

Spectroscopic Properties and Magnetic Behavior of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$

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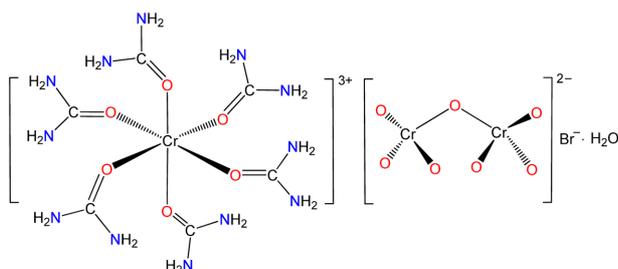
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INTRODUCTION

Chromium in compounds can exist in various oxidation states, ranging from II to VI. In particular, chromium(VI) in CrO_4^{2-} or $\text{Cr}_2\text{O}_7^{2-}$ is highly cytotoxic substance and a potential carcinogen.¹ A number of treatment methods for the removal of toxic heavy metal ions in water have been described.² It may be possible that the $[\text{Cr}(\text{urea})_6]^{3+}$ is suitable to target the oxoanion. In a recent communication, we described concerning synthesis and crystal structure of the $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$ (Scheme 1).³

The complex crystallized in the monoclinic space group $P2_1/n$ with $Z = 4$. It consists of the isolated complex cation $[\text{Cr}(\text{urea})_6]^{3+}$, together with $\text{Cr}_2\text{O}_7^{2-}$ and Br^- counter ions. For convenience, a perspective drawing together with the atomic labeling is depicted in Fig. 1. It is found that the Cr(III) ion is coordinated by six urea ligands through oxygen atoms with the CrA-OA bond lengths ranging from 1.9534 (13) to 1.9776 (12) Å, and with OA-CrA-OA bond angles in the range of 85.10 (5)°–92.95 (5)°. The $\text{Cr}_2\text{O}_7^{2-}$ anion is in a nearly staggered conformation. The Cr1B–O7B–Cr2B bridging angle in the anion is 130.26 (10)°. However, the detailed physical properties of the complex have not been published yet. In the present work we are reporting on the spectroscopic and magnetic studies of title complex by using UV- visible and IR spectroscopy and by measuring magnetic susceptibility.



Scheme 1. Chemical structure of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$.

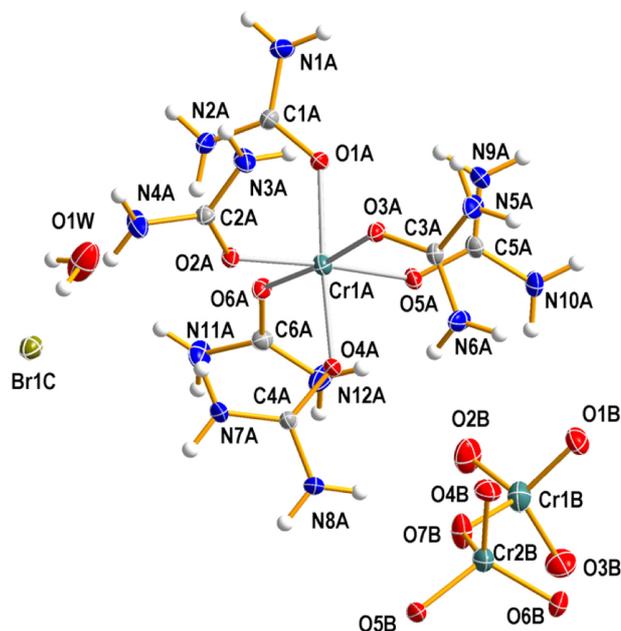


Figure 1. Molecular structure of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$.

EXPERIMENTAL

Materials and Synthesis

The chromium(III) bromide hexahydrate was obtained from Aldrich Chemical Co. and used as supplied. All chemicals were reagent-grade materials and used without further purification. $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$ was prepared as described previously.³ Before the spectra were recorded, the complex was purified from aqueous solution by recrystallization. *Anal.* Found: C, 10.32; H, 3.08; N, 23.38; Calc. for $[\text{Cr}\{\text{CO}(\text{NH}_2)_2\}_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$: C, 9.92; H, 3.61; N, 23.14%. UV-visible data, λ_{max} in nm: 274, 291, 367 (*sh*), 380, 441 (*sh*), 605. IR data (KBr, cm^{-1}): 3634 (*vs*) (ν OH), 3450 (*vs*) (ν_{as} NH), 3352 (*vs*) (ν_{s} NH), 3352 (*vs*) (ν NH...H bonded), 1652 (*s*) (ν_{s} C=O + δ_{as} NH₂), 1638 (*s*) (ν_{s} CO + δ_{s} NH₂), 1151 (*s*) (ρ NH₂), 1035 (*s*) (ν_{s} C=N), 940 (*vs*) (ν Cr–

O), 924 (*s*) (ν Cr–O), 881 (*s*) (ν Cr–O), 797 (*s*), 776 (*m*) (ω CO), 689 (*w*), 633 (*s*), 598 (*m*), 531 (*sh*), 465 (*m*), and 452 (*w*) [ν Cr–O(urea)].

Physical Measurements

Diffuse reflectance electronic spectra were measured on a JASCO V-570 UV/VIS/NIR spectrophotometer, equipped with an integrating sphere in the range of 200–1500 nm. The mid-infrared spectrum was obtained from a KBr pellet using a JASCO 460 plus series FT-IR spectrometer. The magnetic properties were investigated with a Quantum Design MPMS-XL superconducting quantum interference device SQUID magnetometer at an applied field of 0.5 T and a temperature range of 5–300 K. Powder samples were measured in a pharmaceutical cellulose capsule. Diamagnetic correction was applied with Pascal's method. Analyses for C, H, and N were performed on a Perkin-Elmer 2400II CHNS/O analyzer at the Tokyo University of Science.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The FT-IR spectrum of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$ is presented in *Fig. 2*.

The FT-IR spectrum showed a very strong sharp absorption band at 3634 cm^{-1} due to the O–H stretching mode of the hydrate water molecule. The symmetric and asymmetric modes of the noncoordinated NH_2 group appeared at 3450 and 3352 cm^{-1} , respectively, along with an additional less intense band at 3218 cm^{-1} . The absorption band observed near 1507 cm^{-1} is assigned to CO + CN vibrations. This indicates the formation of a CrA–OA(urea) bond instead of the CrA–NA(urea) bond reported in literature⁴ for $[\text{Cr}(\text{urea})_6]\text{Cl}_3$. The strong absorption bands at 1638 and 1151 cm^{-1} can be

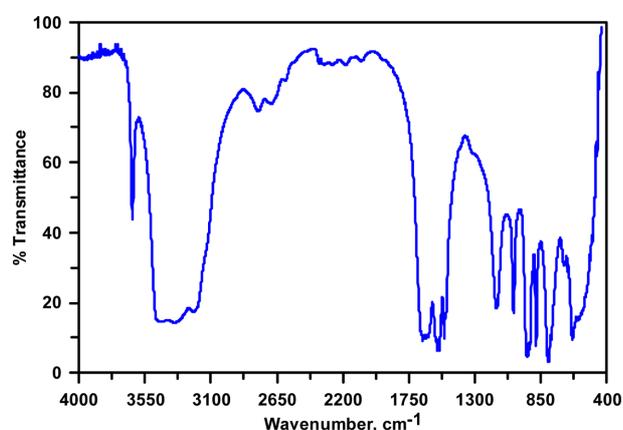


Figure 2. FT-IR spectrum of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$.

assigned to NH_2 bending and rocking modes, respectively. However, for $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ the NH_2 rocking vibration value is 1175 cm^{-1} . The 24 cm^{-1} lowering in the vibrational frequency indicates the weakening of the N–H bonds due to the presence of strong hydrogen bonding between the NH_2 groups and $\text{Cr}_2\text{O}_7^{2-}$ (i.e., NA–H...OB). The strong absorption at 1035 cm^{-1} and the medium absorption at 622 cm^{-1} are assigned to $\nu_s(\text{C}=\text{N})$ and $\delta(\text{NCO})$, respectively. In compound (I), a sharp peak for the CrB–OB bond in $\text{Cr}_2\text{O}_7^{2-}$ was observed at 881 cm^{-1} . This is lower than that in the free dichromate ion.⁵ Sharp peaks were observed at 940 , 881 , and 776 cm^{-1} that are assigned to the asymmetric, symmetric stretch for $\text{Cr}_2\text{O}_7^{2-}$, and the symmetric Cr1B–O1B–Cr2B stretching modes, respectively (Hilliard *et al.*, 1982). The lowering in all these values is attributed to the weakening of the CrB–OB bond due to the formation of NA–H...OB hydrogen bonds.

Electronic Absorption Spectroscopy

The solid-state UV-visible spectrum of compound (I) is shown in *Fig. 3*.

Two bands corresponding to the ${}^4A_{2g} \rightarrow {}^4T_{1g} ({}^4F)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g} ({}^4P)$ transitions in the complex cation $[\text{Cr}(\text{urea})_6]^{3+}$ are believed to be obscured by the intense bands of the $\text{Cr}_2\text{O}_7^{2-}$ moiety. In order to have some point of reference for the splitting of the electron bands containing the dichromate anion, we have fitted the band profiles using six main Gaussian curves, as shown in *Fig. 3*. A deconvolution procedure on the experimental band pattern yielded maxima at 16530 , 21505 , 23475 , 27100 , 35090 , and 38025 cm^{-1} for $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$. Three electronic bands observed at 21505 , 27100 , and 38025 cm^{-1} can be assigned as the lowest-energy singlet transitions of the dichromate ion: ${}^1A_1 \rightarrow {}^1E^a$, ${}^1A_1 \rightarrow {}^1A_1 + {}^1E^b$, and ${}^1A_1 \rightarrow {}^1E^c$ because the UV–

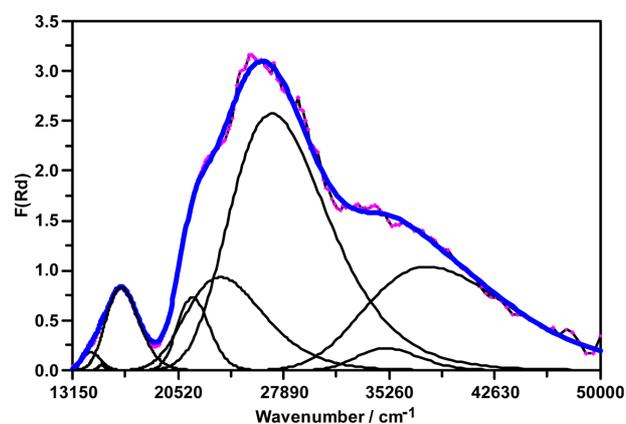


Figure 3. Diffuse reflectance electronic spectrum and the resolved overlapping peaks of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$.

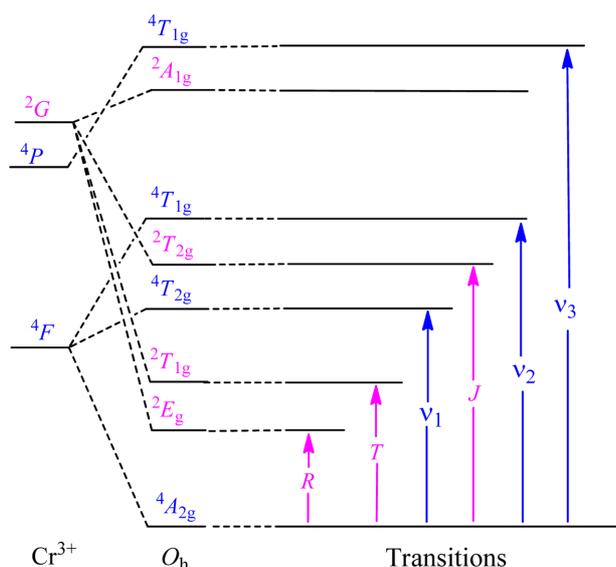


Figure 4. State energy level diagram and electronic transitions of chromium(III) complex with octahedral symmetry.

visible spectrum of K₂Cr₂O₇ having a Cr(VI) metal center shows absorption bands at 22320, 28010, and 38910 cm⁻¹, respectively.^{7,8}

The three lowest terms of the Cr(III) free ion 3d³ configuration, i.e., ⁴F, ⁴P and ²G (⁴F is the ground state) are reduced in an octahedral environment as follows:

$${}^4F \rightarrow {}^4A_{2g} + {}^4T_{2g} + {}^4T_{1g}$$

$${}^4P \rightarrow {}^4T_{1g}$$

$${}^2G \rightarrow {}^2E_g + {}^2T_{1g} + {}^2T_{2g} + {}^2A_{1g}$$

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. 4.

In Fig. 3, two intense bands located at 16530 and 23475 cm⁻¹ correspond to the ⁴A_{2g}→⁴T_{2g} (v₁) and ⁴A_{2g}→⁴T_{1g} (⁴F) (v₂) transitions for the [Cr(urea)₆]³⁺ moiety. The electronic bands for the [Cr(urea)₆]³⁺ moiety are almost in agreement with those reported for [Cr(urea)₆]Cl₃.⁹

For octahedral d³ system, the formula between three spin-allowed electronic transition energies and ligand field parameters is as followings.¹⁰

$${}^4A_{2g} \rightarrow {}^4T_{2g}, v_1 = 10Dq \quad (1)$$

$${}^4A_{2g} \rightarrow {}^4T_{1g}({}^4F), v_2 = 7.5B + 10Dq - 1/2(225B^2 + 100Dq^2 - 180Dq \times B)^{1/2} \quad (2)$$

$${}^4A_{2g} \rightarrow {}^4T_{1g}({}^4P), v_3 = 7.5B + 15Dq + 1/2(225B^2 + 100Dq^2 - 180Dq \times B)^{1/2} \quad (3)$$

The first spin allowed transition directly gives the value of 10Dq. For [Cr(urea)₆]³⁺ moiety, the crystal field splitting parameter, Dq and Racah interelectronic repulsion param-

eter, B were obtained as 1653 cm⁻¹ and 707 cm⁻¹, respectively. These parameters were calculated from the values of v₁ and v₂ by means of following eqs. (4) and (5).

$$Dq = v_1/10 \quad (4)$$

$$B = (2v_1^2 + v_2^2 - 3v_1v_2)/(15v_2 - 27v_1) \quad (5)$$

The nephelauxetic parameter, β of 0.77 was calculated by the eq. (6).

$$\beta = B(\text{complex})/B(\text{free ion}) \quad (6)$$

where B (free ion) is 918 cm⁻¹ for chromium(III) ion.¹¹ The β value indicates that there is an appreciable covalent character in the metal–ligand σ bond.

The third spin allowed transition, ⁴A_{2g}→⁴T_{1g} (⁴P) (v₃) from eq. (3) is predicted to appear at 36715 cm⁻¹. Therefore, the remaining main band of 35090 cm⁻¹ may be assigned to the ⁴A_{2g}→⁴T_{1g} (⁴P) (v₃) transition.

The second derivative of a spectral peak generally results in a peak of greater intensity than the original, but inverted. In the second derivative spectrum, the minima correspond to the maxima in the original spectrum, and hence, the minima are described as the positions of the peaks.¹² The spin-forbidden ⁴A_{2g}→²E_g(R), ²T_{1g}(T), ²T_{2g}(J) bands were found at 14125, 14950, and 20750 cm⁻¹, respectively, from the second derivative of the solid-state absorption spectrum (Fig. 5), but could not be resolved into separate components.

The Racah parameter, C can be calculated from the position of the ⁴A_{2g} ²E_g absorption band and the eq. (7).¹³

$$C = (B/3.05)[\{E(^2E_g)/B\} - 7.90 + 1.80(B/Dq)] \quad (7)$$

The value of C is evaluated to be 2979 cm⁻¹, which is significantly reduced from the free ion value of Cr(III), C (free ion) = 4133 cm⁻¹. A comparison of the two values

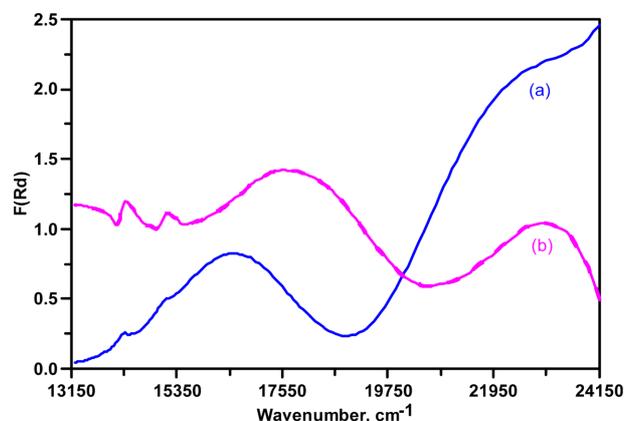


Figure 5. Absorption spectrum (a) and second derivative (b) of [Cr(urea)₆][Cr₂O₇]Br·H₂O.

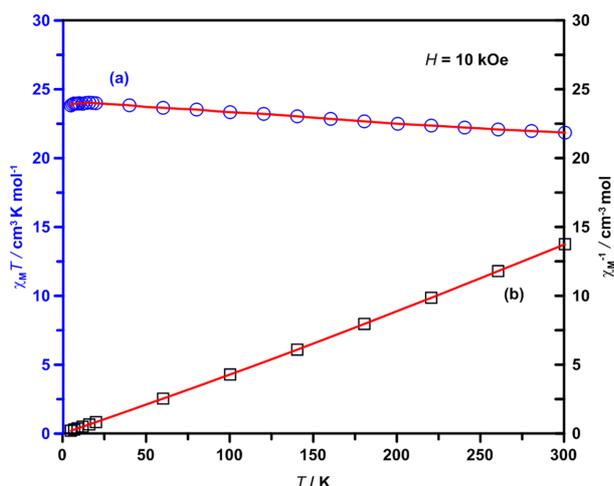


Figure 6. Temperature dependent magnetic susceptibility of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$ measured at 10 kOe.

reveals that C is decreased by 28 % from C (free ion).¹¹ This decrease is also due to effect of bond covalency. The values of Dq , B and C parameters obtained in here are comparable to those reported for $[\text{Cr}(\text{chxn})_3]^{3+}$ ($Dq = 2175 \text{ cm}^{-1}$, $B = 703 \text{ cm}^{-1}$ and $C = 2953 \text{ cm}^{-1}$).¹⁴ The spin-orbit coupling can be calculated from the Cole and Garret empirical relation.¹⁵

$$\lambda_{\text{eff}} = 11 \times 10^{-9} (B + 1080)^3 + 6.2 \quad (8)$$

Using B and Eq. (8) yields $\lambda_{\text{eff}} = 69 \text{ cm}^{-1}$, which is in good agreement with the value expected for chromium(III) ion in crystals.¹⁶ The deviation of λ_{eff} from λ_0 (87 cm^{-1} for free ion) is due to the bonding effects of urea ligands toward chromium(III) ion in the crystal.¹⁷

The magnetic susceptibility of $[\text{Cr}(\text{urea})_6](\text{Cr}_2\text{O}_7)\text{Br}\cdot\text{H}_2\text{O}$ was measured in the temperature range of 5-300 K at 10 kOe. The plots of $\chi_M T$ vs. T (a), and χ_M^{-1} vs. T (b) are shown in Fig. 6. The value of $\chi_M T$ at 300 K is $21.9 \text{ cm}^3 \text{ K mol}^{-1}$. On decreasing the temperature, the $\chi_M T$ value slightly increases to a maximum of $24.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 15 K and decreases again down to $23.8 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. The effective magnetic moment values, μ_{eff} , were calculated from the equation:

$$\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2} \quad (9)$$

where χ_M is the molar magnetic susceptibility (emu mol^{-1}) and T is the absolute temperature.

The observed effective magnetic moments are in the range $3.73 \mu_B - 3.89 \mu_B$, as shown in Fig. 7. The chromium(III) ion ($3d^3$) has three unpaired electrons in the $3d$ shell, therefore its compounds were considered to have magnetic moments close to the spin-only value, $3.88 \mu_B$ and consistent with S

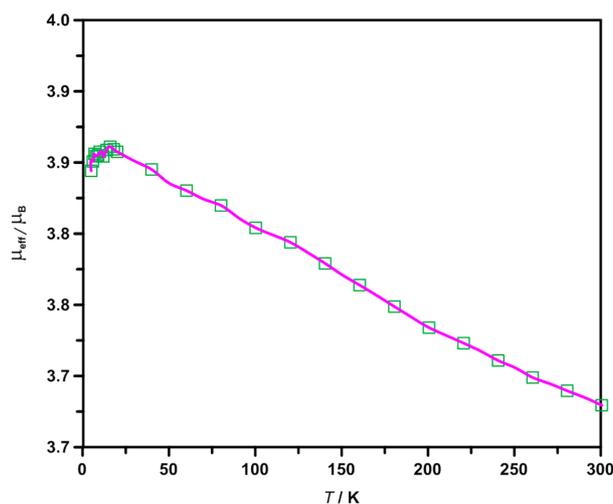


Figure 7. Temperature dependent magnetic moment of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$.

$= 3/2$ spin state of a mononuclear Cr(III) d^3 center.¹⁷

CONCLUSIONS

The FT-infrared and diffuse reflectance electronic spectra including magnetic properties of $[\text{Cr}(\text{urea})_6][\text{Cr}_2\text{O}_7]\text{Br}\cdot\text{H}_2\text{O}$ have been measured. The physical properties are in good agreement with the results obtained from X-ray crystallography that show that the Cr(III) ion is coordinated by six oxygen atoms deriving from urea ligands. Crystal field parameter Dq , nephelauxetic parameter β , Racah B and C parameters have been evaluated. The $[\text{Cr}(\text{urea})_6]^{3+}$ moiety may be used as a potential anion receptor for $\text{Cr}_2\text{O}_7^{2-}$ due to its high positive charge and the large number of hydrogen bond donor groups of its six urea ligands.

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REFERENCES

- Cohen, M. D.; Kargacin, B.; Klein, C. B.; Costa M. *Crit. Rev. Toxicol.* **1993**, *23*, 255.
- Kalidhasan, S.; Kumar, A. S. K.; Rajesh, V.; Rajesh, N. *Coord. Chem. Rev.* **2016**, *317*, 157.
- Moon, D.; Tanaka, S.; Akitsu, T.; Choi, J. H. *Acta Crystallogr. Sect. E* **2015**, *71*, 1336.
- Penland, R.B.; Mizushima, S.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1957**, *79*, 1575.
- Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 5th Ed.; John Wiley & Sons: New York, 1997.
- Hilliard, L. J.; Rice, M. R.; Gold H. S. *Spectrochim. Acta*

- Part A*, **1982**, 68, 611.
7. Cieslak-Golonka, M. *Coord. Chem. Rev.* **1991**, 109, 223-249.
 8. Bala, R.; Kashyap, M.; Kaur, A.; Golobic, A. *J. Mol. Struct.* **2013**, 1031, 246.
 9. Górska, N.; Mikuli, E.; Kótai, L. *Eur. Chem. Bull.* **2014**, 3, 474.
 10. Dou, Y.-S. *J. Chem. Edu.* **1990**, 67, 134.
 11. Powell, R. C. *Physics of Solid-State Laser Materials*; Springer-Verlag: New York, 1998; p. 224.
 12. Choi, J. H.; Hoggard, P. E. *Polyhedron* **1992**, 11, 2399.
 13. Kripal, R.; Yadav, A. K. *Chem. Phys. Lett.* **2014**, 612, 245.
 14. Choi, J. H. *Bull. Korean Chem. Soc.* **1994**, 15, 145.
 15. Cole, G. M.; Garret, B. B. *Inorg. Chem.* **1970**, 9, 1898.
 16. Figgis, B. N.; Hitchman, M. A. *Ligand Field Theory and Its Applications*; Wiley-VCH: New York, 2000.
 17. Gispert, J. R. *Coordination Chemistry*; Wiley-VCH Verlag GmbH & Co KGaA, Weinheim: Germany, 2008.
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