

Electronic Spectroscopy and Ligand Field Analysis of *cis*-[Cr(*cycb*)Cl₂]Cl

Jong-Ha Choi*, In-Gyung Oh, Subodh Kumar and Keon Sang Ryoo
Department of Chemistry, Andong National University, Andong 760-749, Korea

The sharp-line absorption spectrum of microcrystalline samples of *cis*-[Cr(*cycb*)Cl₂]Cl (*cycb* = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) has been measured between 13000 and 16000 cm⁻¹ at temperatures down to 5K. The 77K emission and excitation spectra, and 298 K infrared and visible absorption spectra have also been measured. The nine electronic bands due to spin-allowed and spin-forbidden transitions were assigned. Using the observed transitions, a ligand field analysis has been performed to probe the ligand field properties of coordinated atoms in the title chromium(III) complex. The zero-phonon line in the sharp-line absorption spectrum splits into two components by 240 cm⁻¹, and the large ²E_g splitting can be reproduced by the modern ligand field theory. It is confirmed that nitrogen atoms of the macrocyclic *cycb* ligand have a strong σ-donor character, but chloride ligand has weak σ- and π-donor properties toward chromium(III) ion.

key words: Chromium(III); Electronic transitions; AOM parameters, Ligand field properties

INTRODUCTION

It has been recognized that the narrow bands due to spin-forbidden electronic transitions may be useful in determining the metal-ligand bonding properties as well as the molecular geometry. In particular, the splittings of sharp-line electronic transitions are very sensitive to the exact bond angles around the metal. Thus, it is possible to obtain structural information from the electronic spectra without the benefit of X-ray structure determination [1, 2]. In the past two decades, a considerable amount of data concerning the ligand field analysis and the highly resolved optical spectra of chromium(III) complexes have been accumulated [3-8]. The chromium(III)-doped crystals are promising materials for a tunable solid state laser in the near-IR spectral region [9]. As a prerequisite for these applications, a detailed study of the spectroscopic and ligand field properties is needed. The synthesis, kinetics and absorption spectral data of the *cis*-[Cr(*cycb*)Cl₂]Cl system have been reported [10]. However, the vibrational and electronic energy levels based on the emission and sharp-line electronic spectroscopy of this complex have not been published yet.

In this work, the emission, electronic absorption and infrared spectra of *cis*-[Cr(*cyc b*)Cl₂]Cl were measured. The pure electronic origins due to spin-allowed and spin-forbidden transitions were assigned by analyzing the visible and sharp-line absorption spectra. Using the observed electronic transitions, a ligand field analysis has been performed to determine the detailed bonding properties for the coordinated chloride and nitrogen atoms toward chromium(III) ion. The second

objective of this research is to create a spectroscopic basis for the development of a new efficient tunable solid-state lasers.

MATERIALS AND METHODS

The synthetic methods of *cis*-[Cr(*cycb*)Cl₂]Cl·H₂O have been described in the literature [10]. The sample was generously supplied by Professor O. Mønsted at University of Copenhagen.

The room-temperature visible absorption spectrum was recorded with Cary 5000 UV-VIS-NIR spectrophotometer. The mid-infrared spectrum was obtained with a Mattson Infinities series FT-IR spectrometer using a KBr pellet. The sharp-line absorption spectrum was measured on a Microcrystal spectrometer [11]. The samples were cooled to 5K by a helium flow-tube cryostat. The 77K emission and excitation spectra were measured on a Spex Fluorolog-2 spectrofluorometer under the conditions previously described in detail [12].

RESULTS AND DISCUSSION

Infrared and emission spectra

The mid-infrared spectrum of *cis*-[Cr(*cycb*)Cl₂]Cl·H₂O recorded at room temperature is presented in Fig. 1.

The strong band at 3438 cm⁻¹ can readily be assigned to the O-H stretching of the H₂O molecule in the hydrated complex. The two sharp peaks at 3200 and 3079 cm⁻¹, and 3000-2800 cm⁻¹ regions are due to the symmetric and antisymmetric N-H and C-H stretching modes, respectively [13]. The strong peaks at 482 and 431 cm⁻¹ can be assigned to the Cr-N stretching mode [13, 14].

The infrared spectroscopy is one of the useful tool in the configuration assignment of *cis* and *trans* isomers of chromium(III) complexes with macrocyclic ligand. It is well

*To whom correspondence should be addressed.

E-mail : jhchoi@andong.ac.kr

Received November 27, 2003; Accepted March 15, 2004

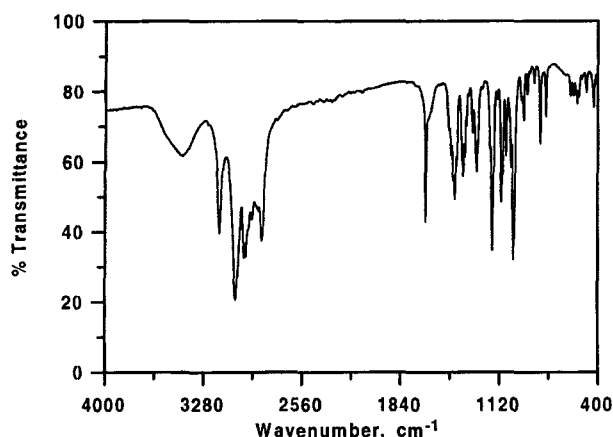


Figure 1. The mid-infrared spectrum of *cis*-[Cr(*cycb*)Cl₂]Cl at 298 K.

known that *cis* isomer exhibits at least three bands in the 920–830 cm⁻¹ region due to the N-H wagging modes while the methylene vibration splits into two peaks in the 830–780 cm⁻¹ region. However, *trans* isomer shows two groups of bands, a doublet near 890 cm⁻¹ arising from the secondary amine vibration and only one band near 810 cm⁻¹ due mainly to the methylene vibration [15]. The present complex exhibits three bands at 914, 895 and 863 in the N-H wagging frequency region. Two CH₂ rocking bands at 820 and 781 cm⁻¹ are also observed. These vibrational modes are not affected by differing counter anions [14]. The infrared spectrum of the title complex is clearly consistent with a *cis* configuration.

An experimental problem lies with the difficulty in distinguishing pure electronic components from the vibronic bands that also appear in the sharp-line absorption spectrum. It is required that the vibrational intervals of the electronic ground state can be obtained by comparing the emission spectral data. The 554 nm excited 77 K emission spectrum of *cis*-[Cr(*cycb*)Cl₂]Cl is shown in Fig. 2. The band positions relative to the lowest zero phonon line, R₁, with corresponding infrared frequencies,

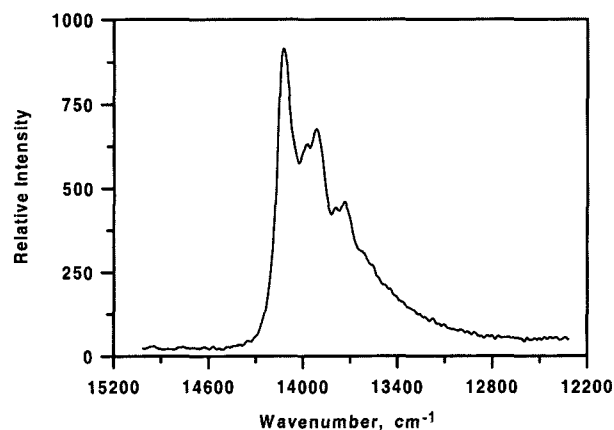


Figure 2. The 77K emission spectrum of *cis*-[Cr(*cycb*)Cl₂]Cl ($\lambda_{\text{ex}} = 554 \text{ nm}$).

Table 1. Vibrational frequencies from the 77 K emission and 298 K infrared spectra for *cis*-[Cr(*cycb*)Cl₂]Cl^a

Emission ^b	Infrared	Assignment
-227 m		R ₂
0 vs		R ₁
151 m		Lattice vibration
209 s		Skeletal bending
335 m		$\nu(\text{Cr-Cl})$
388 m		$\nu(\text{Cr-Cl})$
	431 s	$\nu(\text{Cr-N})$
	482 m	$\nu(\text{Cr-N})$
508 w	516 w, 538 m	$\nu(\text{Cr-N})$ +Ring def.
568 m	551 s, 577 m, 599 s	$\nu(\text{Cr-N})$ +Ring def.
681 vw		
	781 vs, 820 vs	$\gamma(\text{NH})$
	863 s, 895 m, 914 s	$\rho(\text{CH}_2)$
954 m	940 s	
1027 w	1019 vs	
1135 w	1106 vs	

^aData in cm⁻¹.

^bMeasured from zero-phonon line at 14214 cm⁻¹.

are listed in Table 1. The emission spectrum was independent of the exciting wavelength within the first spin-allowed transition region.

The very strong peak at 14124 cm⁻¹ can be assigned to the zero-phonon line, R₁ because a corresponding strong peak is found at 14120 cm⁻¹ in the sharp-line absorption spectrum. The vibrational intervals from the 77 K luminescence spectrum, which consists mainly fundamentals are summarized in Table 1 relative to the zero phonon line at 14124 cm⁻¹. The relatively strong bands at 335 and 388 cm⁻¹ in the emission spectrum can be assigned as a Cr-Cl stretching mode [13]. Absorption bands below 209 cm⁻¹ can be presumed to involve primarily the lattice vibration and skeletal bending modes.

Absorption spectra

In the case of chromium(III) complex with octahedral symmetry, several transitions due to spin-allowed and spin-forbidden are possible as shown in Fig. 3.

The visible absorption spectrum (solid line) of *cis*-[Cr(*cycb*)Cl₂]⁺ in aqueous solution at room temperature is presented in Fig. 4.

It exhibits two bands, one at 18870 cm⁻¹ (ν_1) and the other at 25975 cm⁻¹ (ν_2), corresponding to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (O_h) transitions, respectively [14]. The quartet bands have nearly symmetric profiles. In order to obtain some points of reference for the splittings of the two bands, the band profiles were fitted by using six Gaussian curves (dotted line), as seen in Fig. 4. The contribution from outside bands was corrected for the fine deconvolution. A deconvolution procedure on the experimental band pattern yielded maxima at 16735, 19110, 25350 and 26270 cm⁻¹ for the noncubic splittings of ${}^4T_{2g}$ and ${}^4T_{1g}$. These resolved peak positions were used as the spin-allowed transition energies in the ligand field optimization. In

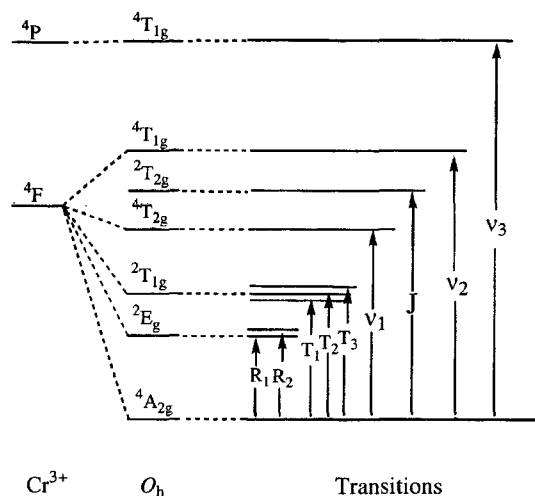


Figure 3. State energy level diagram of chromium(III) complex with octahedral symmetry.

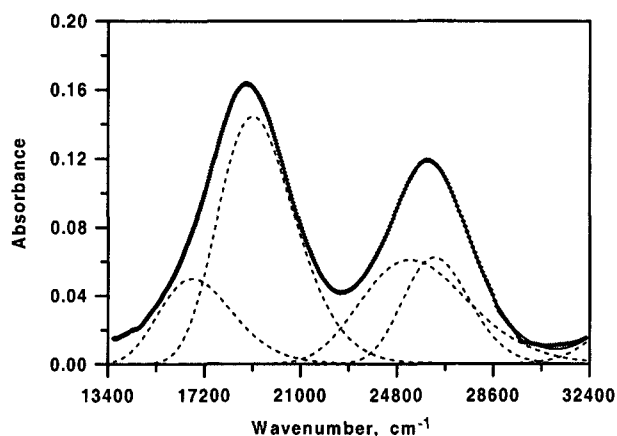


Figure 4. The resolved electronic absorption spectrum of *cis*-[Cr(*cycb*)Cl₂]⁺ in aqueous solution at 298 K.

fact, using just one Gaussian curve instead of two yields a east squares error only four times that of the best fit.

Intraconfigurational $t_{2g}^3 \rightarrow t_{2g}^3$ transitions in chromium(III) complexes, when measured at sufficiently low temperatures, may give rise to narrow zero-phonon lines as well as a series of vibronic induced sharp-lines due to spin-forbidden transitions from the $^4A_{2g}$ ground state into the higher doublets 3E_g , $^2T_{1g}$ and $^2T_{2g}$. The 5K sharp-line absorption spectrum of *cis*-[Cr(*cycb*)Cl₂]Cl is shown in Fig. 5.

Two strong peaks at 14120 and 14360 cm^{-1} in the sharp-line absorption spectrum are assigned to the two components (R_1 and R_2) of the $^4A_{2g} \rightarrow ^2E_g$ transition. The lowest-energy zero-phonon line coincides with the emission origin within 4 cm^{-1} . The 240 cm^{-1} splitting of the 2E_g state can be compared to the 50 cm^{-1} and 144 cm^{-1} observed for *cis*-[Cr(*cycb*)(ox)]ClO₄ and *cis*-[Cr(*cycb*)(O₂CO)]Cl complexes, respectively [17].

In general, it is not easy to locate positions of the other electronic components because the vibronic sidebands of the

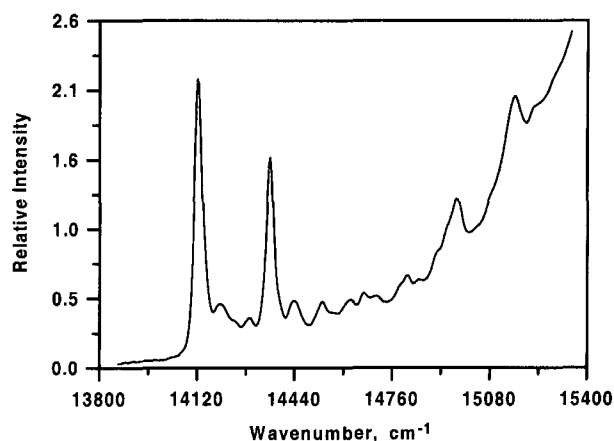


Figure 5. The sharp-line electronic absorption spectrum of *cis*-[Cr(*cycb*)Cl₂]Cl at 5K.

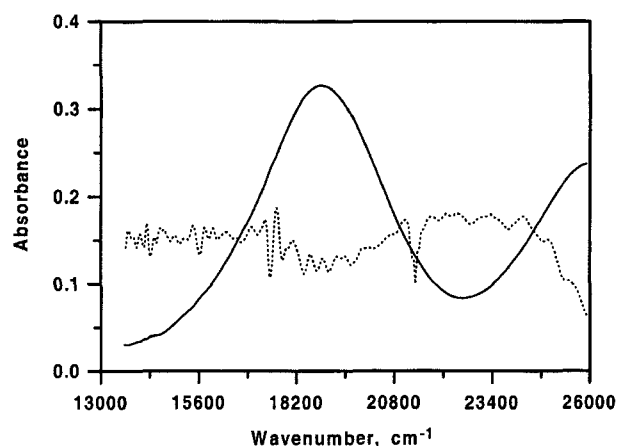


Figure 6. Absorption spectrum (solid line) and second derivative (dotted line) of *cis*-[Cr(*cycb*)Cl₂]⁺ in aqueous solution at 298 K.

2E_g levels overlap with the zero phonon lines of $^2T_{1g}$. However, the three tentative components of the $^4A_{2g} \rightarrow ^2T_{1g}$ electronic origin (T_1 , T_2 and T_3) are assigned to relatively intense peaks at 690, 850 and 1041 cm^{-1} from the lowest electronic line, R_1 . Vibronic satellites based on these origins have similar frequencies and intensity patterns to those of the 2E_g components. These three electronic lines are somewhat less intense than the 2E_g lines, but they are relatively intense compared to other chromium(III) complexes.

The higher energy $^4A_{2g} \rightarrow ^2T_{2g}$ (J) band was found at 21368 cm^{-1} from the second derivative of the solution absorption spectrum, as shown with dotted line in Fig. 6. But it could not be resolved into the separate components.

Ligand-field calculations

The ligand field analysis was carried out through an optimized fit of experimental to calculated transition energies. The ligand field parameters were calculated using the AOMX program [18]. The doublet and quartet energies with the appropriate degeneracies are calculated by diagonalizing the

full 120×120 secular matrix which arises from the perturbed d^3 system. Eigenvalues were assigned to the quartet or doublet states based on a spin analysis of the corresponding eigenfunctions. The amount of quartet character in the doublet states was estimated by comparing the eigenfunctions of the excited doublet states with and without spin-orbit coupling. The ligand field potential matrix was generated for *cis*-[Cr(*cycb*)Cl₂]⁺ from four coordinated nitrogen and two chloride atoms. The crystal structure for any salt of the complex is not solved, thus the positional parameters were adapted from the structure of *cis*-[Cr(*cyclam*)Cl₂]Cl [19]. The coordinates were then rotated so as to maximize the projections of the six-coordinated atoms on the Cartesian axes centered on the chromium. The parameters varied during the optimization were the interelectronic repulsion parameters *B*, *C* and the Trees correction parameter, the spin-orbit coupling parameter ζ , the AOM parameters $e_{\sigma}(\text{Cl})$ and $e_{\pi}(\text{Cl})$ for the chloride-chromium, and $e_{\sigma}(\text{N})$ for the macrocyclic *cycb* nitrogen-chromium. The π -interaction of amine nitrogens with sp^3 hybridization in the trien was assumed to be negligible. However, it is noteworthy that the peptide nitrogen with sp^2 hybridization has a weak π -donor character [3]. Schmidtke's π -expansion parameter was also included in the treatment of the interelectronic repulsion term. In Schmidtke's approximation, the electrostatic terms are modified by a factor τ for each constituent metal wavefunction that overlaps with a ligand π -orbital. The π -orbital expansion parameter, τ was fixed at the value 0.989 [7]. All parameters, except $e_{\sigma}(\text{Cl})$ and $e_{\pi}(\text{Cl})$, were constrained to reasonable limits based on the data from other chromium(III) complexes. The seven parameters were used to fit eleven experimental energies: the five ${}^4A_{2g} \rightarrow \{{}^2E_g, {}^2T_{1g}\}$ components, identified in Table 2, the average energy of the transition to the ${}^2T_{2g}$ state, the four ${}^4A_{2g} \rightarrow \{{}^4T_{2g}, {}^4T_{1g}\}$ components, and the splitting of the 2E_g state.

The Powell parallel subspace optimization procedure was used to find the global minimum [20]. The optimization was repeated several times with different sets of starting parameters to verify that the same global minimum was found. The results of the optimization and the parameter set used to generate the best-fit energies are also listed in Table 2. The error margins reported for the best-fit parameters in Table 2 are based only on the propagation of the assumed uncertainties in the observed peak positions [21]. The quartet terms were given a very low weight to reflect the very large uncertainty in their position.

The deduced ligand field parameters are $e_{\sigma}(\text{N})=7419 \pm 21$, $e_{\sigma}(\text{Cl})=5079 \pm 35$, $e_{\pi}(\text{Cl})=860 \pm 25$, $B=791 \pm 8$, $C=2809 \pm 14$, $\alpha_{\tau}=76 \pm 5$, and $\zeta=275 \pm 17 \text{ cm}^{-1}$. The AOM parameters are plausible and reproduce the spectrum pretty well. The $e_{\sigma}(\text{N})$ value for amine nitrogen is located in the normal range. A ligand field analysis of the sharp-line absorption and broad-band absorption spectra indicates that the chloride is a weak σ - and π -donor. The value of 7419 cm^{-1} for $e_{\sigma}(\text{N})$ is comparable to values for other amines [22-26]. It is suggested that the four nitrogen

Table 2. Experimental and calculated electronic transition energies for *cis*-[Cr(*cycb*)Cl₂]Cl^a

State (O_h)	Exptl	Calcd ^b
2E_g	14120	14125
	14360	14352
${}^2T_{1g}$	14810	14825
	14970	14991
	15160	15128
${}^2T_{2g}$	21368	21305
${}^4T_{2g}$	16735 ^c	16807
	19110 ^c	18934
${}^4T_{1g}$	25350 ^c	25383
	26270 ^c	26361

^aData in cm^{-1} .

^b $e_{\sigma}(\text{N})=7419 \pm 21$, $e_{\sigma}(\text{Cl})=5079 \pm 35$, $e_{\pi}(\text{Cl})=860 \pm 25$, $B=791 \pm 8$, $C=2809 \pm 14$, $\alpha_{\tau}=76 \pm 5$, $\zeta=275 \pm 17$.

^cObtained from the Gaussian component deconvolution.

atoms of the macrocyclic *cycb* ligand have strong σ -donor properties toward chromium(III). An orbital population analysis yields a configuration of $(xy)^{0.998}(xz)^{0.972}(yz)^{0.985}(x^2-y^2)^{0.027}(z^2)^{0.018}$ for the lowest component of the 2E_g state. The relative *d*-orbital ordering from the calculation is $E(xy) = 885 \text{ cm}^{-1} < E(xz) = 1234 \text{ cm}^{-1} < E(yz) = 1740 \text{ cm}^{-1} < E(x^2-y^2) = 18709 \text{ cm}^{-1} < E(z^2) = 20706 \text{ cm}^{-1}$. The value of Racah parameter, *B* is about 86 % of the value for a free chromium(III) ion in the gas phase. These factors plus AOM parameters can be used in predicting the photolabilized ligand and the relative quantum yields of the photoinduced reaction [27]. The 240 cm^{-1} of observed 2E_g splitting in the sharp-line absorption spectrum is more larger than the 139 and 198 cm^{-1} of *cis*-[Cr(*cyclam*)Cl₂]Cl and *cis*-[Cr(*trien*)Cl₂]Cl, respectively [28, 29]. It is also shown that this large 2E_g splitting can be reproduced by the modern ligand field theory. The parameter values reported here appear to be significant, as deduced on the basis of the manifold of sharp-line transitions which were obtained from the highly resolved absorption spectrum

ACKNOWLEDGEMENT

We wish to thank Professor O. Mønsted for a gift of the samples. We should like to thank Prof. E. Krausz for use of his microcrystal spectrometer at Australian National University. We also acknowledge financial support from the Andong National University (2003).

REFERENCES

- Hoggard, P. E (1986) Sharp line electronic transitions and metal-ligand angular geometry. *Coord. Chem. Rev.* **70**, 85-120.
- Choi, J. H (1994) Spectroscopic properties and ligand field analysis of tris(*trans*-1,2-cyclohexanediamine)chromium (III) chloride. *Bull. Korean Chem. Soc.* **15**, 145-150.

- Choi, J. H. and P. E. Hoggard (1992) Ligand field properties of the peptide nitrogen. *Polyhedron* **11**, 2399-2407.
- Choi, J. H. (1999) High resolution optical spectroscopy of *mer*-[Cr(dpt) (Gly-Gly)]ClO₄. *Bull. Korean Chem. Soc.* **20**, 436-440.
- Choi, J. H., Hong, Y. P. and Y. C. Park (2002) Spectroscopic properties and ligand field analysis of [di(3-aminopropyl)amine][prolylglycinato]chromium(III) perchlorate. *Spectrochim. Acta* **58A**, 1599-1606.
- Choi, J. H. (2000) Spectroscopic properties and ligand field analysis of *cis*-diazido(1,4,8,11-tetraazacyclotetradecane)chromium(III) azide. *Spectrochim. Acta* **56A**, 1653-1660.
- Schönherr, T. (1997) Angular overlap model applied to transition metal complexes and d^N-ions in oxide host lattices. *Top. Curr. Chem.* **191**, 87-152.
- Choi, J. H. (2002) Electronic spectroscopy and ligand field analysis of *mer*-[Cr(progly)(2,2-tri)ClO₄]. *J. Photosci.* **9**, 51-55.
- Powell, R. C. (1998) *Physics of Solid-State Laser Materials*, Springer-Verlag, New York.
- Erick, J. and O. Mønsted (1983) Preparation and properties of chromium(III) complexes of *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. *Acta Chem. Scand.* **37A**, 579-584.
- Krausz, E. (1993) A single-beam approach to the absorption spectroscopy of microcrystals. *Aust. J. Chem.* **46**, 1041-1054.
- Choi, J. H. (2000) Spectral properties and ligand field analysis of *cis*-dinitrito(1,4,8,11-tetraazacyclotetradecane)chromium(III) nitrate. *Chem. Phys.* **256**, 29-35.
- Nakamoto, K. (1997) *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 5th Ed., John Wiley & Sons, New York.
- Choi, J. H. (1993) Spectroscopic properties of *cis*-(1,4,8,11-tetraazacyclotetradecane)(1,2-propanediamine)chromium(III). *Bull. Korean Chem. Soc.* **14**, 118-122.
- Poon, C. K. and K. C. Pun (1980) Improved syntheses of *trans* isomers of chromium(III) complexes with 1,4,8,11-tetraazacyclotetradecane. *Inorg. Chem.* **19**, 568-569.
- Lever, A. B. P. (1984) *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam.
- Choi, J. H. I.G. Oh, R. Linder and T. Schönherr (2004) Electronic spectroscopy and ligand field analysis of *cis*-carbonato(*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride. *Chem. Phys.* **297**, 7-12.
- Adamsky, H. (1996) AOMX, A FORTRAN computer program for ligand field parameterization, Univ. of Duesseldorf.
- Forsellini, E., T. Parasassi, M. L. Tobe and M. E. Sosa (1986) *cis*-Dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) chloride. *Acta Cryst.* **C42**, 563-565.
- Kuester, J. L. and J. H. Mize (1973) *Optimization Techniques with Fortran*, McGraw-Hill, New York, pp. 331-343.
- Clifford, A. A. (1973) *Multivariate Error Analysis*, Wiley-Hasted, New York.
- Choi, J. H. (1999) Spectroscopic properties and ligand field analysis of pentaammine(imidazole)chromium(III) perchlorate. *Bull. Korean Chem. Soc.* **20**, 81-84.
- Choi, J. H. (1997) Spectroscopic properties and ligand field analysis of *cis*-dinitrato(1,4,8,11-tetraazacyclotetradecane)chromium(III) nitrate. *Bull. Korean Chem. Soc.* **18**, 819-823.
- Choi, J. H. and Y. C. Park (2003) Electronic and vibrational spectroscopy of *cis*-diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)chromium(III) thiocyanate. *Bull. Korean Chem. Soc.* **14**, 348-352.
- Choi, J. H. and I. G. Oh (1997) Sharp-line electronic spectroscopy and ligand field analysis of [Cr(*trans*-diammac)](ClO₄)₃. *Bull. Korean Chem. Soc.* **18**, 23-27.
- Choi, J. H. and I. G. Oh (1993) Sharp line electronic spectroscopy and ligand field analysis of *cis*-(1,4,8,11-tetraazacyclotetradecane)(ethylenediamine)chromium(III). *Bull. Korean Chem. Soc.* **14**, 348-352.
- Vanquickenborne, L. G. and A. Ceulemans (1983) Ligand field model of and the photochemistry of coordination compounds. *Coord. Chem. Rev.* **48**, 157-202.
- Choi, J. H. (1995) A spectroscopic study on the electronic structure of *cis*-[Cr(cyclam)Cl₂]Cl. *J. Korean Chem. Soc.* **39**, 501-507.
- Choi, J. H. (1998) Emission, excitation and far-infrared spectroscopy of *cis*- α -dichlorotriethyleneteraminechromium(III) Chloride. *Bull. Korean Chem. Soc.* **19**, 575-579.