

## Spectroscopic Properties and Ligand Field Analysis of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>

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**Key words:** Chromium(III) complex, IR spectroscopy, Absorption spectroscopy, AOM parameter

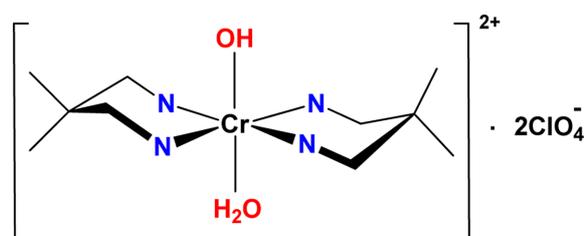
### INTRODUCTION

Tunable solid state laser materials in the near-infrared spectral range are interesting for a variety of applications, for instance, displays technology, medicine and spectroscopy.<sup>1</sup> 2,2-Dimethyl-1,3-propanediamine (Me<sub>2</sub>tn) is a bidentate ligand that can coordinate to the central metal ion by forming six-membered chelate ring with a chair conformation. The [Cr(Me<sub>2</sub>tn)<sub>2</sub>X<sub>2</sub>]<sup>n+</sup> (X = monodentate) cation can adopt either the *trans* or the *cis* geometry. In addition, two different kinds of conformation with respect to the chelate rings of Me<sub>2</sub>tn are seen in the *trans* isomer. The carbon atoms of the two chelate rings of the two conformers may be on the same side (*syn* conformer) or on the opposite side (*anti* conformer) of the coordination plane. In the case of *trans-anti/syn*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]Cl, *trans-anti/syn*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Br<sub>2</sub>]Br<sub>2</sub>·HClO<sub>4</sub>·H<sub>2</sub>O and *trans-anti/syn*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Br<sub>2</sub>]Br, independent *syn* and *anti* conformational isomers were found within the same crystals.<sup>2-4</sup> However, structural analyses of *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(NCS)<sub>2</sub>]NCS·0.5H<sub>2</sub>O, *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>, and *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]ZnCl<sub>4</sub> indicated that two chelate rings of Me<sub>2</sub>tn ligands were only in the *anti* chair-chair conformation.<sup>5-8</sup> The different conformations of the two six-membered chelate rings of Me<sub>2</sub>tn ligands may be dependent on the crystallographic disorder, packing forces, hydrated molecules and counter anions in the crystals. The factors which determine the stability of these geometric conformations are subtle and complicated.<sup>2-8</sup>

The preparation and characterization of novel chromium (III) systems have received much attention in recent years because chromium(III)-doped crystals are promising materials for tunable solid state lasers in the spectral region between 600 and 1100 nm.<sup>9</sup> As a prerequisite for these applications, a detailed study of the spectroscopic and ligand field properties is needed. It has been recognized

that the intraconfiguration *d-d* transitions may be useful to determine metal-ligand bonding property as well as molecular geometry.<sup>10-19</sup> In particular, the sharp-line splitting and its pattern are very sensitive to the exact bond angles around the metal. Thus it is possible to extract geometric information from the electronic spectroscopy in noncrystalline environments.<sup>20,21</sup>

Previously, we have described concerning synthesis and conformational structure of the *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (Scheme 1).<sup>22</sup> It indicated that the chromium atom was in a distorted octahedral environment, coordinated by two bidentate, 2,2-dimethyl-1,3-propanediamine ligands and two O atoms of hydroxy group and water molecule in *trans* position. The average Cr–N(Me<sub>2</sub>tn) and Cr–O bonds were 2.086 (2) and 1.907 (9) Å, respectively. The carbon atoms of the two Me<sub>2</sub>tn chelate rings in the complex adopted a stable *anti* conformation on the coordination plane not including *syn* conformer. However, the detailed IR and electronic absorption spectral properties have not been published yet. In this study, the four electronic bands due to spin-allowed transitions were assigned. Using the observed electronic transitions, a ligand field analysis was performed to determine the metal-ligand bonding properties for the coordinated atoms toward chromium (III).



**Scheme 1.** Chemical structure of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>.

## EXPERIMENTAL

**Caution!** Although we experienced no difficulty with the perchlorate salt described in this study, the compound is potentially explosive, and should be handled with very great care.

### Materials and Synthesis

The free ligand 2,2-dimethyl-1,3-propanediamine was obtained from Aldrich Chemical Co. and used as supplied. All chemicals were reagent grade materials and used without further purification. *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> was prepared as described previously.<sup>22</sup> Before the spectra were recorded, the complex was purified from aqueous solution by recrystallization. *Anal.* Found: C, 24.40; H, 6.31; N, 11.35; Calc. for Cr(C<sub>10</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>)(ClO<sub>4</sub>)<sub>2</sub>: C, 24.45; H, 6.57; N, 11.40%.

### Physical Measurements

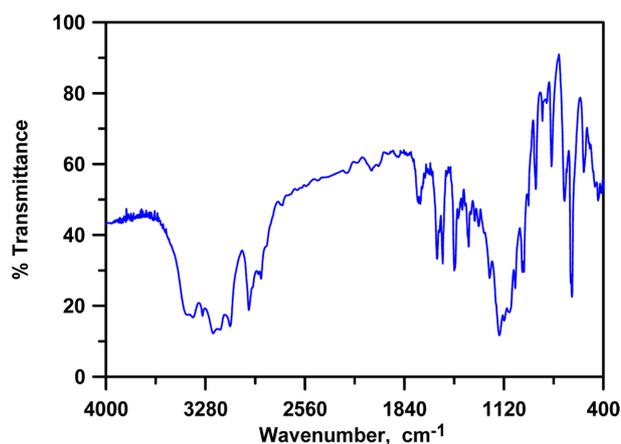
The room-temperature visible absorption spectrum was recorded on a HP 8453 diode array spectrophotometer. The mid-infrared spectrum was obtained on a Mattson Infinities series FT-IR spectrometer using a KBr pellet. Analyses for C, H, and N were carried out on a Carlo Erba 1108 elemental analyzer.

## RESULTS AND DISCUSSION

### Infrared Spectroscopy

Infrared spectroscopy is useful in assigning the configuration of *cis* and *trans* isomers of diacidobis (diamine) type complexes.<sup>23</sup> The infrared absorption spectrum of the *trans* isomer reveals a simpler pattern than that of the *cis* isomer. This pattern may be rationalized on the basis of the higher symmetry of the *trans* isomer. The FT-infrared spectrum of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> is presented in Fig. 1.

Two intense bands at 3423 and 3371 cm<sup>-1</sup> are assigned to the asymmetric and symmetric stretching vibrations, ν(O–H) of hydroxy group and water molecule. The broadness of these bands indicates that hydrogen bonds are present in this structure complex. The infrared spectrum shows strong bands in the region 3100–3300 cm<sup>-1</sup> and 2800–3000 cm<sup>-1</sup> due to the symmetric and antisymmetric N–H and C–H stretching modes, respectively. The assignment of NH<sub>2</sub> and CH<sub>2</sub> deformations follows the frequency sequence proposed for some chromium(III) complexes according to which these vibrational modes have the energetic order<sup>31</sup>



**Figure 1.** FT-infrared spectrum of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>.

bending ( $\delta$ ) > wagging ( $\omega$ ) > twisting ( $\gamma$ ) > rocking ( $\rho$ )

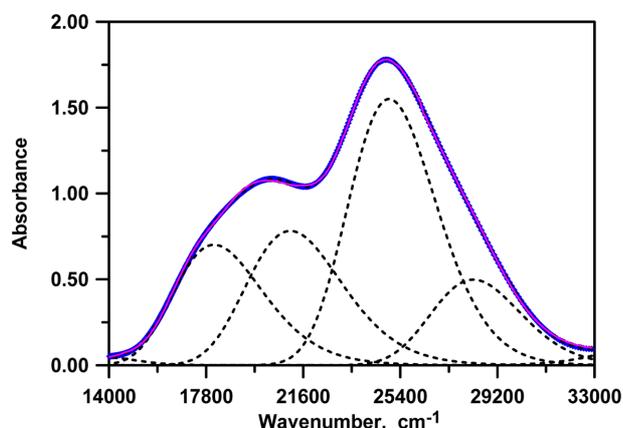
Two strong absorption bands at 1604 and 1563 cm<sup>-1</sup>, and the single band at 1479 cm<sup>-1</sup> can be assigned to NH<sub>2</sub> and CH<sub>2</sub> bending modes, respectively. Medium to weak absorptions in the region 1260–1390 cm<sup>-1</sup> can be assigned to the symmetric NH<sub>2</sub> deformation and the ring C–C stretching mode, respectively. The strong absorption at 1038 cm<sup>-1</sup> may be assigned to CH<sub>2</sub> twisting mode. It has been suggested that the *cis* isomer exhibits at least three bands in the 830–890 cm<sup>-1</sup> region due to the NH<sub>2</sub> rocking mode while the methylene vibration splits into two peaks in the 760–830 cm<sup>-1</sup> region. However, the *trans* isomer shows two groups of bands, one band near 890 cm<sup>-1</sup> arising from the amine vibration and a doublet near 800 cm<sup>-1</sup> due mainly to the methylene vibration.<sup>2,4,5</sup> The title complex exhibits two bands at 889 and 841 cm<sup>-1</sup> in the NH<sub>2</sub> rocking frequency region. The CH<sub>2</sub> rocking bands at 775 cm<sup>-1</sup> are observed. The absorption positions of bending ( $\delta$ ), wagging ( $\omega$ ), twisting ( $\gamma$ ) and rocking ( $\rho$ ) bands of NH<sub>2</sub> and CH<sub>2</sub> deformations are not significantly affected by differing counter anions. The very strong absorptions at 1081 cm<sup>-1</sup> and 627 cm<sup>-1</sup> are assigned to  $\delta$ (ClO<sub>4</sub><sup>-</sup>) and  $\nu_{as}$ (ClO) of the ionic perchlorate.<sup>17,24</sup> The broadening or split of the perchlorate peaks results from the reduction in the symmetry of the ClO<sub>4</sub><sup>-</sup> ion to C<sub>3v</sub> or C<sub>2v</sub> due to its interaction with the amine hydrogen atoms and the formation of partial H–bonding. The metal-ligand stretching and ring-deformation bands occur in the far infrared range. The two strong peaks at 460 and 428 cm<sup>-1</sup> can be assigned to the Cr–N stretching modes. The infrared spectral properties of the new complex would strongly support the assignment of the *trans* configurational geometry, but the spectroscopic

data do not give any evidence whether *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> has the *syn* or *anti* conformation of the two six-membered chelate rings.

### Electronic Absorption Spectroscopy

The assignment of the geometrical configuration of some chromium(III) complexes with mixed ligands can be suggested by inspection of the *d-d* absorption spectra.<sup>10–15</sup> The position of the spin-allowed transitions in the electronic spectra, the number of bands, and their extinction coefficients are usually reliable indicators for distinguishing the *trans* and *cis* isomers. Electronic absorption spectroscopy of a tetragonally distorted chromium(III) complexes is revealing, with significant splitting under the <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>2g</sub> envelope occurring for the *trans* geometrical isomers, but small or undetected splitting observed for the *cis* isomers. In general, the *trans* chromium(III) complexes with two monodentate and two diamine ligands that are more symmetrical have three bands in the visible region, and these bands are located at higher wavelengths and have lower extinction coefficients than those of the less symmetrical *cis* isomers. The visible absorption spectrum (solid line) of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> in aqueous solution at room temperature is presented in Fig. 2.

It exhibits two main bands, one at 19 920 cm<sup>-1</sup> (ν<sub>1</sub>), and the other at 24 890 cm<sup>-1</sup> (ν<sub>2</sub>), corresponding to the <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>2g</sub> and <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>1g</sub>(O<sub>h</sub>) transitions, respectively. The <sup>4</sup>A<sub>2g</sub>→<sup>4</sup>T<sub>1g</sub>(<sup>4</sup>P) transition corresponds to a higher energy range, and could not be observed under our experimental condition. The third band (ν<sub>3</sub>) may be obscured by the charge-transfer and ligand-specific transition bands. The one quartet band shows an asymmetric profile and has a shoulder at 17360 cm<sup>-1</sup>. This is indicative of the *trans* configuration. In order to have some point of reference for the splitting of



**Figure 2.** Visible absorption spectrum (solid line) of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>.

the bands, we have fitted the band profiles using four Gaussian curves, as shown in Fig. 2. A deconvolution procedure on the experimental band pattern yielded maxima at 18 115, 21 095, 25 000 and 28 250 cm<sup>-1</sup> for the non-cubic (*D*<sub>4h</sub>) split levels (<sup>4</sup>E<sub>g</sub><sup>a</sup> + <sup>4</sup>B<sub>2g</sub> and <sup>4</sup>A<sub>2g</sub> + <sup>4</sup>E<sub>g</sub><sup>b</sup>) of <sup>4</sup>T<sub>2g</sub> and <sup>4</sup>T<sub>1g</sub>(O<sub>h</sub>), respectively. These deconvoluted band positions were used as the observed spin-allowed transition energies in the ligand field calculation.

### Ligand Field Optimization

The ligand field analysis was carried out through an optimized fit of experimental to calculated transition energies using the AOMX program.<sup>25</sup> The ligand field potential matrix was generated for *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)]<sup>2+</sup> from the coordinated four primary amine nitrogen atoms of the Me<sub>2</sub>tn and the two oxygen atoms of hydroxy group and water molecule. Throughout the ligand field optimization, we assumed the *D*<sub>4h</sub> tetragonal symmetry for the title complex. In the framework of the angular overlap model the metal-ligand interactions are described in terms of localized bonding parameters of σ- and π-type. The parameters that were varied during the optimization were the interelectronic repulsion parameter *B* plus the AOM parameters e<sub>σ</sub>(O) and e<sub>π</sub>(O) of hydroxy group and water molecule for the oxygen-chromium interaction, and e<sub>σ</sub>(N) for the Me<sub>2</sub>tn nitrogen-chromium interaction. The π-interaction of the hydroxy group and water molecule with the metal ion was considered to be isotropic.

The π-interaction of amine nitrogen with *sp*<sup>3</sup> hybridization in the Me<sub>2</sub>tn ligand was assumed to be negligible. However, it is worth nothing that peptide nitrogen with *sp*<sup>2</sup> hybridization has a weak π-donor character.<sup>26,27</sup> The results of the optimization and the parameter set used to generate the best-fit energies (cm<sup>-1</sup>) are listed in Table 1. The following values were finally obtained for the ligand field parameters: e<sub>σ</sub>(N) = 7032; e<sub>σ</sub>(O) = 7367; e<sub>π</sub>(O) = 1735 and

**Table 1.** Observed band positions and calculated transition energies (cm<sup>-1</sup>) in the electronic spectrum of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)]

| Assignment   | Observed <sup>a</sup> | Calculated <sup>b</sup> |
|--|-----------------------|-------------------------|
| <sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> <sup>a</sup>  | 18115                 | 18115                   |
| <sup>4</sup> B <sub>1g</sub> → <sup>4</sup> B <sub>2g</sub>              | 21095                 | 21095                   |
| <sup>4</sup> B <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub> <sup>a</sup> | 28250                 | 28249                   |
| <sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> <sup>b</sup>  | 25000                 | 25000                   |
| <sup>4</sup> B <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub> <sup>b</sup> | ?                     | 39713                   |
| <sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>g</sub> <sup>c</sup>  | ?                     | 42473                   |

<sup>a</sup>Obtained from the Gaussian compound deconvolution. <sup>b</sup>Calculated using the following parameters: e<sub>σ</sub>(N) = 7032; e<sub>σ</sub>(O) = 7367; e<sub>π</sub>(O) = 1735; *B* = 685. All in cm<sup>-1</sup>

**Table 2.** The AOM parameters ( $\text{cm}^{-1}$ ) for  $\text{trans-}[\text{Cr}(\text{Me}_2\text{tn})_2\text{XY}]^{n+}$ 

| XY                     | $e_{\sigma}(\text{N})$ | $e_{\sigma}(\text{L})$ | $e_{\pi}(\text{L})$ | Ref.      |
|------------------------|------------------------|------------------------|---------------------|-----------|
| F <sub>2</sub>         | 7 175                  | 7 510                  | 1 710               | 28        |
| Cl <sub>2</sub>        | 7 360                  | 5 265                  | 860                 | 2         |
| Br <sub>2</sub>        | 7 280                  | 4 985                  | 945                 | 29        |
| (NCS) <sub>2</sub>     | 7 130                  | 6 160                  | 32                  | 5         |
| (OH)(H <sub>2</sub> O) | 7 032                  | 7 367                  | 1 735               | This work |

$B = 685 \text{ cm}^{-1}$ . The AOM parameters are reasonable and reproduce the absorption spectrum well. The  $e_{\sigma}(\text{N})$  value for primary amine nitrogen is slightly smaller than expected. Table 2 contains the comparison of the AOM parameters with the values reported in the literature<sup>2,6,28,29</sup> for the  $\text{trans-}[\text{Cr}(\text{Me}_2\text{tn})_2\text{XY}]^{n+}$  with neutral and anionic ligands. A ligand field analysis of the solution absorption spectrum indicates that the hydroxy group and water molecule are much stronger  $\sigma$ - and  $\pi$ -donor than chloride, bromide or isothiocyanate. The four nitrogen atoms of the two bidentate  $\text{Me}_2\text{tn}$  ligand have still strong  $\sigma$ -donor characteristics toward chromium(III) but it is smaller than those of other amines.

The values for  $e_{\sigma}(\text{O})$  and  $e_{\pi}(\text{O})$  are comparable to the values for various ligands.<sup>30–34</sup> The value of the Racah parameter  $B$  is about 75% of the value for a free chromium (III) ion in the gas phase. These factors as well as the AOM parameters can be used in determining the labilization modes of the photoreaction in the chromium(III) complexes and in predicting the relative efficiency of the  $3d-4f$  energy transfer in heterometal dinuclear complexes.<sup>35,36</sup>

## CONCLUSIONS

The infrared and UV-visible absorption spectra of  $\text{trans-}[\text{Cr}(\text{Me}_2\text{tn})_2(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2$  have been measured. The four electronic bands due to spin-allowed transitions were assigned. Using the observed electronic transitions, a ligand field analysis was performed in the framework of the angular overlap model. The resolved band maxima of the electronic  $d-d$  spectrum were fitted with a secular determinant for a quartet energy state of the  $d^3$  configuration in a tetragonal field including configurational but neglecting spin-orbit coupling. It was confirmed that the nitrogen atoms of the  $\text{Me}_2\text{tn}$  ligand were a strong  $\sigma$ -donor character, and the oxygen atoms of OH or H<sub>2</sub>O have strong  $\sigma$ - and  $\pi$ -donor properties toward the chromium (III).

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