J. of Basic Sciences, Cheju Nat'l Univ.
19(1), 79~87, 2006

기초과학연구 제주대학교
19(1), 79~87, 2006

Lanthanide (Gd^{3+} and Dy^{3+}) Complexes with Tetraazadioxa Macrocyclic Ligand : Template Synthesis and Characterization Studies

Chung Hun Han, Sung Bin Han, Chang Hee Kang, Sun Joo Lee, Nam Ho Lee and Jong Chul Byun

Department of Chemistry, College of Natural Sciences, Cheju National University

Abstract

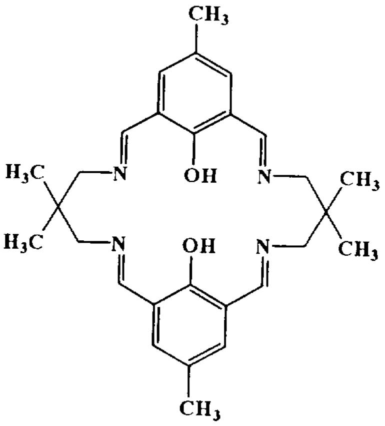
The lanthanide ions were found to act as templates for the cyclic [2+2] condensation of 2,6-diformyl-*p*-cresol with 2-dimethyl-1,3-propandiamine to yield 22-membered hexadentate Schiff base macrocyclic complexes, $[Ln(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot xH_2O$ (Ln = $Gd^{3+}$and Dy^{3+} ; $H_2[22]$-HMTADO;5,5,11,17,17,23-hexamethyl-3,7,15,19-tetraazatricyclo$[19,3,1,1^{9,13}]$hexacosa-1(25),2,7,9,11, 13(26),14,19,21,23-decane-25,26-diol}), with an N_4O_2 set of donor atoms. The complexes were charaterized by elemental analysis, molar conductance, and spectral data (UV/Vis, FT-IR, FAB-MS). The macrocyclic entity changed slowly up to 360℃, and then those complexes have been changed to Ln_2O_3.

Key words : lanthanide complex, compartmetal macrocyclic ligand

Ⅰ. Introduction

The macrocyclic and macroacyclic lanthanide complexes are currently attracting considerable attention because of their possibility of using as supramolecular devices, suitable bioinorganic probes for the active sites in metallo-biomolecules, as contrast agents in magnetic resonance imaging, potential radioimmuno-pharmaceutical for monoclonal antibody technology and sensitizers for photodynamic therapy, as synthetic nucleases for *in vivo* application [1-17]. The Schiff base macrocyclic complexes of rare earth elements obtained by us [18-20] have found to be very effective catalysts for hydrolytic cleavage or transesterification of RNA phosphate diester backbone [21,22]. Many of the synthetic routes to Schiff base macrocycles involve the use of the metal ion template to orient the reacting groups of the substrates in the desired conformation for optimum ring closure [23-26]. The 4*f* cations have found to be very effective as template agents because they have little or no stereochemical requirements and can be accommodated by the particular stereochemical constrains enforced by the template process.

We now report the template synthesis and characterization of the lanthanide(Gd^{3+} and Dy^{3+}) complexes containing 22-membered tetraazadioxa macrocyclic Schiff base ligand H_2[22]-HMTADO, where H_2[22]-HMTADO is 5,5, 11,17,17,23-hexamethyl-3,7,15,19-tetraazatricyclo$[19,3,1,1^{9,13}]$-hexacosa-1(25),2,7,9,11,13(26),14,19,21,23-decane-25,26-diol, formed in the metal-promoted cyclocondensation reaction of 2,6-diformyl-*p*-cresol with 2-dimethyl-1, 3-propandiamine.



H_2[22]-HMTADO

Ⅱ. Experimental

1. Chemicals and Physical Measurements

All chemicals were commercial analytical reagents and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods. Nanopure quality water was used throughout this work. Microanalyses of C, H, and N was carried out using LECO CHN-900 analyzer. Conductance measurement of the complex was performed at 25±1℃ using an ORION 162 conductivity temperature meter. IR spectrum was recorded with a Bruker FSS66 FT-IR spectrometer in the range 4000-370 cm^{-1} using KBr pellets. Electronic absorption spectrum was measured at 25℃ on a UV-3150 UV-VIS-NIR Spectrophotometer (SHIMADZU). 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. TGA was carried out on a TGA 2050 thermal analyzer. The thermogravimetric curves of complexes were recorded in 30~1000℃ range under nitrogen atmosphere. The heating rate was 10℃/min.

2. Preparations of lanthanide(III) complexes

The synthesis of 2,6-diformyl-*p*-cresol was prepared according to the literature methods previously reported [27, 28].

1) $[Gd(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot 2H_2O$.

A solution of 2,6-diformyl-*p*-cresol (0.328 g) in the boiling acetonitrile (30 mL) was dropwise added to the yellow solution formed by mixing 2,2-dimethyl-1,3-propandiamine (0.206 g) with a solution of $Gd(NO_3)_3 \cdot 6H_2O$ (0.451 g) in acetonitrile (50 mL). The resulting yellow mixture was stirred at the reflux temperature for 3 h to give an yellow microcrystalline powder. It was collected by suction filtration, thoroughly washed with acetonitrile and dried *in vacuo*. Yield 88%. Anal. Calc. (Found) % for $Gd(C_{28}H_{36}N_4O_2)(NO_3)_3(H_2O)_2$: C, 40.14 (39.65) ; H, 4.57 (4.02); N, 11.70 (11.81). Solubility : hot methanol, DMSO, DMF. UV-Vis (CH_3OH) [λ_{max} (ε, $M^{-1}cm^{-1}$) : 398 (17,910). Λ_M (methanol) : 256 ohm^{-1} cm^{2}mol^{-1}.

2) $[Dy(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot H_2O$.

A solution of 2,6-diformyl-*p*-cresol (0.328 g) in the boiling acetonitrile (30 mL) was dropwise added to the yellow solution formed by mixing 2,2-dimethyl-1,3-propandiamine (0.206 g) with a solution of $Dy(NO_3)_3 \cdot 5H_2O$ (0.439 g) in acetonitrile (50 mL). The resulting yellow mixture was stirred at the reflux temperature for 3 h to give an yellow microcrystalline powder. It was collected by suction filtration, thoroughly washed with acetonitrile and dried *in vacuo*. Yield 75%. Anal. Calc. (Found) % for $Dy(C_{28}H_{36}N_4O_2)(NO_3)_3(H_2O)$: C, 40.66 (41.82); H, 4.63 (4.08); N, 11.85 (11.99). Solubility : hot methanol, DMSO, DMF. UV-Vis (DMF) [λ_{max} (ε, $M^{-1}cm^{-1}$) : 398 (16,820). Λ_M (methanol) : 326 ohm^{-1} cm^{2}mol^{-1}.

Ⅲ. Results

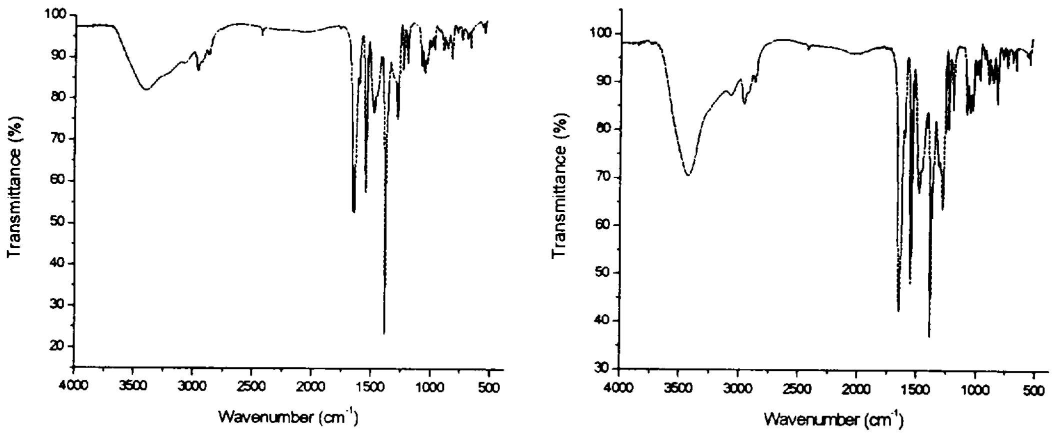
1. IR spectra of the lanthanide(III) complexes

IR spectra of the lanthanide(III) complexes were presented Figure 1. The strong and sharp absorption bands occurring at 1645 cm^{-1} in the IR spectra of the complexes are attributed to υ(C=N) of the coordinated [22]-HMTADO ligand [29,30], and the absence of any carbonyl bands associated with the diformyl-phenol starting materials or nonmarcrocyclic intermediates. The IR spectra displayed C-H stretching vibrations from 3000 to 2800 cm^{-1}. The present complexes exhibited three C-H deformation bands at 1478, 1390, and 1317 cm^{-1} regions and two out-of-plan vibration bands at 825 and 781 cm^{-1} regions. The absorption bands occurring in the IR spectra of the complexes in the 3430 cm^{-1} region may probably be due to the υ(OH) vibration of the lattice water.

The absorption bands occurring in the IR spectra of the complexes in the 1460, 1284 and 1035 cm^{-1} regions are assignable to the υ(N=O) (υ_1), υ_a(NO$_2$) (υ_5) and υ_s(NO$_2$) (υ_2) vibrations, respectively, of the chelating bidentate nitrate ion [30-32]. The absorption band observed at 815 cm^{-1} in the complexes is also characteristic of chelating bidentate nitrate [31]. The larger separation of 176-177 cm^{-1} between the two higher frequency bands (υ_1 and υ_5) indicates strong interaction of the oxygen atoms of the nitrate with the lanthanide ions and is typical of bidentate coordination [32,33]. The absorption band at 1385 cm^{-1} is characteristic of ionic nitrate present in the outer-coordination sphere [31].

2. FAB mass spectra

The FAB mass spectra of the lanthanide(III) complexes were shown in Figure 2 and 3. The FAB mass spectra of two complexes contain peaks corresponding to the molecular ion [Ln(H$_2$[22]-HMTADO)(NO$_3$)]$^+$ for Ln = Gd^{3+} (m/z 677.7) and Dy^{3+} (m/z 683.8). The molecular ion loses the exocyclic nitrate ligand resulting in the formation of the fragment [Ln(H$_2$[22]-HMTADO)]$^+$ for Ln = Gd^{3+} (m/z 615.7) and Dy^{3+} (m/z 621.8). These species are well observed in the FAB mass spectra. Removal of nitrate ion from the molecular ion is observed with a mass loss of 63 as HNO$_3$. For each metal containing species there is a set of peaks due to the different isotopes of the metal. In the FAB mass spectra of all the complexes there is a peak at m/z 460.8 corresponding to the



(a) (b)

Figure 1. FT-IR spectra of [Ln(H$_2$[22]-HMTADO)O$_2$NO](NO$_3$)$_2$ · xH$_2$O {Ln = (a) Gd and (b) Dy}.

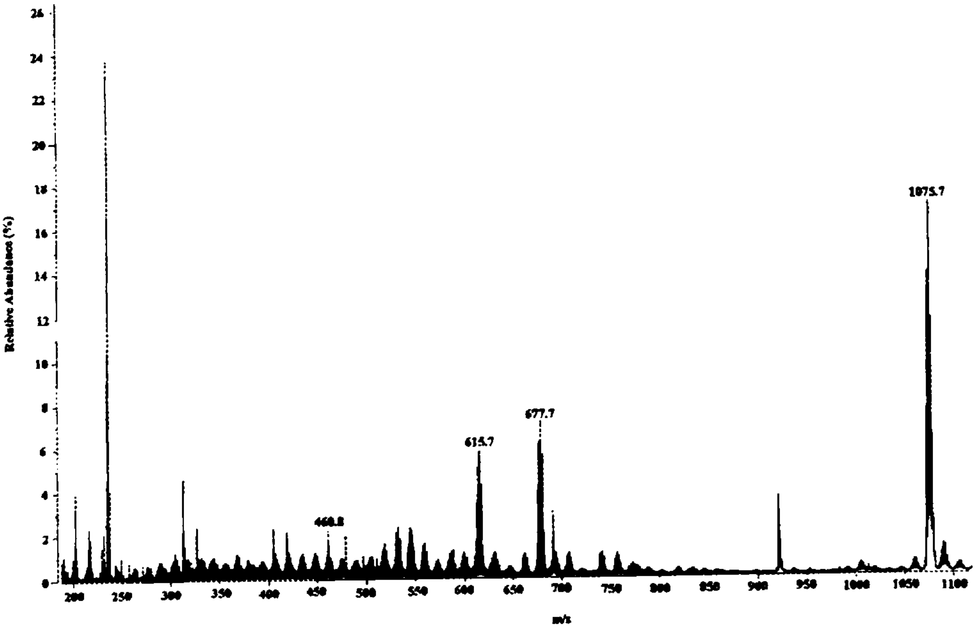


Figure 2. FAB-mass spectrum of $[Gd(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot 2H_2O$.

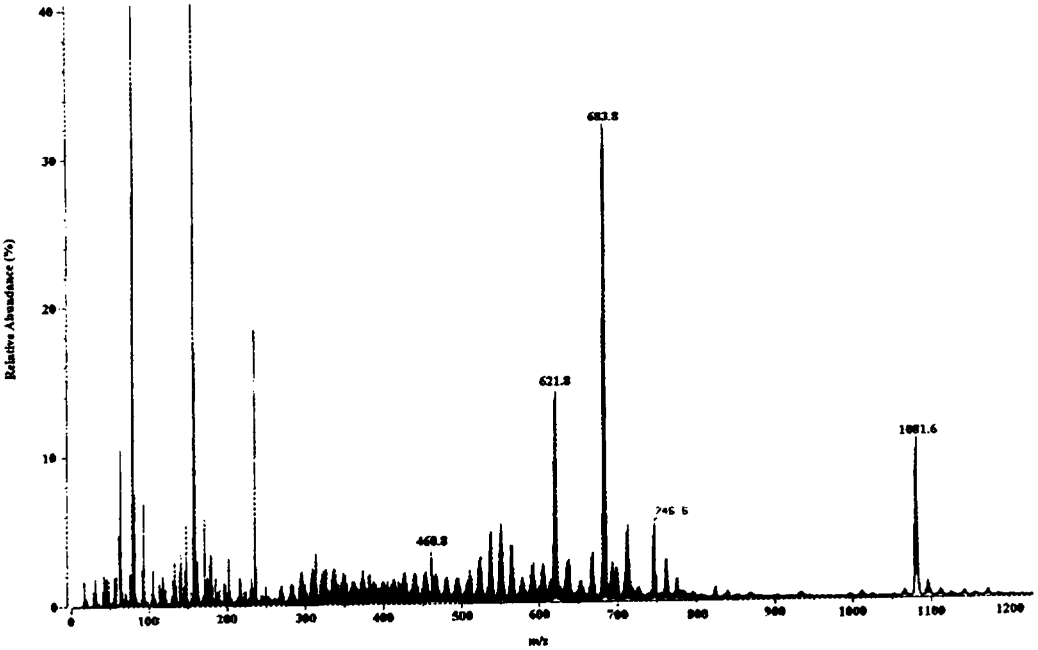


Figure 3. FAB-mass spectrum of $[Dy(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot H_2O$.

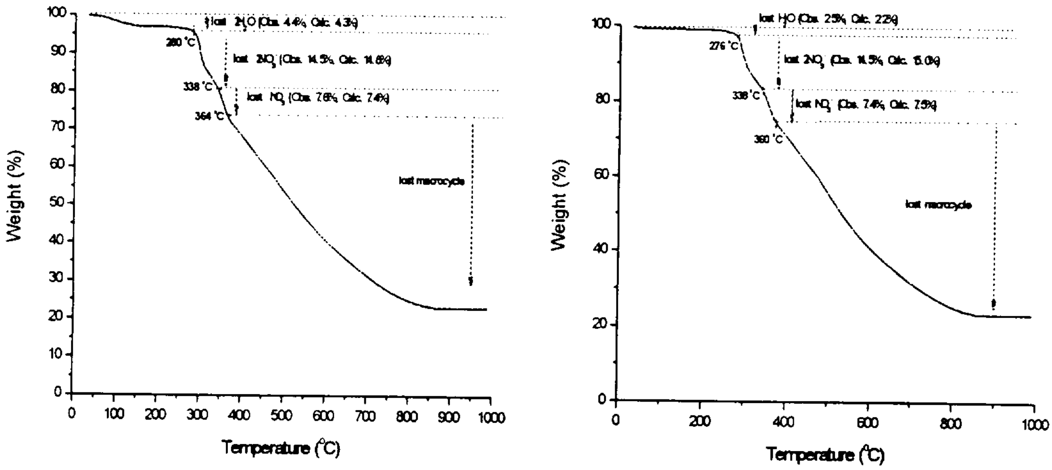
species $[H_2[22]\text{-HMTADO}]^+$. This indicates that the species $[Ln(H_2[22]\text{-HMTADO})]^+$ undergoes demetallation to give the tetraazadioxa macrocycle $H_2[22]$-HMTADO under FAB conditions. Peaks corresponding to sandwich complexes of the type $[Ln(H_2[22]\text{-HMTADO})_2]^+$ for Ln = Gd^{3+} (m/z 1075.7) and Dy^{3+} (m/z 1081.6) are observed in FAB mass spectra. These sandwich complexes might gave been formed during the FAB fragmentation process [30].

3. Thermal stability of lanthanide complexes

Thermogravimetry analysis (TGA) have been carried out simultaneously for the lanthanide complexes (Figure 4). Thermo-gravimetric details were given in Table 1. It was found out from the results that the prepared macrocycle compounds have relatively high thermal stability. The lattice water molecules were lost at ~280 ℃ ranges. The two nitrate ions were lost at 280~338 ℃ range. The coordinated nitrate ion was lost at 338~360 ℃ range. The macrocyclic entity changed slowly up to 360 ℃, and then those complexes have been changed to Ln_2O_3.

Table 1. TGA data of Pr^{3+} and Sm^{3+} complexes

Complexes	Temperature range (℃)	Moieties lost
$[Gd(H_2[22]\text{-HMTADO})O_2NO]\text{-}(NO_3)_2 \cdot 2H_2O$	~280	$2H_2O$
	280~338	$2NO_3^-$
	338~360	NO_3^-
	360~	macrocycle
$[Dy(H_2[22]\text{-HMTADO})O_2NO]\text{-}(NO_3)_2 \cdot H_2O$	~276	$2H_2O$
	276~338	$2NO_3^-$
	338~360	NO_3^-
	360~	macrocycle



(a) (b)

Figure 4. TGA curves of $[Ln(H_2[22]\text{-HMTADO})O_2NO](NO_3)_2 \cdot 2H_2O$ {Ln = (a) Gd and (b) Dy}.

IV. Discussion

The formation of lanthanide(III) complexes of H_2[22]-HMTADO demonstrates the template potential of these metal ions in the assembly of oxaaza macrocycles. As the size of the lanthanide(III) cations decreases along the lanthanide series the metal ions adopt different geometries in the complexes. Thus the template potential of the lanthanide(III) cations in the assembly of H_2[22]-HMTADO is due to the adaptability of the macrocycle to the geometrical requirements of the metal ions. The electronic and steric requirements of the central metal ions appear to be fully satisfied by coordination of the four nitrogen and two oxygen donors of the macrocycle and to the oxygen donors of a bidentate chelating nitrate ion. The coordination of the nitrate ion in each complex illustrates the influence of oxygen donor ligands to stabilize the lanthanide(III) cations in the macrocyclic framework. The remarkable ability of this macrocycle to coordinate with all the lanthanide(III) cations despite the large differences in their ionic radii is attributed to the flexibility of the macrocycle to fold according to the steric demands of the metal ions and the exocyclic ligands. The yield of the complexes of H_2[22]-HMTADO increases with decreasing ionic radii of the metal ions. In the present case the increase in the yield of the complexes along the lanthanide series is attributed to the better match between the size of the heavier lanthanide(III) cations and the macrocyclic cavity.

The two OH protons of H_2[22]-HMTADO remain intact in the complexes. Thus the ligand acts as a neutral species even though it has two ionizable protons. Such a behavior is also observed in the case of the lanthanide (III) complexes of the [2+2] symmetric macrocycles obtained by the Schiff base condensation of 2,6-diformyl-4-chlorophenol with diethylenetriamine, 1,5-diamino-3-thiapentane [34,35] or N-dodecyldiethylenetriamine [36] by the metal template method or by the reaction of the respective preformed macrocycle with the hydrated lanthanide(III) nitrate.

Reference

[1] Y. Bretonnière, R. Wietzke, C. Lebrun, M. Mazzanti and J. Pècaut, *Inorg. Chem* 39 (2000), 3499.

[2] D. Parker, *Coord. Chem. Rev.* 205 (2000) 109.

[3] T. Gunnlaugsson, D.A. Mac Dónaill and D. Parker, *J. Am. Chem. Soc.* 123 (2001) 12866.

[4] L. Thunus and R. Lejeune, *Coord. Chem. Rev.* 184 (1999) 125.

[5] K. Wang, R. Li, Y. Cheng, and B. Zhu, *Coord. Chem. Rev.* 190-192 (1999) 297.

[6] M.K. Moi and C.F. Meares, *J. Am. Chem. Soc.* 110 (1988) 6224.

[7] C.D. Hall, J.H. Tucker, A. Sheridan, Y.F. Chu, and D.J. Williams, *J. Chem. Soc., Dalton Trans.* (1992) 3133.

[8] M. Botta, *Eur. J. Inorg. Chem.* (2000) 399.

[9] S. Rigault and C. Piguet, *J. Am. Chem. Soc.* 122 (2000) 9304.

[10] M. Woods, S. Aime, M. Botta, J.A.K. Howard, J.M. Moloney, M. Navet, D. Parker, M. Port, and O. Rousseaux, *J. Am. Chem. Soc.* 122 (2000) 9781.

[11] L. Xu, S. Rettig, and Ch. Orvig, *Inorg. Chem.* 40 (2001) 3734.

[12] F. Alhaique, I. Bertini, M. Fragai, M. Carafa, C. Luchinat, G. Parigi, Inorg. Chim. Acta 331 (2002) 151.

[13] S. Aime, L. Frullano, and S.G. Crich, *Angew. Chem.*, Int. Ed. 41 (2002) 1017.

[14] M.K. Thompson, M. Vuchokv, and I.A. Kahwa, *Inorg. Chem.* 40 (2001) 4332.

[15] S. Arndt, T.P. Spaniol, and J. Okuda, *Chem. Commun.* (2002) 896.

[16] R. Häner and J. Hall, *Antisense Nucleic Acid Drug Dev.* 7 (1997) 423.

[17] S.W.A. Bligh, N. Choi, E.G. Evagorou, M. McPartlin, and K.N. White, *J. Chem. Soc., Dalton Trans.* (2001) 3169.

[18] W. Radecka-Paryzek, *Inorg. Chim. Acta* 45 (1980) L147.

[19] W. Radecka-Paryzek, *Inorg. Chim. Acta* 54 (1981) L251.

[20] W. Radecka-Paryzek, *Inorg. Chim. Acta* 109 (1985) L21.

[21] J.R. Morrow, L.A. Buttrey, V.M. Shelton, K.A. Berback, *J. Am. Chem. Soc.* 114 (1992) 1903.

[22] N. Hayashi, N. Takeda, T. Shiiba, M. Yashiro, K. Watanabe, and M. Komiyama, *Inorg. Chem.* 32 (1993) 5889.

[23] N.V. Gerbeleu, V.B. Arion, and J. Burges, *Template Synthesis of Macrocyclic Compounds*, Wiley-VCH, Weinheim, 1999.

[24] B. Dietrich, P. Viout, and J.-M. Lehn, *Macrocyclic Chemistry*, VCH Verlagsgesell-schaft, Weinheim, 1993.

[25] E.C. Constable, *Metals and Ligand Reactivity*, VCH Verlagsgesellschaft, Weinheim, 1996.

[26] J.R. Fredericks, A.D. Hamilton, in: A.D. Hamilton (Ed.), *Supramolecular Control of Structure and Reactivity*, Wiley, Chichester, 1996 (Chapter 1).

[27] T. Shozo, *Bull. Chem. Soc. Jpn.* 57 (1984), 2683.

[28] J.C. Byun, Y.C. Park, and C.H. Han, *J. Kor. Chem. Soc.* 43/3 (1999), 267.

[29] L.A. Kahwa, J. Selbin, T.C.Y. Hsieh and R. A. Laine, *Inorg. Chim. Acta* 118 (1986), 179.

[30] D. Suresh Kumar and V. Alexander, *Inorg. Chim. Acta* 238 (1995), 63.

[31] P. Guerriero, U. Casellato, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta* 129 (1987), 127.

[32] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination*

Compounds. 3rd edn., Wiley, New York, 1997.

[33] W. Radecka-Paryzek, *Inorg. Chim. Acta* 109 (1985), L21.

[34] P. Guerriero, U. Casellato, S. Tamburini, P.A. Vigato and R. Graziani, *Inorg. Chim. Acta*, 129 (1987) 127.

[35] J.-C.G. Bunzli, E. Moret, U. Casellato, P. Guerriero and P.A. Vigato, *Inorg. Chim. Acta*, 150 (1988) 133.

[36] E. Bullita, P. Guerriero, S. Tamburini and P.A. Vigato, *J. Less Common Met.*, 153 (1989) 211.