ligands possessing two metal-binding sites with respect to the nature of donor atoms, the cavity size, and the steric requirement for coordination.^{8,9} The use of designed macrocyclic ligands is of great advantage for the purpose because dinuclear cores can be thermodynamically stabilized by macrocyclic effect.¹⁰

Our interest has been directed towards the study of the dinuclear metal oxa-azamacrocyclic complexes, in which the [2+2] symmetrical N₄O₂ compartmental macrocycle {H₂[22]-HMTADO; 5,5,11,17,17,23-hexamethyl-3,7,15,19-tetraazatricyclo[19,3,1,1^{9,13}]hexacos-1(25),2,7,9,11,13(26),14,19,21,23-decane-25,26-diol} by the reaction between 2,6-diformyl-*p*-cresol (DFPC) and 2,2-dimethyl-1,3-propanediamine with methyl groups on the lateral chains is involved. To our knowledge, work has never been carried out on the preparation and characterization of the dinuclear Cu(II) complex [Cu(II)₂-([22]-HMTADO)(L_a)] with auxiliary ligands (L_a). In the light of above discussion, the present work concerns the synthesis, physicochemical characterization and crystal structure of the dinuclear Cu(II) oxa-azamacrocyclic complex [Cu₂([22]-HMTADO)(H₂O)₄]-Cl₂·10H₂O.

Experimental Section

Measurements. Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurement of the complex was performed in water at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectrum was recorded with a Bruker FSS66 FT-IR spectrometer as KBr pellets. Electronic absorption spectrum was measured at 25 °C on a HP model 8453 UV-VIS Spectrophotometer. FAB-mass spectrum was 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 spectrum was calibrated by Alkali-CsI positive.

Synthesis of [Cu₂([22]-HMTADO)(H₂O)₄]-Cl₂·8H₂O. A methanolic solution (30 mL) of 2,6-diformyl-*p*-cresol (1.312 g, 8 mmol) was added to a suspension of the 2,2-dimethyl-1,3-propanediamine (0.824 g, 8 mmol) and the cupric chloride dihydrate (1.364 g, 8 mmol) in methanol (30 mL).

The mixture was refluxed for 20 min whereupon the solution turned immediately to dark green, and then the solvent was partially evaporated. The pale green precipitate obtained by addition of tetrahydrofuran (200 mL) filtered, washed with tetrahydrofuran and dried *in vacuo*. The products can be further purified by warm water. Yield: 92%. Anal. Calcd (Found) % for $C_{28}H_{58}N_4O_{14}Cl_2Cu_2$: C, 38.53 (38.51); H, 6.70 (6.38); N, 6.42 (6.46). λ_M (water): $218 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

X-ray crystallography of complex. Crystals of $[Cu_2([22]\text{-HMTADO})(H_2O)_4]Cl_2 \cdot 10H_2O$ suitable for X-ray diffraction study were obtained by slow evaporation of warm aqueous solution of the complex. The dark green crystal of complex 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. Cell constants and an orientation matrix were obtained by least-squares refinement of the data for 4935 reflections of the 13200 unique reflections measured, in the range $2.06^\circ \leq 2\theta \leq 28.29^\circ$ for complex. The data were corrected for Lorentz and polarization effects during data reduction. The structure was solved by the direct method,¹¹ and refined by full-matrix least-squares refinement with use of the SHELXS program of the SHELXTL package.¹² All non-hydrogens atoms of the copper(II) complex were refined on F^2 by the full matrix least-squares procedure using anisotropic displacement parameters. Hydrogen atoms were inserted in the calculated positions, assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached [$U_{iso} = 1.2U_{eq}$ (parent atom)] and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for complex is listed in Table 1.

Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC 256434). The data can be

obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Description of crystal structure. The ORTEP representation of the $[Cu_2([22]\text{-HMTADO})(H_2O)_4]Cl_2 \cdot 10H_2O$ complex is shown in Figure 1 together with the numbering scheme. The selected bond lengths and angles relevant to the copper coordination sphere are summarized in Table 2. The dinuclear Cu(II) complex consists of a $[Cu_2([22]\text{-HMTADO})(H_2O)_4]^{2+}$ cation, two chloride ions as counter ions and ten water molecules crystallizing as solvent, corresponding to the formula $[Cu_2([22]\text{-HMTADO})(H_2O)_4]Cl_2 \cdot 10H_2O$. In other words, the structure consists of two copper centers bridged by two endogenous phenolic oxygen atoms with two secondary imine nitrogen donors completing the CuN_2O_2 basal plane. Each of the metal centers achieves a pseudo-octahedral configuration through the axial coordination of water molecules, which are *trans* to each other. Therefore, complex has a centrosymmetric structure with center of inversion at the middle of Cu_2O_2 plane.

The two copper atoms are separated by $3.0482(4) \text{ \AA}$, which is comparative to the other dinuclear Cu(II) complexes,¹³ with a Cu-O(1)-Cu bridge angle of $102.32(8)^\circ$. The bond lengths of Cu-O are slightly longer than those of Cu-N in the macrocyclic ring, and the axial Cu-O (water) bond lengths are much longer than those of Cu-O and Cu-N in the macrocyclic plane; this is elongated owing to the Jahn-Teller effect.¹⁴ The bond angles of N(1)-Cu-O(2), N(2)-Cu-O(1), O(3W)-Cu-O(4W) and O(2)-Cu-O(4W) are $170.36(6)$,

Table 1. Crystal data and details of the structure determination for $[Cu_2([22]\text{-HMTADO})(H_2O)_4]Cl_2 \cdot 10H_2O$

Empirical formula	$C_{28}H_{58}Cl_2Cu_2N_4O_{16}$
Temperature, K	173(2)
Crystal system, Space group	Monoclinic, $C2/m$
a, \AA Unit cell dimensions	$a = 16.3781(6)$
b, \AA	$b = 25.3716(9)$
c, \AA	$c = 9.9589(3)$
Z	4
Density (calculated)	1.468 g/cm^3
Absorption coefficient	1.233 mm^{-1}
$F(000)$	1912
Theta range for data collection	2.06 to 28.29°
Reflections collected	13200
Independent reflections	4935 [$R(\text{int}) = 0.0393$]
Goodness-of-fit on F^2	1.094
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0336$, $wR_2 = 0.0803$
R indices (all data)	$R_1 = 0.0394$, $wR_2 = 0.0834$

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}, w = 1/[\sigma^2(F_o^2) + (0.00282P)^2 + 7.1613P], P = (F_o^2 + 2F_c^2)/3$$

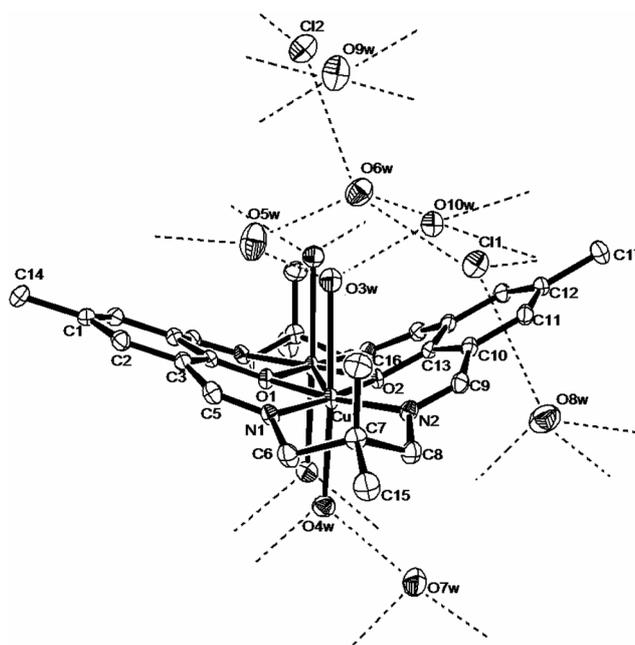


Figure 1. ORTEP drawing with atom-labelling scheme for $[Cu_2([22]\text{-HMTADO})(H_2O)_4]Cl_2 \cdot 10H_2O$.

Table 2. Selected bond lengths (Å) and angles (°) for [Cu₂([22]-HMTADO)(OH₂)₄]Cl₂·10H₂O

Cu(1)-N(1)	1.9490(15)	Cu(1)-O(3W)	2.5798(14)
Cu(1)-N(2)	1.9503(15)	Cu(1)-Cu(1) [#]	3.0482(4)
Cu(1)-O(1)	1.9567(11)	O(1)-Cu(1) [#]	1.9567(11)
Cu(1)-O(2)	1.9638(11)	O(2)-Cu(1) [#]	1.9638(11)
Cu(1)-O(4W)	2.4792(14)		
N(1)-Cu(1)-N(2)	97.75(7)	O(1)-Cu(1)-O(3W)	84.36(6)
N(1)-Cu(1)-O(1)	92.61(6)	O(2)-Cu(1)-O(3W)	86.22(6)
N(2)-Cu(1)-O(1)	169.15(6)	O(4W)-Cu(1)-O(3W)	172.68(5)
N(1)-Cu(1)-O(2)	170.36(6)	N(1)-Cu(1)-Cu(1) [#]	131.37(4)
N(2)-Cu(1)-O(2)	91.79(6)	N(2)-Cu(1)-Cu(1) [#]	130.87(4)
O(1)-Cu(1)-O(2)	77.79(6)	O(1)-Cu(1)-Cu(1) [#]	38.84(4)
N(1)-Cu(1)-O(4W)	90.40(6)	O(2)-Cu(1)-Cu(1) [#]	39.10(4)
N(2)-Cu(1)-O(4W)	94.49(6)	O(4W)-Cu(1)-Cu(1) [#]	86.66(3)
O(1)-Cu(1)-O(4W)	88.63(6)	O(3W)-Cu(1)-Cu(1) [#]	86.55(3)
O(2)-Cu(1)-O(4W)	90.25(6)	Cu(1)-O(1)-Cu(1) [#]	102.32(8)
N(1)-Cu(1)-O(3W)	92.03(6)	Cu(1) [#] -O(2)-Cu(1)	101.81(7)
N(2)-Cu(1)-O(3W)	92.03(6)		

Symmetry transformations used to generate equivalent atoms: [#]*x*, -*y*+1, *z*.

169.15(6), 172.68(5) and 90.25(6)°, respectively. These bond lengths and bond angles are in good agreement with those in related [CuPbL_{m1}(BzO)(dmf)]ClO₄ (L_{m1} = heterodinucleating macrocycle, BzO⁻ = C₆H₅COO⁻, dmf = *N,N*-dimethylformamide).¹⁵

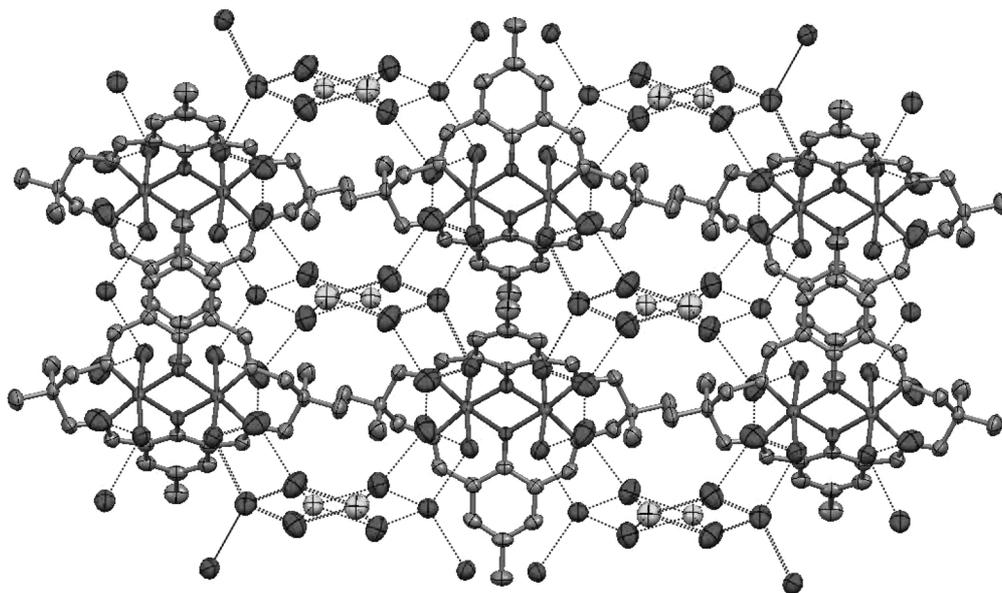
As shown in Figure 2 and Table 3, there are four types of intermolecular hydrogen bonds. The coordinated water forms hydrogen bonds of the type O-H...O with the coordinated water (O3W-H3C...O3W; 2.738 Å, etc.) and lattice water (O3W-H3A...O5W; 2.773 Å, etc.). The structure of the compound is further consolidated by another hydrogen bond of the type O-H...Cl between the counter anion and lattice water (O6W-H6C...Cl2; 3.261 Å, etc.). These interactions

Table 3. Hydrogen bonding interactions in Cu₂([22]-HMTADO)(OH₂)₄]Cl₂·10H₂O

D-H...A	d(D-H), Å	d(H...A), Å	<DHA, °	d(D...A), Å
between coordinated waters				
O3W-H3C...O3W ^a	0.897	1.876	160.45	2.738
O4W-H2C...O4W ^a	0.91	1.852	174.75	2.759
coordinated water - lattice water				
O3W-H3A...O5W	0.789	2.001	165.9	2.773
O3W-H3B...O10W	0.737	2.141	157.69	2.836
O4W-H4A...O7W	0.717	2.023	162.33	2.715
O4W-H4B...O9W ^b	0.788	2.141	161.92	2.9
O5W-H5C...O3W	0.819	1.982	162.09	2.773
chloride ion - lattice water				
O6W-H6C...Cl2	0.784	2.476	179.69	3.261
O6W-H6D...Cl1	0.845	2.423	167.38	3.252
O8W-H8C...Cl1	0.825	2.391	170.17	3.207
O8W-H8D...Cl2 ^c	0.91	2.311	165.92	3.202
between lattice waters				
O5W-H5B...O6W	0.869	2.094	155.5	2.907
O7W-H7A...O8W ^d	0.965	1.909	159.73	2.834
O7W-H7B...O5W ^c	0.735	1.983	162.69	2.693
O9W-H9B...O8W ^e	0.808	2.03	172.6	2.833
O10W-H10A...O6W	0.783	2.101	166.62	2.869

Symmetry transformations used to generate equivalent atoms: ^a*x*, -*y*+1, *z*; ^b-*x*+1/2, -*y*+1/2, -*z*+1; ^c*x*, *y*, *z*+1; ^d-*x*+1/2, -*y*+1/2, -*z*+2; ^e*x*, *y*, *z*-1.

result in a formation of polymer in the packing of the complex (Figure 2). Namely, the ordered chloride anion and lattice water participate in mediating between the [Cu₂([22]-HMTADO)(H₂O)₄]²⁺ units to form the polymer through hydrogen bonds. Hydrogen bonding interactions through coordinated waters, anions and lattice water are crucial for the formation of three-dimensional supramolecular network.

**Figure 2.** The molecular packing diagram of [Cu₂([22]-HMTADO)(OH₂)₄]Cl₂·10H₂O along with the hydrogen bonds, indicated by broken lines that contribute to stabilize the lattice.

It is generally understood that the directionality and strength of interactions are essential to assemble building blocks in polymeric chemistry, and usually a hydrogen bond is the interaction of choice.¹⁶⁻¹⁸ These values are comparable with those reported for the $[\text{Cu}_2\text{L}_{m2}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (L_{m2} = phenoxo-bridged macrocyclic ligand).¹⁹

As shown in Figure 2, another interesting feature of the complex resides in the formation of a three-dimensional layered structure in which the stacking pattern is arranged ABABAB... type. The dinuclear oxa-azamacrocyclic ligand in the complex exhibits a slight boat-like conformation and each layer unit (A or B) is consisted of five boat-like monomers due to the complex cation. There are water molecules in the complex, which can act as donors and acceptors for hydrogen bonds in addition to the chloride ions. The two chloride counter ions are bound to the lattice waters through hydrogen bonds and located at the vacancy between A and B layers. These hydrogen bonds in the inter-layers (A and B) consolidate the structure of the present complex. In this lattice water connection it is interesting to compare the previous values reported for $[\text{Cu}_2\text{L}_{m3}(\text{N}_3)_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (L_{m3} = hexaaza macrocycle)²⁰ and $[\text{Cu}_2(\text{bpp})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ { bpp = 3,5-bis(2-pyridyl)pyrazole}.²¹

General properties. The molar conductivity measurement of the complex exhibits $218 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, typical of 2 : 1 electrolytic nature in water solvent. The electronic spectrum of the complex involves an asymmetric broad peak occurring at $17,120 \text{ cm}^{-1}$ with some evidence for a possible low-energy shoulder at approximately $15,240 \text{ cm}^{-1}$, consistent with its six-coordinated distorted octahedral stereochemistry as found in its X-ray crystal structure, and similar to those of the comparable structures in $[\text{Cu}(\text{dpyam})_2(\text{SCN})_2]$ (dpyam = di-2-pyridylamine).²² The complex shows an intense band near $26,300 \text{ cm}^{-1}$ which is assigned to π - π^* transition associated with the azomethine linkage.²³ The binuclear Cu(II) complex reveals another intense band at $23,500 \text{ cm}^{-1}$, which may be assigned to ligand to metal charge-transfer transition associated with the macrocyclic nitrogen donors.²⁴

The suggested one-electron ground state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$ for general complexes. For complex, the transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ for the low-energy peak, arising from the tetragonal splitting of the formally octahedral e_g orbitals and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ for the high-energy peak, with the position of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition being uncertain.²⁵ Therefore, copper(II) complexes in tetragonal symmetry are expected to have three absorption bands in d - d transitions, the spectrum of complex have one major component. Such band is resolved by Gaussian Analysis²⁶ and in the visible region the two peak positions calculated at $15,510$ and $17,560 \text{ cm}^{-1}$ can be assigned to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$, respectively. The ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition band has expected at much lower energy.²⁷

Strong evidence that aldehyde groups had been completely converted into Schiff base residues was provided by the disappearance of the aldehydic C=O stretching band at 1680 cm^{-1} and the appearance of a strong band at $1635 \pm 5 \text{ cm}^{-1}$

assigned to C=N stretching band.²⁸ Sharp C=N stretching vibration bands corresponding to four enamine groups of macrocyclic framework are observed at 1635 - 1640 cm^{-1} . Wide bands resulting from O-H stretching vibration of the coordinated water molecules and lattice waters emerge at 3412 cm^{-1} and 3549 cm^{-1} , respectively.²⁹ In the FAB mass spectrum of complex there is a peaks at m/z 585.7 and 522.5 corresponding to the $[\text{Cu}_2([\text{22}]\text{-HMTADO})]^+$ and $[\text{Cu}([\text{22}]\text{-HMTADO})]^+$, respectively. These major peaks are associated with peaks of mass one or two greater or less, which are attributed to protonated/deprotonated forms.³⁰

References

- Fraser, C.; Ostrander, R.; White, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 324.
- Guerrieo, P.; Tamburini, S.; Vigato, P. A. *Coord. Chem. Rev.* **1995**, *139*, 17.
- Atkins, A. J.; Black, D.; Blake, A. J.; Marrin-Becerra, A.; Parsons, S. *Chem. Commun.* **1996**, 457.
- Benicni, A.; Jeania, Y.; Julve, M.; Philoche-Levisalles, M. *Inorg. Chem.* **1990**, *29*, 962.
- Alexander, V. *Chem. Rev.* **1995**, *95*, 273.
- D'Alpaos, M.; Tamburini, S.; Tomasin, P.; Traldi, P. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1909.
- Brianese, N.; Casellato, U.; Tamburini, S.; Tomasin, P.; Vigato, P. A. *Inorg. Chim. Acta* **1999**, *293*, 178.
- Nishio, J.; Okawa, H.; Ohtsuka, S.; Tomono, M. *Inorg. Chim. Acta* **1994**, *218*, 27.
- McCullum, D. G.; Hall, L.; White, C.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 924.
- Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, 1979; p 145.
- Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
- Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1997.
- Nanda, K. K.; Das, R.; Venkatsubramanian, K.; Paul, P.; Nag, K. *Inorg. Chem.* **1994**, *33*, 1188.
- Hori, A.; Yonemura, M.; Ohba, M.; Okawa, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 495.
- Yonemura, M.; Matsura, Y.; Furutachi, H.; Ohba, M.; Okawa, H. *Inorg. Chem.* **1997**, *36*, 2711.
- Kim, J. C.; Lough, A. J. *Bull. Korean Chem. Soc.* **1999**, *20*, 1241.
- Braga, D.; Grepioni, F. *Acc. Chem. Res.* **2000**, *33*, 601.
- Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.
- Huang, W.; Gou, S.; Hu, D.; Meng, Q. *J. Mol. Struct.* **2001**, *561*, 121.
- Li, S. A.; Li, D. F.; Duan, C. Y.; Tang, W. X. *Inorg. Chem. Comm.* **2001**, *4*, 651.
- Du, M.; Chen, S. T.; Bu, X. H.; Ribas, J. J. *J. Mol. Struct.* **2005**, *737*, 17.
- Youngme, S.; Chaichit, N. *Polyhedron* **2001**, *21*, 247.
- Wada, H.; Aono, T.; Ohba, M.; Matsumoto, N. *Inorg. Chim. Acta* **1996**, *246*, 13.
- (a) Kim, J. C.; Fettinger, J. C.; Kim, Y. I. *Inorg. Chim. Acta* **1999**, *286*, 67. (b) Sharaby, C. M. *Spectrochim. Acta Part A* **2005**, in press.
- Youngme, S.; Chaichit, N.; Pakawatchai, C.; Booncoon, S. *Polyhedron* **2002**, *21*, 1279.
- Byun, J. C.; Han, C. H.; Park, Y. C. *Bull. Korean Chem. Soc.* **2005**, *26*, 1044.
- Ahmed, I. *Spectrochim. Acta Part A* **2005**, in press.
- Zhou, H.; Peng, Z. H.; Pan, Z. Q.; Zhang, Z.; Chi, R. A. *J. Mol. Struct.* **2005**, *743*, 61.
- Kumar, D. S.; Alexander, V. *Inorg. Chim. Acta* **1995**, *238*, 63.
- Fujino, T.; Hoshino, Y.; Igarashi, S.; Masuda, Y.; Yukawa, Y. *Inorg. Chim. Acta* **2004**, *357*, 11.