

## КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF  
TRANS-DICHLOROBIS(1,3-PROPANEDIAMINE)CHROMIUM(III) PERCHLORATE© 2012 J.-H. Choi<sup>1\*</sup>, A. Takayama<sup>2</sup>, T. Suzuki<sup>2</sup><sup>1</sup>Department of Chemistry, Andong National University, Andong 760-749, South Korea<sup>2</sup>Department of Chemistry, Okayama University, Okayama 700-8530, Japan

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The crystal structure of *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> (tn = 1,3-propanediamine) is determined by a single-crystal X-ray diffraction study at 185 K. The Cr atom is in a slightly distorted octahedral environment coordinated by four nitrogen atoms of two tn ligands and two chlorine atoms in *trans* position. The orientations of two six-membered rings in the complex cation are in an *anti chair-chair* conformation with respect to each other. The mean Cr—N(tn) and Cr—Cl bond lengths are 2.0862(2) and 2.3112(6) Å respectively. The ClO<sub>4</sub><sup>-</sup> anions have a slightly distorted tetrahedral geometry with Cl—O lengths and O—Cl—O angles influenced by the hydrogen bonding. The crystal packing is stabilized by several hydrogen bonds. The infrared and electronic absorption spectral properties are also described along with the results of X-ray crystallography.

**Keywords:** crystal structure, *trans*-isomer, chromium(III) complex, 1,3-propanediamine, spectral properties.

The bidentate 1,3-propanediamine (tn) ligand forms a six-membered chelate ring with a flattened chair conformation in chromium(III) complexes [1]. The study of geometrical and conformational isomers in octahedral transition metal complexes with bidentate amines has been an area of intense activity and has provided much basic structural information and spectroscopic properties [2]. The [Cr(tn)<sub>2</sub>L<sub>2</sub>]<sup>+</sup> cation adopts *trans* or *cis* geometric isomers. Furthermore, the *trans* isomer can exist in either of two conformations, as shown in Fig. 1. The carbon atoms of the two chelate rings of tn ligands can be located on the same side (*syn* conformer) or on the opposite side (*anti* conformer) of the equatorial plane. We have recently described the crystal structure and spectral properties of *trans*-dichlorobis(2,2-dimethyl-1,3-propanediamine)chromium(III) system [3,4]. The structural analysis of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]Cl (2,2-dimethyl-1,3-propanediamine = Me<sub>2</sub>tn) shows that there are two crystallographically independent Cr complex cations that are *anti* and *syn* conformational isomers with respect to the two *chair-chair* chelate rings [3]. However, the case of *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> indicates that two chelate rings of Me<sub>2</sub>tn ligands are only in the *anti chair-chair* conformation [4]. These different conformational arrangements of the two six-membered chelate rings may be dependent on the packing forces and counter anions in the crystal structure [5]. The elucidation of the factors that stabilize either the *syn*- or *anti*-conformation in this type complex continues to be of interest.

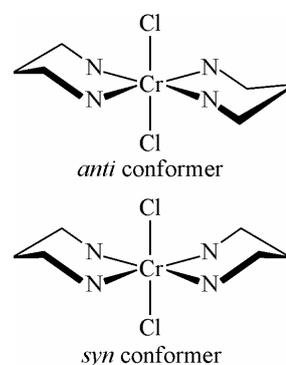


Fig. 1. Two possible conformational isomers of *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>

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X-ray crystallography is generally used to establish the presence of either conformation because this cannot be established using the methods such as infrared and electronic absorption spectroscopy.

The preparation, hydrolysis kinetics, and spectral data of dichlorochromium(III) complexes containing propane-1,3-diamine as a bidentate ligand have been reported, but have not been structurally characterized [ 6—8 ].

As part of our ongoing research, in this paper, we describe the spectroscopic and structural properties of *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> with the purpose of obtaining information on the conformation of the two six-membered chelate rings and verify its geometrical assignment by the spectroscopic method.

**Experimental. Reagents, synthesis, and physical measurements.** 1,3-Propanediamine was obtained from Aldrich Chemical Co. and used as supplied. All chemicals were reagent grade materials and used without further purification. As starting materials, *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]Br was prepared as described in the literature [ 8 ]. Recrystallization of the crude bromide salt from 0.5 M hydrochloric acid at 40 °C and 60 % HClO<sub>4</sub> solution afforded green crystals suitable for X-ray analysis.

The mid-infrared spectrum was obtained with a Mattson Infinities series FT—IR spectrometer using a KBr pellet. The room-temperature UV-visible absorption spectrum was recorded with a HP 8453 diode array spectrophotometer. Analyses for C, H, and N were determined on a Carlo Erba 1108 Elemental Vario EL analyzer. *Anal.* Found: C, 19.55; H, 5.23; N, 14.91 %. *Calc.* for *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]·ClO<sub>4</sub>: C, 19.45; H, 5.44; N, 15.12 %.

**Crystal structure analysis.** Single crystal X-ray diffraction data were collected on a Rigaku R-Axis Rapid II diffractometer using graphite—monochromated MoK<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $-88(2) \text{ }^\circ\text{C}$ . Data were processed by the Process-Auto program package [ 9 ] and absorption correction was applied by the numerical integration method from the crystal shape [ 10 ]. The structure was solved by direct methods using SIR2004 [ 11 ] and refined by full-matrix least-squares on  $F^2$  using SHELXL97 [ 12 ]. Non-hydrogen atoms were refined anisotropically. The H atoms were placed geometrically and refined using a riding model (with N—H = 0.92 and C—H = 0.99  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N or C})$ ). All calculations were carried out using the CrystalStructure software package [ 13 ]. The crystal data and details of data collection together with the refinement procedure are given in Table 1. Molecular graphics were produced using DIAMOND-3 [ 14 ].

**Results and Discussion. Structural properties.** The single crystal X-ray structure determination was carried out at 185(2) K. The structure analysis demonstrated the monoclinic  $P2_1/c$  space group with  $Z = 4$ . Selected bond lengths and angles are listed in Table 2. An ellipsoid plot (50 % probability level) of *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>, together with the atom labeling scheme, is depicted in Fig. 2.

In the title complex, the chromium ion adopts an octahedral geometry, where four nitrogen atoms of two tn ligands occupy the equatorial sites and two chlorine atoms coordinate to the Cr metal centre in *trans* configuration. The complex cation has an approximately molecular  $C_i$  symmetry. The six-membered rings are in stable *chair* conformations, and the N1—Cr1—N5 and N6—Cr1—N10 angles are  $91.11(5)^\circ$  and  $90.48(5)^\circ$  respectively. Two chelate rings in the chromium(III) complex cation adopt *anti chair-chair* conformation with respect to each other.

The Cr—N bond distances in the tn complex are in the range of 2.0868(13)  $\text{\AA}$  to 2.0931(13)  $\text{\AA}$  and these lengths are in agreement with those observed in *trans*-[Cr(Me<sub>2</sub>tn)Cl<sub>2</sub>]Cl, *cis*- $\beta$ -[Cr(2,2,3-tet)Cl<sub>2</sub>]·ClO<sub>4</sub>, and *trans*-[Cr(en)<sub>2</sub>Br<sub>2</sub>]ClO<sub>4</sub> [ 3, 15—17 ]. The Cl—Cr—Cl angle is  $179.079(18)^\circ$ , and the Cr—Cl distances [ 2.3184(4) and 2.3196(4)  $\text{\AA}$  ] are very close to the values of 2.3179(9)  $\text{\AA}$  and 2.3212(4)  $\text{\AA}$  found in *trans*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> [ 6 ].

The uncoordinated ClO<sub>4</sub><sup>−</sup> anions remain outside the coordination sphere. The perchlorate anion shows a distorted tetrahedral arrangement of oxygen atoms around the central chlorine atom with Cl—O distances in the range of 1.4250(14)—1.4354(14)  $\text{\AA}$  and the O—Cl—O angles ranging from  $107.96(9)^\circ$  to  $110.43(10)^\circ$ . Table 3 contains the distances and angles of hydrogen bonds in which the extensive hydrogen-bonded networks are formed. It seems that the whole crystal structure is stabilized by the intermolecular hydrogen bonds and short contacts.

**Spectroscopic Properties.** Infrared spectroscopy is useful in assigning the configuration of *cis* and *trans* isomers of diacidobis(diamine)chromium(III) complexes [ 18 ].

Table 1

Crystal data and structure refinement for *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>

Chemical formula	C <sub>6</sub> H <sub>20</sub> Cl <sub>3</sub> CrN <sub>4</sub> O <sub>4</sub>
Formula weight	370.61
Temperature, K	185(2)
Radiation, wavelength, Å	MoK <sub>α</sub> , 0.71075
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell parameters <i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg.	6.4402(4), 17.2894(13), 13.0851(8); 92.899(2)
Cell volume, Å <sup>3</sup>	1455.12(17)
<i>Z</i>	4
Calculated density, Mg·m <sup>-3</sup>	1.692
Absorption coefficient, mm <sup>-1</sup>	1.35
<i>F</i> (000)	764
Crystal color and size, mm	Green, 0.20×0.15×0.10
Data collection method	Rigaku RAXIS-RAPID diffractometer ω scans
θ range for data collection, deg.	3.1 to 27.5
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	-7 to 8, -22 to 22, -16 to 16
Reflections collected	14159
Independent reflections	3322 ( <i>R</i> <sub>int</sub> = 0.021)
Reflections with <i>F</i> <sup>2</sup> > 2σ	3014
Absorption correction	Numerical integration
Min. and max. transmission	0.774 and 0.877
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Weighting parameters <i>a</i> , <i>b</i>	0.0224 and 0.8553
Data / restraints / parameters	3322 / 0 / 164
Final <i>R</i> indices [ <i>F</i> <sup>2</sup> > 2σ]	<i>R</i> <sub>1</sub> = 0.023, <i>wR</i> <sub>2</sub> = 0.054
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.027, <i>wR</i> <sub>2</sub> = 0.058
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.102
Extinction coefficient	None
Largest difference map peak and hole, e·Å <sup>-3</sup>	-0.23 and 0.46

The O—H stretching absorption near 3435 cm<sup>-1</sup> and broadness of the band indicate that there are hydrogen bonds in this complex. The infrared spectrum shows strong bands in 3100—3300 cm<sup>-1</sup> and 2800—3000 cm<sup>-1</sup> regions due to the symmetric and antisymmetric N—H and C—H stretching modes respectively. The strong absorption bands at 1552 cm<sup>-1</sup> and 1463 cm<sup>-1</sup> and 1445 cm<sup>-1</sup> can be assigned to NH<sub>2</sub> and CH<sub>2</sub> bending modes respectively. The very strong absorptions at 1089 cm<sup>-1</sup> and 627 cm<sup>-1</sup> are due to the ν<sub>a</sub>(Cl—O) stretching and δ<sub>d</sub>(OCIO) bending modes of the perchlorate anion. 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 region from 760 cm<sup>-1</sup> to 900 cm<sup>-1</sup> was found to be one of the best regions for distinguishing the *trans* and *cis* isomers of octahedral chromium(III)

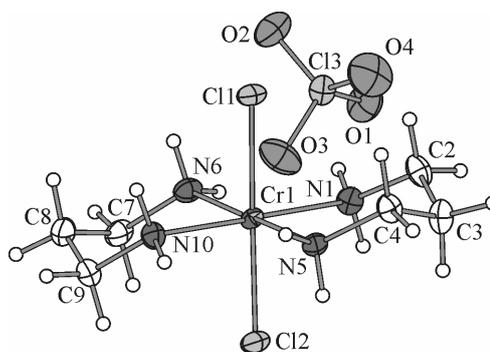


Fig. 2. Perspective view (50% probability level) of *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>

Table 2

Selected bond distances (Å) and angles (deg.) for *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>

Cr1—N1	2.0931(13)	N6—C7	1.491(2)	Cl3—O2	1.4281(14)
Cr1—N6	2.0868(13)	C2—C3	1.515(2)	Cl3—O4	1.4250(14)
Cr1—Cl1	2.3196(4)	C8—C7	1.514(3)	N5—C4	1.493(2)
Cl3—O1	1.4345(14)	Cr1—N5	2.0915(13)	N10—C9	1.495(2)
Cl3—O3	1.4354(14)	Cr1—N10	2.0910(14)	C3—C4	1.516(2)
N1—C2	1.491(2)	Cr1—Cl2	2.3184(4)	C8—C9	1.512(3)
N6—Cr1—N5	178.48(5)	C4—N5—Cr1	119.99(9)	N10—Cr1—Cl1	89.11(4)
N10—Cr1—N5	90.48(5)	N1—C2—C3	111.70(14)	N5—Cr1—Cl1	88.84(4)
N5—Cr1—N1	91.11(5)	N5—C4—C3	112.35(13)	N1—Cr1—Cl1	91.35(4)
N6—Cr1—Cl2	90.71(4)	C9—N10—Cr1	119.41(11)	C2—N1—Cr1	120.34(10)
N5—Cr1—Cl2	90.33(4)	N6—Cr1—N10	88.39(6)	C2—C3—C4	113.64(14)
N1—Cr1—Cl2	88.26(4)	N6—Cr1—N1	90.02(5)	C9—C8—C7	114.78(14)
N10—Cr1—Cl2	91.30(4)	N10—Cr1—N1	178.35(5)	N10—C9—C8	112.40(14)
C7—N6—Cr1	120.50(10)	N6—Cr1—Cl1	90.12(4)	N6—C7—C8	111.39(14)

complexes [19–21]. It has been suggested that the *cis* isomer exhibits at least three bands in the 830–900 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> mainly due to the methylene vibration [3, 22, 23]. The title complex exhibits one band at 879 cm<sup>-1</sup> in the NH<sub>2</sub> rocking frequency region. The CH<sub>2</sub> rocking band is observed at 807 cm<sup>-1</sup>.

Metal-ligand stretching bands occur in the far infrared range. Differences in the 560–400 cm<sup>-1</sup> region are of interest as they can be used to distinguish the *cis* and *trans* isomers of diacidobis(diamine)chromium(III) complexes. All *trans* complexes show three bands in this region, whereas all the *cis* complexes show four strong bands. In the far IR spectral range of *trans*-[CrN<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> complex with *D*<sub>4h</sub> symmetry, the group theory analysis predicts two Cr—N and one Cr—Cl infrared-active stretching vibrations respectively. The title complex shows a pattern of three main bands: one strong band at 501 cm<sup>-1</sup> and other medium bands at 488 cm<sup>-1</sup> and 434 cm<sup>-1</sup>. The latter two absorptions can be assigned to the Cr—N stretching modes. The IR spectral properties are in agreement with the geometry of *trans* configuration.

The *d-d* absorption spectra have also been used to distinguish between the geometrical isomers of some chromium(III) complexes with mixed ligands [24]. The visible absorption spectrum of *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub> in an aqueous solution exhibits two main bands; one at 16260 cm<sup>-1</sup> ( $\nu_1$ ) and another at 25640 cm<sup>-1</sup> ( $\nu_2$ ), corresponding to <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 one quartet band has a shoulder peak at 21505 cm<sup>-1</sup> and shows an asymmetric profile. This property of the

Table 3

Hydrogen bonding geometry (Å, deg.) for *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]ClO<sub>4</sub>

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>	<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O2 <sup>i</sup>	0.92	2.33	3.195 (2)	156	N5—H5B...Cl1 <sup>i</sup>	0.92	2.62	3.379 (1)	140
N1—H1B...O4	0.92	2.32	3.152 (2)	151	N10—H10A...O1 <sup>iii</sup>	0.92	2.19	3.045 (2)	154
N1—H1B...O3	0.92	2.53	3.331 (2)	146	N6—H6A...Cl2 <sup>iv</sup>	0.92	2.55	3.323 (1)	142
N5—H5A...Cl1 <sup>ii</sup>	0.92	2.77	3.540 (1)	142	N6—H6B...O3	0.92	2.13	3.006 (2)	160

Symmetry codes: (i) *x*+1, *y*, *z*; -*x*+1, -*y*, -*z*+1; (iii) -*x*+1, *y*-1/2, -*z*+1/2; (iv) *x*-1, *y*, *z*.

quartet band is indicative of *trans* configuration. The UV-visible and infrared spectral properties of the complex are consistent with the *trans* geometry, but the spectroscopic data do not give any evidence whether *trans*-[Cr(tn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> has *syn* or *anti* conformation of the two six-membered chelate rings in the crystals.

**Conclusions.** The infrared and electronic spectroscopic properties of the title complex are in good agreement with the result of X-ray crystallography, which shows that the chromium atom is in the octahedral environment, coordinated by two bidentate 1,3-propanediamine ligands and two chlorine atoms in *trans* positions. The carbon atoms of the two tn chelate rings in the chromium(III) complex cation adopt a stable *anti* conformation on the equatorial coordination plane.

**Supplementary material.** Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 798641. Copies of this information may be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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