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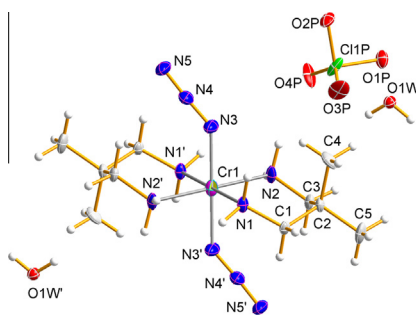
# Synthesis, conformational structure and spectroscopic properties of *trans*-diazidobis(2,2-dimethyl-1,3-propanediamine)chromium(III) perchlorate

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## HIGHLIGHTS

- Synthesis of a new chromium(III) complex with diazido groups.
- Crystal structure from synchrotron radiation.
- Spectral properties by IR and electronic absorption spectroscopy.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new complex *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O, where Me<sub>2</sub>tn = 2,2-dimethyl-1,3-propanediamine was synthesized and characterized, and its molecular structure was established by single-crystal X-ray diffraction at 95 K. The complex crystallized in the space group C2/c of the monoclinic system with four mononuclear formula units in a cell of dimensions  $a = 16.600$  (3),  $b = 7.709$  (2),  $c = 16.865$  (3) Å, and  $\beta = 99.07$  (3)°. The chromium(III) atom was in a distorted octahedral coordination with four N atoms of two chelating Me<sub>2</sub>tn ligands and two N atoms of the azido group in the *trans* axial position. The two six-membered rings in the complex adopted only *anti* chair–chair conformations with respect to each other. The important bond lengths are Cr–N(azide) 2.007 (2), Cr–N(Me<sub>2</sub>tn) 2.081 (2), 2.082 (2), N–N(azide) 1.184 (2) and 1.156 (2) Å, respectively. The crystal lattice is stabilized by hydrogen bonding interactions among the ClO<sub>4</sub><sup>-</sup>, hydrate molecule, N<sub>3</sub><sup>-</sup>, and NH groups of the Me<sub>2</sub>tn ligand. The ligand field analysis as well as the IR and electronic spectral properties were described.

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## Introduction

The study of conformational isomerism in octahedral transition metal complexes with mixed ligands has generated considerable interest, and has provided much basic structural information and spectroscopic properties [1]. Information about geometrical isom-

erism and conformation of various ligands in the metal complexes is important in medical applications, and likely to be a major factor in determining antiviral activity and related side-effect [2–4]. 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 a six-membered chelate ring with a chair conformation [5]. 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 (Fig. 1).

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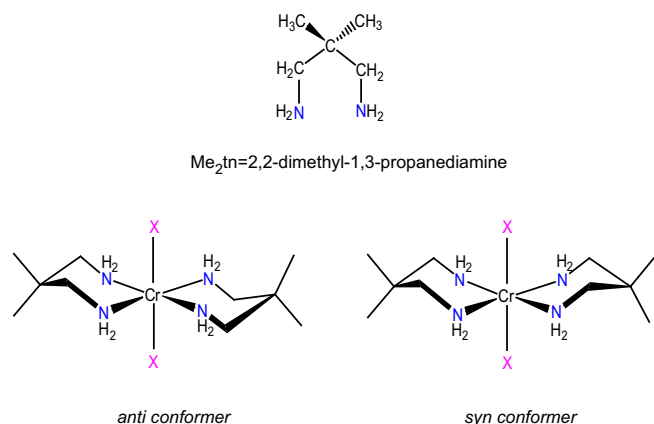
E-mail address: [jhchoi@anu.ac.kr](mailto:jhchoi@anu.ac.kr) (J.-H. Choi).

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 and *trans-anti/syn*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Br<sub>2</sub>]<sub>2</sub>Br<sub>2</sub>·HClO<sub>4</sub>·H<sub>2</sub>O, crystallographically independent *syn* and *anti* conformational isomers were found within the same crystals [6–8]. However, structural analyses of *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>, *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(NCS)<sub>2</sub>]NCS·1/2H<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>]<sub>2</sub>ZnCl<sub>4</sub> indicated that two chelate rings of the Me<sub>2</sub>tn ligands are only in the *anti* chair–chair conformation [8–11]. The different arrangements of the two six-membered chelate rings of Me<sub>2</sub>tn ligands may be dependent on the crystallographic disorder, packing forces, hydrate molecules and counter anions in the crystal structure. The factors that determine the stability of these geometric conformations are subtle, and complicated [6–11]. X-ray crystallography is typically used to determine the presence of either conformation, as infrared and visible absorption spectroscopy cannot readily discriminate between the *syn* or *anti* conformers of the six-membered chelate rings. The coordination behavior of the azido ion (N<sub>3</sub><sup>-</sup>) is also of interest because the azide can bind to metal ions in a number of coordination modes, giving rise to mononuclear, dinuclear and polynuclear complexes. Multiple types of azido ligand bonding have been observed in metal complexes, including simple monodentate and bridging end-on (1,1-μ) or end-to-end (1,3-μ) ligands. The coordination mode of the azido ligand depends on the nature and oxidation state of the central metal ion, as well as the steric and electronic effects of other ligands present [12]. However, the geometric assignment and determination of coordinating mode based on spectral properties are not always conclusive [13,14].

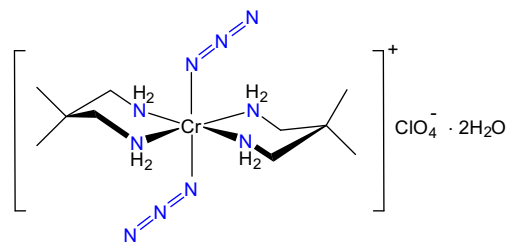
Elucidation of the factors that stabilize the *syn*- or *anti*-conformation in these complex cations continues to be of interest. In this paper, we report the synthesis, crystal structure and spectroscopic characterization of *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O (Scheme 1) in order to obtain definite information on the conformation referring to the position of the carbon atoms of the Me<sub>2</sub>tn chelate rings with respect to the equatorial coordination plane and confirm the bonding mode of the azido ligand in axial positions.

## Experimental

**Caution!** Although we experienced no difficulty with the perchlorate salt of the azido complex described in this paper, this should be regarded as a potentially explosive compound and treated with care.



**Fig. 1.** Structure of ligand Me<sub>2</sub>tn and two possible conformational isomers of *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>X<sub>2</sub>]<sup>+</sup>.



**Scheme 1.** Chemical structure of *trans-anti*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>·2H<sub>2</sub>O.

## 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. The starting material, *trans-anti/syn*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]Cl was prepared as described previously [27]. The *trans-anti/syn*-[Cr(Me<sub>2</sub>tn)<sub>2</sub>Cl<sub>2</sub>]Cl (1.8 g, 5 mmol) and NaN<sub>3</sub> (0.65 g, 10 mmol) were suspended in 10 ml of water and the mixture was heated at 60 °C for 10 min. Then 2 ml of saturated solution of NaClO<sub>4</sub> was added and heating was continued for a further 90 min to produce a violet solution. The solution was allowed to stand at room temperature for 1–2 days to give the purple crystals suitable for X-ray structural analysis. Yield 62%. Anal. Calcd. for Cr(C<sub>10</sub>H<sub>28</sub>N<sub>10</sub>)ClO<sub>4</sub>·2H<sub>2</sub>O (%): C, 25.24; H, 6.78; N, 29.43. Found: C, 25.61; H, 6.44; N, 29.02. Visible spectral data for an aqueous solution, λ<sub>max</sub> in nm (ε in M<sup>-1</sup> cm<sup>-1</sup>): 397 (99.1), 544 (162.6). IR spectrum (KBr, cm<sup>-1</sup>): 3575 br and 3466 br and 539 s (ν OH), 3270 vs and 3109 vs (ν NH), 2964 vs and 2878 m (ν CH), 2065 vs (ν<sub>as</sub> N<sub>3</sub>), 1590 vs (δ NH<sub>2</sub>), 1476 vs (δ CH<sub>2</sub>), 1417 s, 1357 m (ν<sub>s</sub> N<sub>3</sub>), 1345 m, 1276 m, 1223 s, 1142 vs 1120 vs (ν CN), 1089 vs (ν<sub>as</sub> ClO), 1040 vs 987 vs 896 s (ρ NH<sub>2</sub>), 778 s (ρ CH<sub>2</sub>), 667 s, 636 vs 627 vs (δ OClO), 554 s, 443 s and 417 s (ν Cr–N).

## Physical measurements

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

## Crystal structure analysis

A block-shaped purple crystal of the title complex with approximate dimensions 0.22 mm × 0.15 mm × 0.14 mm was coated with paratone-*N* oil to prevent crystallinity losses on exposure to air. The diffraction data were measured with synchrotron radiation on a 2D SMC ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator (0.62998 Å) at the Pohang Accelerator Laboratory, Korea and a nitrogen cold stream (100 K). The ADSC Quantum-210 ADX program [15] was used for data collection, and HKL3000sm (Ver. 703r) [16] was used for cell refinement, reduction, and absorption correction. The structures were solved by direct methods with SHELX-XS (2013) program and refined by full-matrix least-squares calculations with the SHELX-XL (2013/2) program package [17]. Molecular graphics were produced using DIAMOND-3 [18]. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were first located in a difference map, then N–H hydrogen atoms were refined with distance restraints and C–H hydrogen atoms were constrained to ride on the parent carbon atom, with C–H = 0.98 Å and U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C) for methyl groups, and C–H = 0.99 Å and U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C) for methylene

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