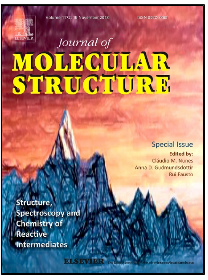

# Synthesis, molecular structure, and spectroscopic properties of tris[*trans*-diazidobis(2,2-dimethylpropane-1,3-diamine)chromium(III)]bis[tertaazido(2,2-dimethylpropane-1,3-diamine)chromium(III)] perchlorate

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# Synthesis, molecular structure, and spectroscopic properties of tris[*trans*-diazidobis(2,2-dimethylpropane-1,3-diamine)chromium(III)]bis[tertaazido(2,2-dimethylpropane-1,3-diamine)chromium(III)] perchlorate

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## Abstract

A new double complex, [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$ ($Me_2tn$ = 2,2-dimethylpropane-1,3-diamine), was prepared, and its structure determined through single-crystal X-ray diffraction at 100 K. The complex crystallizes in the space group *C2/c* of the monoclinic system with $a$ = 34.255(7), $b$ = 11.067(2), $c$ = 24.137(5) Å, and $\beta$ = 120.64(3)°. The asymmetric unit contains one half of a centrosymmetric *trans*-*anti*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cation, one independent *trans*-*syn*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cation, one *cis*-$[Cr(N_3)_4(Me_2tn)]^-$ anion, and one half of a perchlorate anion. In two independent complex cations, the $Cr^{III}$ ions are each coordinated by four N atoms of two chelating $Me_2tn$ and two N atoms of the azido group in a distorted octahedral geometry, whereas the $Cr^{III}$ ion in *cis*-$[Cr(N_3)_4(Me_2tn)]^-$ has a distorted octahedral coordination with two N atoms of one $Me_2tn$ and four N atoms of the azido group. Interestingly, the six-membered rings in two *trans*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cations adopt *anti* and *syn* chair-chair conformations, independently. The Cr–N($Me_2tn$) bond lengths vary from 2.0556 (15) to 2.0992 (19) Å, whereas the Cr–N(azido) bond lengths range from 2.0205(16) to 2.0428 (16) Å. The perchlorate anion is disordered over two sets of sites, and has a distorted tetrahedral geometry. The crystal lattice is stabilized through hydrogen bonding interactions between the nitrogen of $N_3^-$ and the NH groups of the $Me_2tn$ ligand. The IR and electronic absorption spectral properties are also discussed herein.

*Keywords:*

Crystal structure

*anti*-*syn*-Conformers

Double chromium(III) complex

$N_3^-$ Coordination mode

Spectral properties

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## 1. Introduction

The study on geometrical and conformational isomerism in transition metal complexes with chelating ligands has been an area of intense activity, and has provided a significant amount of basic structural information and insight into their spectroscopic properties [1-3]. The geometrical isomers or conformers of various ligands in metal complexes are quite important in terms of medical application, and are likely to be a major factor in determining an antiviral activity and toxic effect [4-7]. 2,2-dimethylpropane-1,3-diamine ($Me_2tn$) and propane-1,3-diamine (tn) can act as a bidentate ligand to a central metal ion through its two nitrogen atoms, forming a six-membered chelate ring with a chair, a boat, and a twist or skew-boat conformation [1, 2]. A $[CrX_2(Me_2tn)_2]^+$ (X = monodentate) cation can form either a *trans* or *cis* geometric isomer. In addition, two different types of conformations with respect to the chelate rings of $Me_2tn$ ligand occur in a *trans* isomer, as shown at the bottom of Fig. 1. The carbon atoms of the two chelate rings of the two conformers can be on the same side (*syn* conformer) or on opposite sides (*anti* conformer) of the equatorial coordination plane.

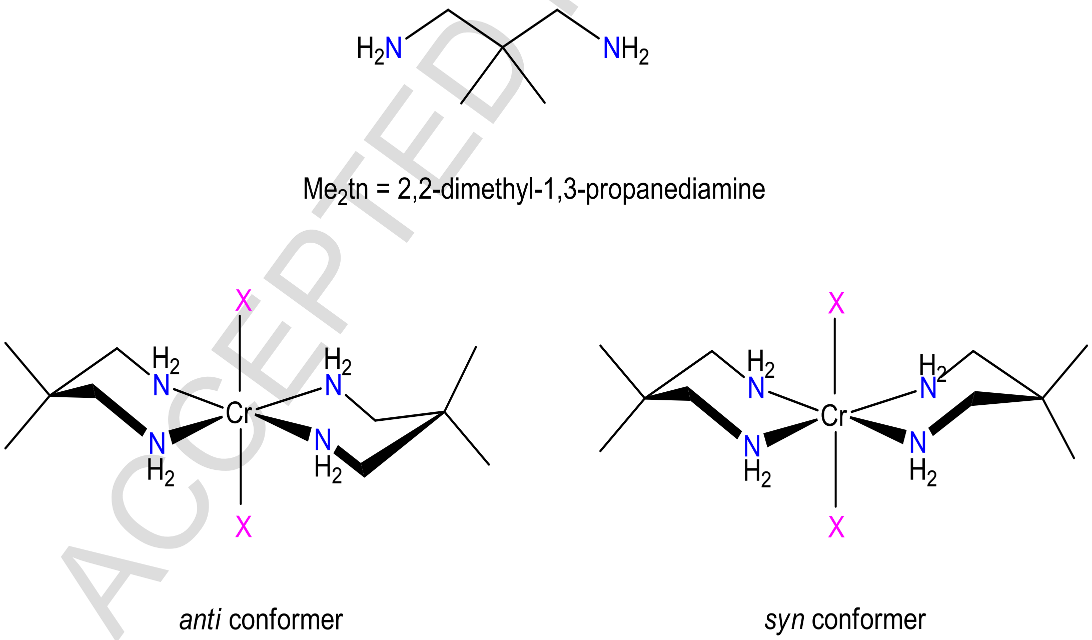
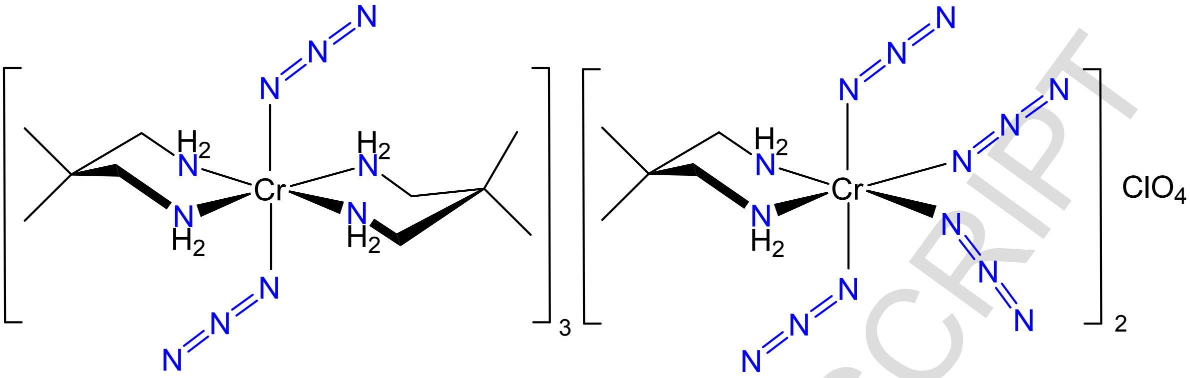


**Fig. 1.** The structures of $Me_2tn$ and two possible conformational isomers of *trans*-$[CrX_2(Me_2tn)_2]^+$

Structural analyses of *trans-anti*-$[CrCl_2(Me_2tn)_2]ClO_4$, *trans-anti*-$[CrBr_2(Me_2tn)_2]ClO_4$, *trans-anti*-$[CrCl_2(Me_2tn)_2]_2ZnCl_4$, *trans-anti*-$[Cr(NCS)_2(Me_2tn)_2]NCS\cdot 1/2H_2O$, *trans-anti*-$[Cr(N_3)_2(Me_2tn)_2]ClO_4\cdot 2H_2O$, and *trans-anti*-$[Cr(OH)(H_2O)(Me_2tn)_2](ClO_4)_2$ revealed that two chelate rings of $Me_2tn$ ligands adopt only an *anti* chair-chair conformation [8-13]. However, in the case of *trans-anti/syn*-$[CrCl_2(Me_2tn)_2]Cl$, *trans-anti/syn*-$[CrBr_2(Me_2tn)_2]Br$, and *trans-anti/syn*-$[CrBr_2(Me_2tn)_2]_2Br_2\cdot HClO_4\cdot H_2O$, both independent *syn* and *anti* conformers were found within the same crystal [14-16]. Additionally, the two chelate rings of $Me_2tn$ ligands in *trans-syn*-$[Cr(N_3)_{0.8}Cl_{1.2}(Me_2tn)_2]ClO_4$ were found to be only in a *syn* chair-chair conformation [17]. The different arrangements of the two six-membered chelate rings of a $Me_2tn$ ligand may be dependent on the packing force, hydrate molecule, and counter anion within the crystal. It seems that the factors determining the stability of these geometric conformations are subtle and more complicated. Because infrared and electronic absorption spectroscopy cannot readily discriminate between *syn* and *anti* conformers of the six-membered chelate rings, X-ray crystallography is typically used to determine the presence of either conformation.

Furthermore, the coordination behavior of an azide ion ($N_3^-$) is of interest because it can bind to metal ions in a number of coordination modes, giving rise to mononuclear, dinuclear, and polynuclear complexes [18]. 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 the other ligands present. It should be noted that, based on spectroscopic studies, the geometric assignment and determination of the coordinating mode are much less conclusive.

The elucidation of the factors stabilizing either a *syn* or *anti* conformation continues to be of interest. As an extension of our investigation on chromium(III) complexes with different conformers, we describe herein the preparation, crystal structure, and spectroscopic properties of the title compound (**Scheme 1**) to determine the bonding mode of the azido ligand, and obtain definite information on the conformation referring to the position of the carbon atoms of the $Me_2tn$ chelate rings.



**Scheme 1.** Chemical structure of [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$

## 2. Experimental

Although we experienced no difficulty when applying the perchlorate salt of the azido complex described in this paper, as a cautionary measure, it should be regarded as a potentially explosive compound and treated with significant care.

### *2.1. Materials and synthesis*

The free ligand 2,2-dimethylpropane-1,3-diamine 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*-$[CrCl_2(Me_2tn)_2]Cl$, was prepared as previously described [19]. Sodium azide (0.65 g, 10 mmol) was added to an aqueous suspension (10 mL) of *trans*-$[CrCl_2(Me_2tn)_2]Cl$ (0.73 g, 2 mmol). The mixture was heated at 55 °C for 10 minutes. Sodium perchlorate (1.22 g, 10 mmol) was then added, and heating was continued for a further 120 min. The resulting solution was filtered, and the filtrate was allowed to stand at room temperature for 5 days to afford single crystals of [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$ suitable for a structural X-ray analysis. *Anal.* Found: C, 26.94; H, 6.24; N, 46.43%. Calc. for $[C_{10}H_{28}N_{10}Cr]_3[C_5H_{14}N_{14}Cr]_2ClO_4$: C, 27.22; H, 6.40; N, 46.02%. The visible spectral data for an aqueous solution, $\lambda_{max}$ in nm ($\varepsilon$ in $M^{-1}$ $cm^{-1}$), are as follows: 428 (343), 557 (427). The IR spectrum (KBr, $cm^{-1}$) shows the following: 3379 m and

3330 w ($\nu_a$ $N_3$ + $\nu_s$ $N_3$), 3290 s, 3277 vs, 3243 vs, 3166 s and 3098 s ($\nu$ NH), 2959 vs, 2913 m and 2875 s ($\nu$ CH), 2110 vs and 2050 vs ($\nu_a$ $N_3$), 1591 vs ($\delta$ $NH_2$), 1476 vs ($\delta$ $CH_2$), 1414 s, 1367 m, 1341 vs and 1293 m ($\nu_s$ $N_3$), 1223 s, 1194 m, 1160 vs, 1132 vs ($\nu$ CN), 1107 vs and 1094 vs ($\nu_a$ Cl–O), 1039 s, 987 vs, 895 s (ρ $CH_2$), 781 s (ρ $NH_2$), 768 m, 653 vs, 640 s, 624 s ($\delta$ OClO), 599 w, 551 s ($\nu$ Cr–N + ring def.), 451 m ($\nu$ Cr–N).

### *2.2. Physical measurements*

The UV-visible absorption spectrum was recorded using an HP 8453 diode array spectrophotometer. The mid-infrared spectrum was obtained from KBr pellets using a JASCO 460 plus series FT-IR spectrometer. Analyses for C, H, and N were conducted on a Carlo Erba 1108 Elemental Vario EL analyzer.

### *2.3. Crystal structure analysis*

A plate of cobalt blue crystal of the title complex having approximate dimensions of 0.25 × 0.11 × 0.05 mm was coated with paratone-*N* oil because the crystal loses its crystallinity upon exposure to air. The diffraction data were measured using an ADSC Quantum-210 detector at BL2D-SMC with a silicon (111) double-crystal monochromator (0.62998 Å) at the Pohang Accelerator Laboratory, Korea, using synchrotron radiation and a nitrogen cold stream. The PAL BL2D-SMDC program [20] was used for data collection, and HKL3000sm (Ver. 715) [21] was used for cell refinement, reduction, and absorption correction. The structure was solved using the intrinsic phasing method with SHELXT-2015 program [22] and refined through full-matrix least-squares calculations under the SHELXL-2015 program [22]. Molecular and packing diagrams were produced using DIAMOND-4 [23].

Non-hydrogen atoms were refined anisotropically; hydrogen atoms were first located on a difference map, and N–H hydrogen atoms were then 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 $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl groups, and C–H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the methylene groups. The crystallographic experiment data and refinement parameters are summarized in Table 1.

**Table 1.** Crystallographic data for [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$

| | |
|---|---|
| Empirical formula | $C_{40}H_{112}ClCr_5N_{58}O_4$ |
| Formula weight | 1765.32 g mol$^{-1}$ |
| Temperature | 100(2) K |
| Wavelength | 0.62998 Å |
| Crystal system, space group | Monoclinic, *C*2/*c* |
| Unit cell dimensions | $a$ = 34.255(7) Å |
| | $b$ = 11.067(2) Å $\beta$ = 120.64(3)° |
| | $c$ = 24.137(5) Å |
| Volume | 7873(3) Å$^3$ |
| *Z* | 4 |
| Density (calculated) | 1.489 Mg m$^{-3}$ |
| Absorption coefficient | 0.561 mm$^{-1}$ |
| *F*(000) | 3708 |
| Crystal size | 0.25 × 0.11 × 0.05 mm$^3$ |
| Theta range for data collection | 1.742 to 25.00° |
| Reflections collected | 38561 |
| Independent reflections | 9916 [$R_{int}$ = 0.0330] |
| Completeness to theta = 29.99° | 99.5 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 1.000 and 0.876 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 9916 / 1 / 516 |
| Goodness-of-fit on $F^2$ | 1.055 |
| Final R indices [$F^2 > 2$] | $R_1$ = 0.0425, $wR_2$ = 0.1175 |
| R indices (all data) | $R_1$ = 0.0448, $wR_2$ = 0.1193 |
| Extinction coefficient | 0.0050(3) |
| Largest diff. peak and hole | 2.275 and -0.866 e Å$^{-3}$ |

## 3. Results and discussion

### *3.1. Spectroscopic properties*

The UV-visible absorption spectrum of [*trans*-Cr$(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$ in an aqueous solution at room temperature is presented in Fig. 2.

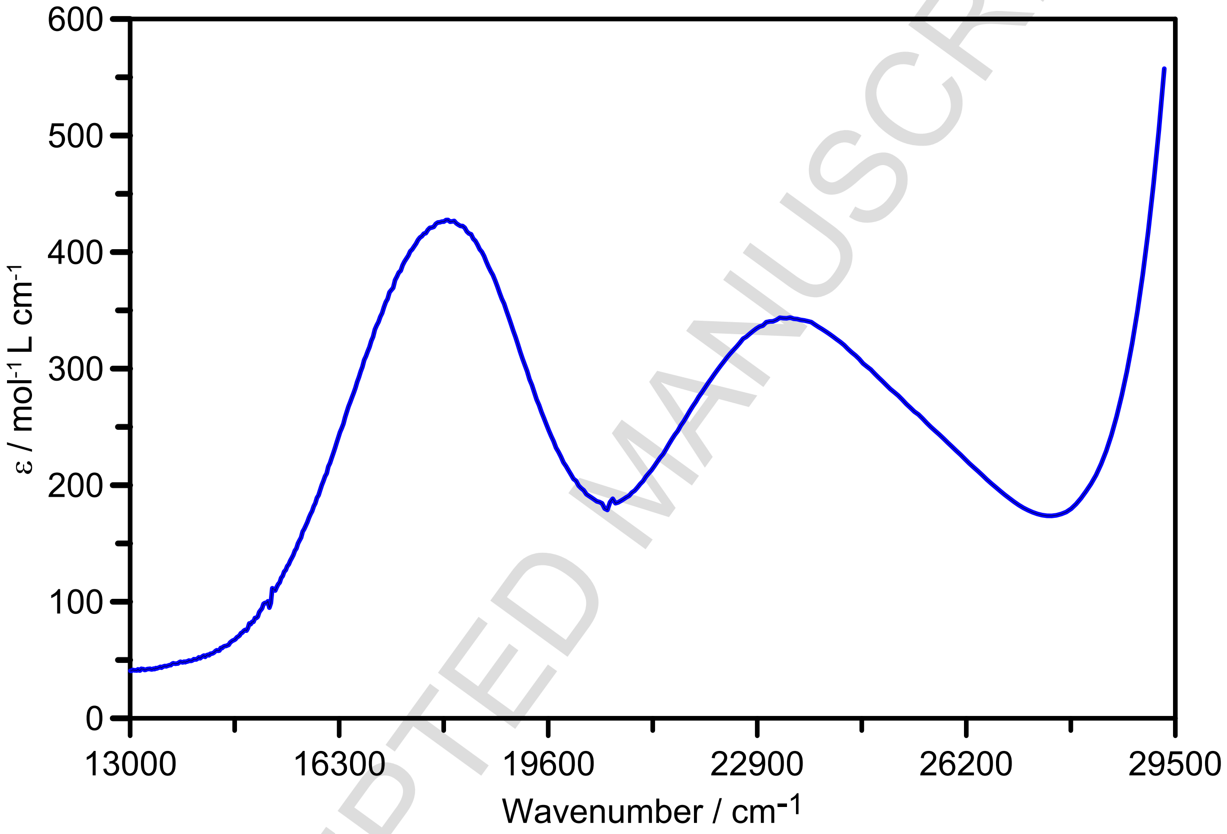


**Fig. 2.** The UV-visible absorption spectrum of [*trans*-Cr$(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$ in aqueous solution.

The three lowest terms of the Cr(III) free ion $3d^3$ configuration, i.e., $^4F$, $^4P$, and $^2G$ (where $^4F$ is the ground state) are reduced in an octahedral environment as follows [24]:

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

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

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

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

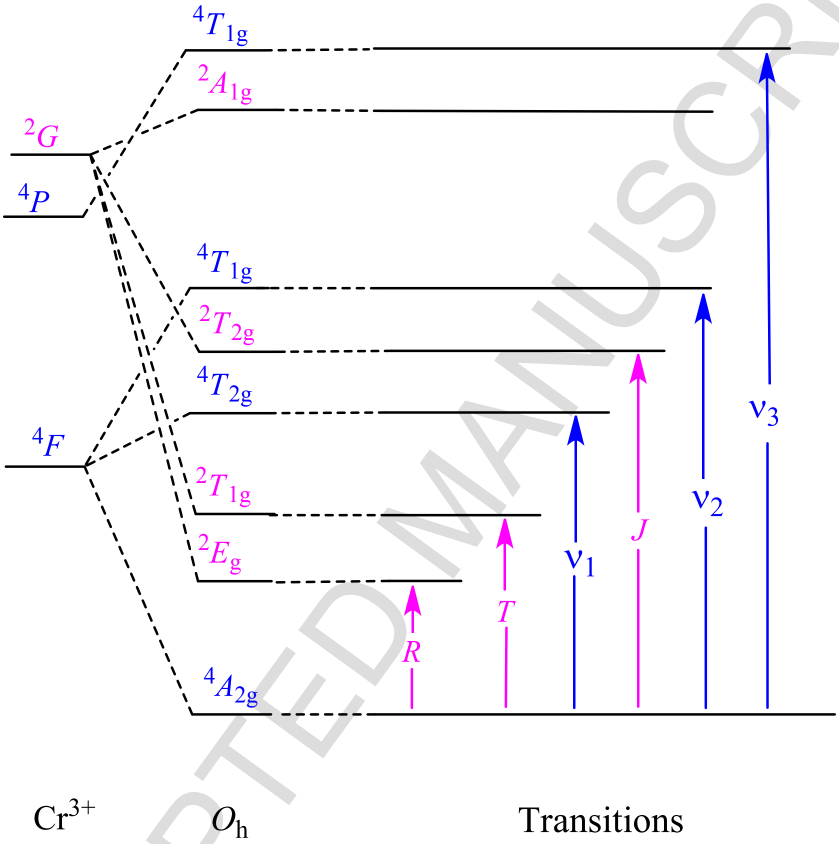


**Fig. 3**. Schematic energy level diagram and electronic transitions of chromium(III) complex in an octahedral symmetry.

In Fig. 2, two intense bands located at 17 953 and 23 365 cm$^{-1}$ corresponding to the $^4A_{2g}\rightarrow{}^4T_{2g}$ ($\nu_1$) and $^4A_{2g}\rightarrow{}^4T_{1g}$ ($^4F$) ($\nu_2$) transitions for the *trans*-$[Cr(N_3)_2(Me_2tn)_2]^+$ and $[Cr(N_3)_4(Me_2tn)]^-$ moieties are shown. The lowering of the transition positions compared to the 18 380 and 25 190 cm$^{-1}$ of pure *trans*-$[Cr(N_3)_2(Me_2tn)_2]ClO_4{\cdot}2H_2O$ might be caused by the $[Cr(N_3)_4(Me_2tn)]^-$ moiety contained in the title double complex. The third spin-allowed transition, $^4A_{2g}\rightarrow{}^4T_{1g}$ ($^4P$)

($\nu_3$), corresponds to a higher energy range, and could not be observed under our experimental conditions. The $^4A_{2g}\rightarrow{}^4T_{1g}(^4P)$ may be obscured owing to the charge-transfer and ligand-specific transition bands. However, two weak spin-forbidden bands $^4A_{2g}\rightarrow{}^2T_{1g}$ ($T$) and $^4A_{2g}\rightarrow{}^2T_{2g}$ ($J$) were found at 15 270 and 20 610 cm$^{-1}$, respectively.

Infrared (IR) spectroscopy is useful in distinguishing between monodentate azido and bridging azido complexes. The FT-IR spectra of (a) *trans*-[CrCl$_2$(Me$_2$tn)$_2$]Cl and (b) [*trans*-Cr(N$_3$)$_2$(Me$_2$tn)$_2$]$_3$[Cr(N$_3$)$_4$(Me$_2$tn)]$_2$ClO$_4$ are shown in Fig. 4. The resulting wavenumbers, intensities, and assignments of the principal IR bands are summarized in Table 2. The assignments were made according to the data found in the literature [8-17, 25, 26].

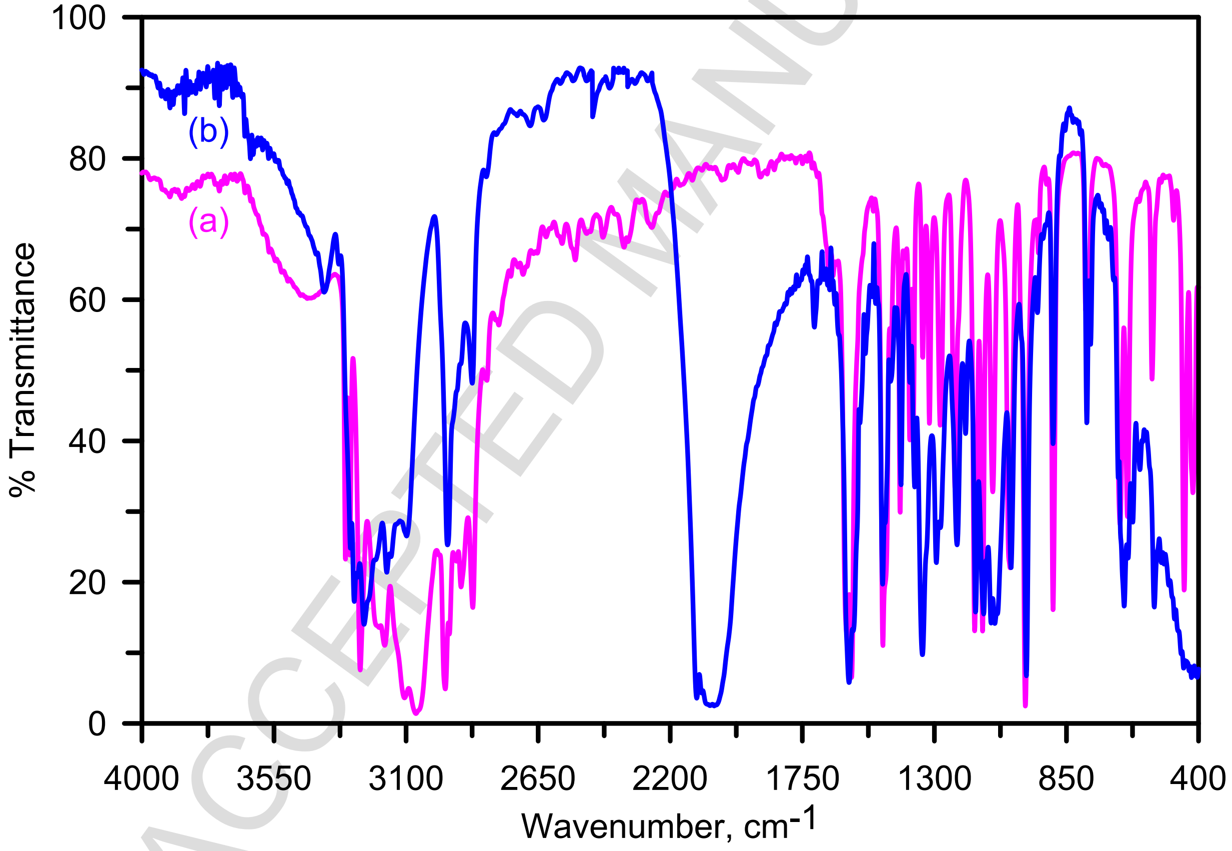


**Fig. 4**. FT-infrared spectra of (a) *trans*-[CrCl$_2$(Me$_2$tn)$_2$]Cl and (b) [*trans*-Cr(N$_3$)$_2$(Me$_2$tn)$_2$]$_3$[Cr(N$_3$)$_4$(Me$_2$tn)]$_2$ClO$_4$, respectively.

**Table 2**

Assignments of the selected bands occurring in the IR spectrum of [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$

| Frequencies(cm$^{-1}$) | Assignment | Frequencies(cm$^{-1}$) | Assignment |
|---|---|---|---|
| 3379 m | $\nu_a(N_3)+\nu_s(N_3)$ | 1160 vs | $\gamma(NH_2)$ |
| 3277 vs, 3243 vs | $\nu(NH)$ | 1132 vs | $\nu(CN)$ |
| 3166 s, 3098 vs | $\nu(NH)$ | 1107 vs | $\nu_a$(Cl–O) |
| 2959 vs | $\nu(CH)$ | 1094 vs | $\nu_a$(Cl–O) |
| 2913 m, 2875 s | $\nu(CH)$ | 1039 s | $\nu(CN)$ |
| 2110 vs, 2050 vs | $\nu_a(N_3)$ | 987 vs | $\nu(CC)$ |
| 1591 vs | $\delta(NH_2)$ | 895 s | $\rho(CH_2)$ |
| 1476 vs | $\delta_a(CH_2)$ | 781 s | $\rho(NH_2)$ |
| 1414 s | $\delta_a(CH_2)$ | 768 m | |
| 1367 m | $\delta_s(CH_2)$ | 653 vs | |
| 1341 m | $\nu_s(N_3)$ | 640 s | |
| 1293 m | $\nu_s(N_3)$ | 624 s | $\delta$(O–Cl–O) |
| 1223 s | $\tau(CH_2)$ | 551 s | $\nu$(Cr–N) + ring def. |
| 1194 m | | 451 m | $\nu$(Cr–N) |

The two absorption peaks at 3379 cm$^{-1}$ and near 3330 cm$^{-1}$ may be due to the $\nu_a(N_3)+\nu_s(N_3)$ combination mode. Strong bands in the 3100–3300 cm$^{-1}$ and 2800–3000 cm$^{-1}$ regions were attributed to the symmetric and anti-symmetric N–H and C–H stretching modes, respectively. Two very strong absorption bands at 2110 and 2050 cm$^{-1}$ for the asymmetric stretching frequency of the azido ligand confirmed that both *trans* and *cis* geometries are contained. Two medium absorptions at 1341 and 1293 cm$^{-1}$ are assigned to the $\nu_s(N_3)$ frequency. It is known that the free azide ions exhibit two bands at 2041 and 1344 cm$^{-1}$, which are attributable to $\nu_a(N_3)$ and $\nu_s(N_3)$, respectively [18, 25, 26].

The assignment of $NH_2$ and $CH_2$ deformations follows the frequency sequence proposed for certain chromium(III) complexes, according to which these vibrational modes have the following energetic order:

$$\text{scissoring }(\delta) > \text{wagging }(\omega) > \text{twisting }(\gamma) > \text{rocking }(\rho)$$

The strong absorption band at 1591 cm$^{-1}$ and the single band at 1476 cm$^{-1}$ can be assigned to the $NH_2$ and $CH_2$ scissoring modes, respectively. Various $NH_2$ and $CH_2$ wagging and twisting vibrations as well as some skeletal modes occur in the region 1000−1450 cm$^{-1}$. The strong absorption at 1039 cm$^{-1}$ may be assigned to the skeletal mode involving C−N stretching. The absorption positions of the scissoring (δ), wagging (ω), twisting (γ), and rocking (ρ) bands of the $NH_2$ and $CH_2$ deformations are not significantly affected by the differing counter anions. It has been suggested that the *cis* isomer exhibits at least three bands within the 830−890 cm$^{-1}$ region owing to the $CH_2$ rocking mode, whereas the $NH_2$ rocking mode splits into two peaks within the 760−830 cm$^{-1}$ region. However, the *trans* isomer shows two groups of bands, namely, one band near 890 cm$^{-1}$ arising from the methylene vibration, and a doublet near 800 cm$^{-1}$ due mainly to the amine vibration [8-17]. The title complex exhibits one band at 895 cm$^{-1}$ within the $CH_2$ rocking frequency region. $NH_2$ rocking bands at 781 cm$^{-1}$ are also observed. The IR spectral data support the geometry of the *trans*-$[Cr(N_3)_2(Me_2tn)_2]^+$ moiety. The very strong absorptions at 1094 and 624 cm$^{-1}$ are assigned to $\delta(ClO_4^-)$ and $\nu_{as}(ClO)$ of the ionic perchlorate, respectively [18]. The positions of the $\nu_a(N_3)$, $\nu_s(N_3)$, $\delta(ClO_4^-)$, and $\nu_{as}(ClO)$ modes could be also determined by comparing the IR spectrum of the *trans*-$[CrCl_2(Me_2tn)_2]Cl$ whose bands are absent (Fig. 4a) [14]. The metal-ligand stretching and ring-deformation bands occur in the far infrared range. The strong peak at 451 cm$^{-1}$ can be assigned to the Cr−N stretching mode. However, the IR and UV-visible spectral properties do not supply any evidence of the *syn* or *anti* conformation of the two six-membered chelate rings in the *trans*-$[Cr(N_3)_2(Me_2tn)_2]^+$ moiety.

### *3.2. Description of the structure*

In order to deteremine the conformations of the six-membered chelate rings unambiguously, the single-crystal structure analysis was performed from synchrotron X-ray data. The title complex crystallizes within the space group *C*2/*c* of the monoclinic system with four mononuclear formula units in a cell with dimensions $a$ = 34.255(7), $b$ = 11.067(2), $c$ = 24.137(5) Å, and $\beta$ = 120.64(3)°.

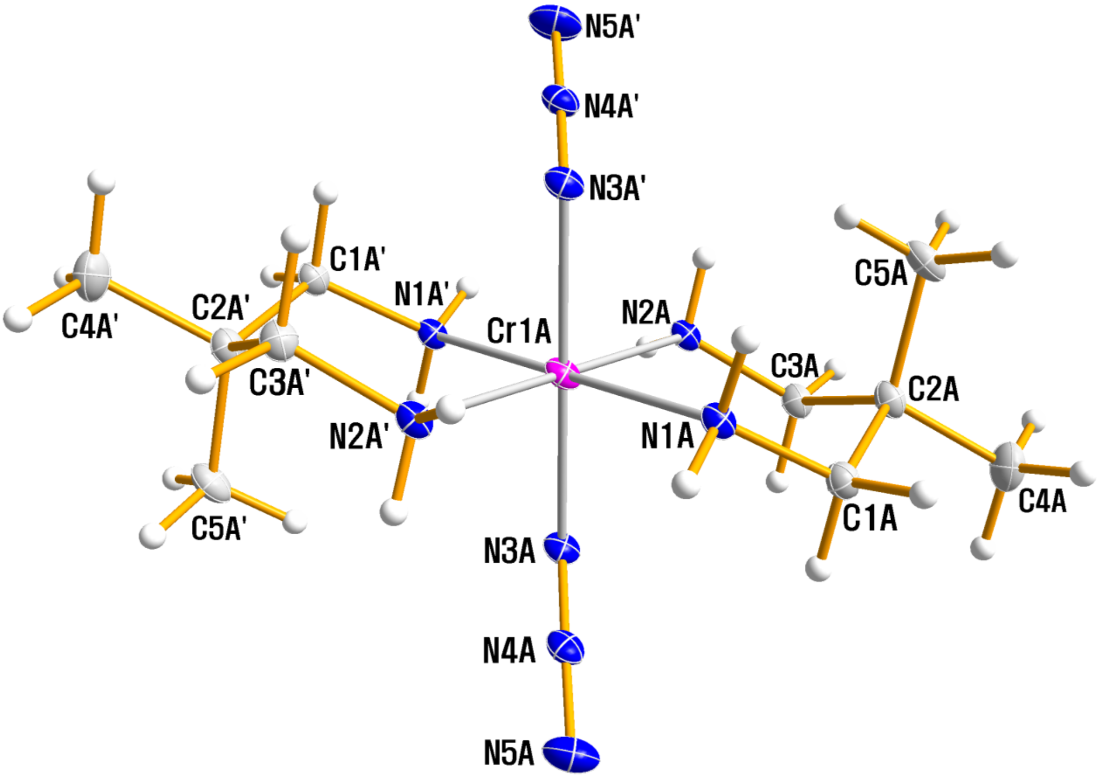


**Fig. 5**. Molecular structure of *trans-anti*-[Cr$(N_3)_2(Me_2tn)_2]^+$ moiety in the title complex. The displacement ellipsoids are shown at the 30% probability level. The atoms labeled with prime symbols are related by symmetry code ($-x+3/2$, $-y+3/2$, $-z+1$).

The asymmetric unit contains one independent half of a *trans-anti*-[Cr$(N_3)_2(Me_2tn)_2]^+$ cation, one other *trans-syn*-[Cr$(N_3)_2(Me_2tn)_2]^+$ cation, one *cis*-[Cr$(N_3)_4(Me_2tn)]^-$ anion, and one half of a perchlorate anion. The selected bond lengths and angles are listed in Tables 3 and 4. The ellipsoid plots of the *trans-anti*-[Cr$(N_3)_2(Me_2tn)_2]^+$ cation, *trans-syn*-[Cr$(N_3)_2(Me_2tn)_2]^+$ cation, and *cis*-[Cr$(N_3)_4(Me_2tn)]^-$ anion together with atomic labelling are illustrated in Figs. 5-7. Hydrogen atoms are shown as circles with arbitrary radii.

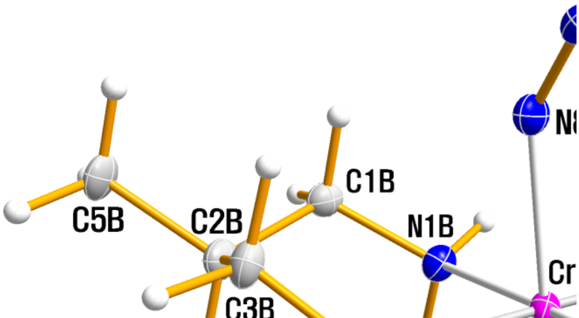


**Fig. 6**. Molecular structure of *trans*-*syn*-[Cr$(N_3)_2$$(Me_2tn)_2$]$^+$ moiety in the title complex. The displacement ellipsoids are shown at the 30% probability level.

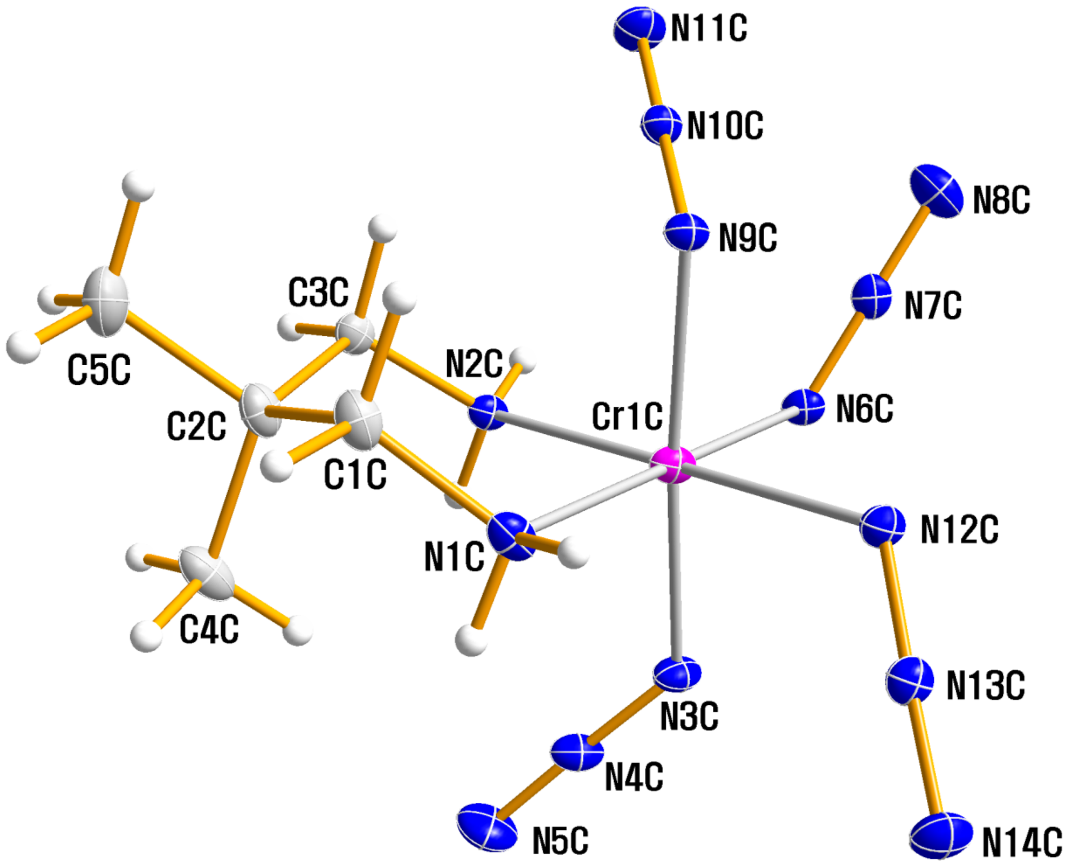



**Fig. 7**. Molecular structure of [Cr$(N_3)_4$$(Me_2tn)$]$^-$ moiety in the title complex. The displacement ellipsoids are shown at the 30% probability level.

**Table 3.** Selected bond distances /Å for [*trans*-Cr$(N_3)_2$$(Me_2tn)_2$]$_3$[Cr$(N_3)_4$$(Me_2tn)$]$_2$ClO$_4$

| | | | |
|---|---|---|---|
| Cr1A—N3A | 2.0312 (15) | N8B—N9B | 1.139 (2) |
| Cr1A—N1A | 2.0821 (14) | N9B—N10B | 1.170 (2) |
| Cr1A—N2A | 2.0929 (14) | Cr1C—N3C | 2.0205 (16) |
| N1A—C1A | 1.488 (2) | Cr1C—N9C | 2.0367 (14) |
| N2A—C3A | 1.487 (2) | Cr1C—N6C | 2.0556 (15) |

| | | | |
|---|---|---|---|
| N3A—N4A | 1.185 (2) | Cr1C—N12C | 2.0659 (15) |
| N4A—N5A | 1.158 (2) | Cr1C—N1C | 2.0759 (15) |
| Cr1B—N8B | 2.0230 (18) | Cr1C—N2C | 2.0858 (15) |
| Cr1B—N5B | 2.0428 (16) | N1C—C1C | 1.486 (3) |
| Cr1B—N2B | 2.0667 (17) | N2C—C3C | 1.486 (2) |
| Cr1B—N3B | 2.0843 (15) | N3C—N4C | 1.195 (2) |
| Cr1B—N1B | 2.0943 (16) | N4C—N5C | 1.154 (2) |
| Cr1B—N4B | 2.0992 (19) | N6C—N7C | 1.207 (2) |
| N1B—C1B | 1.486 (2) | N7C—N8C | 1.148 (2) |
| N2B—C3B | 1.485 (2) | N9C—N10C | 1.210 (2) |
| N3B—C6B | 1.485 (2) | N10C—N11C | 1.150 (2) |
| N4B—C8B | 1.486 (3) | N12C—N13C | 1.206 (2) |
| N5B—N6B | 1.160 (2) | N13C—N14C | 1.153 (2) |
| N6B—N7B | 1.148 (3) | | |

**Table 4.** Selected bond angles /° for [*trans*-Cr(N$_3$)$_2$(Me$_2$tn)$_2$]$_3$[Cr(N$_3$)$_4$(Me$_2$tn)]$_2$ClO$_4$

| | | | |
|---|---|---|---|
| N3A—Cr1A—N1A | 91.12 (6) | N7B—N6B—N5B | 176.8 (2) |
| N3A$^{i}$—Cr1A—N1A | 88.88 (6) | N9B—N8B—Cr1B | 142.76 (14) |
| N3A—Cr1A—N2A | 88.12 (6) | N8B—N9B—N10B | 176.4 (2) |
| N3A$^{i}$—Cr1A—N2A | 91.88 (6) | N1B—C1B—C2B | 114.66 (15) |
| N1A$^{i}$—Cr1A—N2A | 88.13 (6) | N2B—C3B—C2B | 113.75 (16) |
| N1A—Cr1A—N2A | 91.87 (6) | N3B—C6B—C7B | 113.34 (16) |
| N3A—Cr1A—N2A$^{i}$ | 91.88 (6) | N4B—C8B—C7B | 113.61 (18) |
| N1A—Cr1A—N2A$^{i}$ | 88.13 (6) | N3C—Cr1C—N9C | 175.69 (6) |
| C1A—N1A—Cr1A | 119.71 (10) | N3C—Cr1C—N6C | 87.12 (7) |
| C3A—N2A—Cr1A | 119.02 (11) | N9C—Cr1C—N6C | 90.88 (6) |
| N4A—N3A—Cr1A | 124.81 (12) | N3C—Cr1C—N12C | 89.13 (6) |
| N5A—N4A—N3A | 177.4 (2) | N9C—Cr1C—N12C | 87.12 (6) |
| N1A—C1A—C2A | 114.54 (14) | N6C—Cr1C—N12C | 92.03 (6) |
| N2A—C3A—C2A | 114.42 (14) | N3C—Cr1C—N1C | 92.61 (7) |

| | | | |
|---|---|---|---|
| N8B—Cr1B—N5B | 177.41 (7) | N9C—Cr1C—N1C | 89.39 (6) |
| N8B—Cr1B—N2B | 89.86 (7) | N6C—Cr1C—N1C | 179.71 (6) |
| N5B—Cr1B—N2B | 88.55 (7) | N12C—Cr1C—N1C | 88.07 (6) |
| N8B—Cr1B—N3B | 92.98 (7) | N3C—Cr1C—N2C | 92.01 (6) |
| N5B—Cr1B—N3B | 89.05 (6) | N9C—Cr1C—N2C | 91.86 (6) |
| N2B—Cr1B—N3B | 89.32 (6) | N6C—Cr1C—N2C | 91.38 (6) |
| N8B—Cr1B—N1B | 88.16 (7) | N12C—Cr1C—N2C | 176.46 (6) |
| N5B—Cr1B—N1B | 89.78 (7) | N1C—Cr1C—N2C | 88.53 (6) |
| N2B—Cr1B—N1B | 89.84 (6) | C1C—N1C—Cr1C | 118.26 (11) |
| N3B—Cr1B—N1B | 178.58 (7) | C3C—N2C—Cr1C | 119.75 (11) |
| N8B—Cr1B—N4B | 90.49 (7) | N4C—N3C—Cr1C | 129.25 (14) |
| N5B—Cr1B—N4B | 91.14 (7) | N5C—N4C—N3C | 178.2 (2) |
| N2B—Cr1B—N4B | 178.75 (6) | N7C—N6C—Cr1C | 121.76 (12) |
| N3B—Cr1B—N4B | 89.46 (6) | N8C—N7C—N6C | 178.67 (18) |
| N1B—Cr1B—N4B | 91.37 (7) | N10C—N9C—Cr1C | 123.38 (11) |
| C1B—N1B—Cr1B | 118.95 (12) | N11C—N10C—N9C | 178.27 (18) |
| C3B—N2B—Cr1B | 118.20 (12) | N13C—N12C—Cr1C | 118.27 (12) |
| C6B—N3B—Cr1B | 120.00 (11) | N14C—N13C—N12C | 178.15 (19) |
| C8B—N4B—Cr1B | 118.01 (12) | N1C—C1C—C2C | 113.13 (15) |
| N6B—N5B—Cr1B | 127.37 (14) | N2C—C3C—C2C | 114.98 (14) |

Symmetry code: (i) $-x+3/2$, $-y+3/2$, $-z+1$.

In both the *trans-anti*-$[\mathrm{Cr(N_3)_2(Me_2tn)_2}]^+$ and *trans-syn*-$[\mathrm{Cr(N_3)_2(Me_2tn)_2}]^+$ cations, the chromium(III) centers are essentially coplanar with the four N atoms, and adopt an octahedral geometry, where the four nitrogen atoms of two bidentate $\mathrm{Me_2tn}$ ligands occupy the equatorial sites. The two azido groups coordinate with the Cr metal center in the *trans* arrangement. The two chelate rings of the $\mathrm{Me_2tn}$ ligands in *trans-anti*-$[\mathrm{Cr(N_3)_2(Me_2tn)_2}]^+$ are in an *anti* chair-chair conformation, whereas the chelate rings in *trans-syn*-$[\mathrm{Cr(N_3)_2(Me_2tn)_2}]^+$ are in a *syn* conformation. The two conformational arrangements of *trans-anti/syn*-$[\mathrm{Cr(N_3)_2(Me_2tn)_2}]^+$ are comparable to the *anti* conformation, which was found in *trans-anti*-[Cr(NCS)$_2$(Me$_2$tn)$_2$]NCS·1/2H$_2$O, *trans-anti*-[CrCl$_2$(Me$_2$tn)$_2$]ClO$_4$, and *trans-anti*-[CrCl$_2$(Me$_2$tn)$_2$]$_2$ZnCl$_4$ [10-12]. The *anti* conformational arrangement can also be compared with the conformation of [Cu(N$_3$)(Me$_2$tn)$_2$]N$_3$, in which the Cu atom is in a distorted square-pyramidal environment with the four N atoms of two bidentate Me$_2$tn ligands in equatorial positions, and only one azido ligand at the apical position [27].

The *syn* conformational arrangement is consistent with the *syn* conformer observed in *trans-anti/syn*-[CrCl$_2$(Me$_2$tn)$_2$]Cl, *trans-anti/syn*-[CrBr$_2$(Me$_2$tn)$_2$]Br, and *trans-anti/syn*-[CrBr$_2$ (Me$_2$tn)$_2$]$_2$Br$_2$·HClO$_4$·H$_2$O containing the two types of conformers [14-16]. The difference observed in the conformations of the two chelate rings seems to be responsible for the differences in the packing forces and hydrogen-bonding networks among the solvent molecules, complex cations, and anions in the complexes. The Cr–N(Me$_2$tn) bond distances for the nitrogen atoms of the Me$_2$tn in *trans-anti*-[Cr(N$_3$)$_2$(Me$_2$tn)$_2$]$^+$, which vary from 2.0667 (17) to 2.0992(19) Å, are very close to the corresponding bond distances reported in *trans-anti*-[Cr(NCS)$_2$(Me$_2$tn)$_2$]NCS·1/2H$_2$O, *trans-anti*-[CrCl$_2$(Me$_2$tn)$_2$]ClO$_4$, *trans-anti*-[CrCl$_2$(Me$_2$tn)$_2$]$_2$ZnCl$_4$, *trans*-[Cr(nic-*O*)$_2$(cyclam)]ClO$_4$, and [Cr(ox)(cyclam)]ClO$_4$ [3, 8, 10, 11, 28]. The Cr–N(azido) bond lengths of the azido groups in the *trans* position are not equivalent. The 2.0428 (16) Å of Cr1B–N5B is slightly larger than 2.0230 (18) and 2.0312(15) Å for Cr1B–N8B and Cr1A–N3A, which are comparable to the mean distances of 2.007(2) Å 2.021 (7) and 1.977 (4) in the *trans-anti*-[Cr(N$_3$)$_2$(Me$_2$tn)$_2$]ClO$_4$·2H$_2$O, *cis-β*-[Cr(N$_3$)$_2$(2,2,3-tet)]Br, and *trans*-[Cr(N$_3$)$_2$(cyclam)]BPh$_4$, respectively [12, 29, 30]. The Cr1A–N3A–N4A, Cr1B–N5B–N6B, and Cr1B–N8B–N9B bond angles are also different at 124.81(12), 127.37(14) Å, and 142.76(14) Å, respectively. The geometries of the azido groups are essentially linear, the N3A–N4A–N5A angle being 177.4(2)°, which is slightly larger than 176.8(2)° and 176.4(2)° of the N5B–N6B–N7B and N8B–N9B–N10B angles, respectively. The inner and terminal N–N bond lengths are within the 1.139(2)–1.185(2) Å range. It seems that the longer N–N bond lengths are attributed to the hydrogens bonds of the N4A, N6B, N7B, and N10B atoms with the N–H groups of the Me$_2$tn ligand. In the [Cr(N$_3$)$_4$(Me$_2$tn)]$^-$ anion, the chromium(III) ion is in a distorted octahedral environment coordinated by two N atoms of the $Me_2tn$ ligand and four azido ligands in a mutual *cis* geometry. The Cr–N(azido) bond distances in the complex anion are within the range of 2.0205(16) to 2.0659(15) Å, and the mean Cr–N($Me_2tn$) bond distance is 2.0809(15) Å; these lengths are in good agreement with those observed in the *trans-anti/syn*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cations. The geometry of the azido ligands is nearly linear with the $N_\alpha$–$N_\beta$–$N_\gamma$ (azido) angles being 178.15(19)–178.67(18)°. The mean interior $N_\alpha$–$N_\beta$ bond distances of 1.205(2) Å are slightly longer than the mean terminal $N_\beta$–$N_\gamma$ bond lengths of 1.151(2) Å owing to the hydrogen bond interactions. The bonding between chromium(III) and the azido ligand is bent with the Cr1C–$N_\alpha$–$N_\beta$ angle from 118.27(12)° to 129.25(14)°, which is within the expected range for the angle of the $sp^2$ nitrogen. In the title complex, the six-membered rings are in stable chair conformations, with N1A–Cr1A–N2A, N1B–Cr1B–N2B, N1B–Cr1B–N2B, and N1C–Cr1C–N2C angles of 91.87(6), 89.84(6), 89.46(7)°, and 88.53(6)°, respectively. The average Cr–N–C, N–C–C, and C–C–C bond angles in the six-membered chair rings are 118.99(11), 114.05(15), and 111.70 (15)°, respectively. The presence of two substituted methyl groups on the carbon of the $Me_2tn$ molecule does not disturb the essential features of the chelate ring. The mean C–N and C–C distances in the $Me_2tn$ ligand are typical, and are comparable to those observed in other *trans*-$[CrX_2(Me_2tn)]^+$ (X = Cl, Br, NCS, $N_3$) complexes [8-12]. The uncoordinated $ClO_4^-$ anion remains outside the coordination sphere. The perchlorate anion shows a distorted tetrahedral arrangement of oxygen atoms around the central chloride atom with Cl–O distances within the range of 1.443(3)–1.463 (4) Å and the O–Cl–O angles ranging from 106.03(16) to 112.55(18)°. In the title complex, the crystal lattice is stabilized by hydrogen bonding interactions (Table 5) between the NH groups of the $Me_2tn$ ligand and the nitrogen of the azido group. An array of these contacts generates a 3D network, as shown in Fig. 8. Consideration of the crystal packing diagram shows that the N–H…N(azide) hydrogen bonds are the main interactions. Thus, the *trans-anti/syn*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cations and $[Cr(N_3)_4(Me_2tn)]^-$ anion are linked together by a network of these hydrogen bonds. The oxygen atoms of the $ClO_4^-$ anion are not involved in the hydrogen bond or any considerable contact with other neighboring atoms in the crystal. The differences found in the conformations of the two six-membered chelate rings may well be attributed to the different hydrogen bonding networks and crystal packing forces between the chromium(III) complex cation, chromium(III) complex anion, counter anion, and solvated molecule present in the lattice.

**Table 5.** Hydrogen-bonding geometry /Å, ° for [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2A—H2A1···N9C | 0.91 | 2.15 | 3.0246 (19) | 162.1 |
| N2B—H2B2···N6C | 0.91 | 2.08 | 2.987 (2) | 172.5 |
| N3B—H3B1···N3C | 0.91 | 2.68 | 3.168 (3) | 114.9 |
| N3B—H3B1···N6C | 0.91 | 2.18 | 3.081 (2) | 171.2 |
| N4B—H4B1···N6B | 0.91 | 2.63 | 3.154 (2) | 117.5 |
| N2C—H2C2···N4C | 0.91 | 2.65 | 3.223 (2) | 121.3 |
| N1A—H1A1···N8C$^{i}$ | 0.91 | 2.43 | 3.125 (2) | 133.3 |
| N1A—H1A2···N12C$^{i}$ | 0.91 | 2.30 | 3.200 (2) | 170.3 |
| N2A—H2A2···N4A$^{i}$ | 0.91 | 2.66 | 3.186 (3) | 118.0 |
| N1B—H1B1···N7B$^{ii}$ | 0.91 | 2.65 | 3.257 (3) | 124.5 |
| N4B—H4B2···N7B$^{ii}$ | 0.91 | 2.58 | 3.162 (3) | 122.8 |
| N1B—H1B1···N10B$^{iii}$ | 0.91 | 2.42 | 3.247 (3) | 151.0 |
| N4B—H4B2···N10B$^{iii}$ | 0.91 | 2.29 | 3.125 (3) | 151.6 |
| N2B—H2B1···N11C$^{iv}$ | 0.91 | 2.44 | 3.053 (3) | 125.2 |
| N1C—H1C1···N5A$^{v}$ | 0.91 | 2.33 | 3.108 (2) | 143.7 |
| N1C—H1C2···N14C$^{vi}$ | 0.91 | 2.17 | 3.051 (2) | 161.5 |
| N2C—H2C1···N5C$^{vii}$ | 0.91 | 2.17 | 3.048 (2) | 163.3 |

Symmetry codes: (i) $-x+3/2$, $-y+3/2$, $-z+1$; (ii) $-x+1$, $-y$, $-z+1$; (iii) $-x+1$, $-y+1$, $-z+1$; (iv) $-x+3/2$, $y-1/2$, $-z+3/2$; (v) $x$, $y-1$, $z$; (vi) $-x+3/2$, $-y+1/2$, $-z+1$; (vii) $-x+3/2$, $y+1/2$, $-z+3/2$.

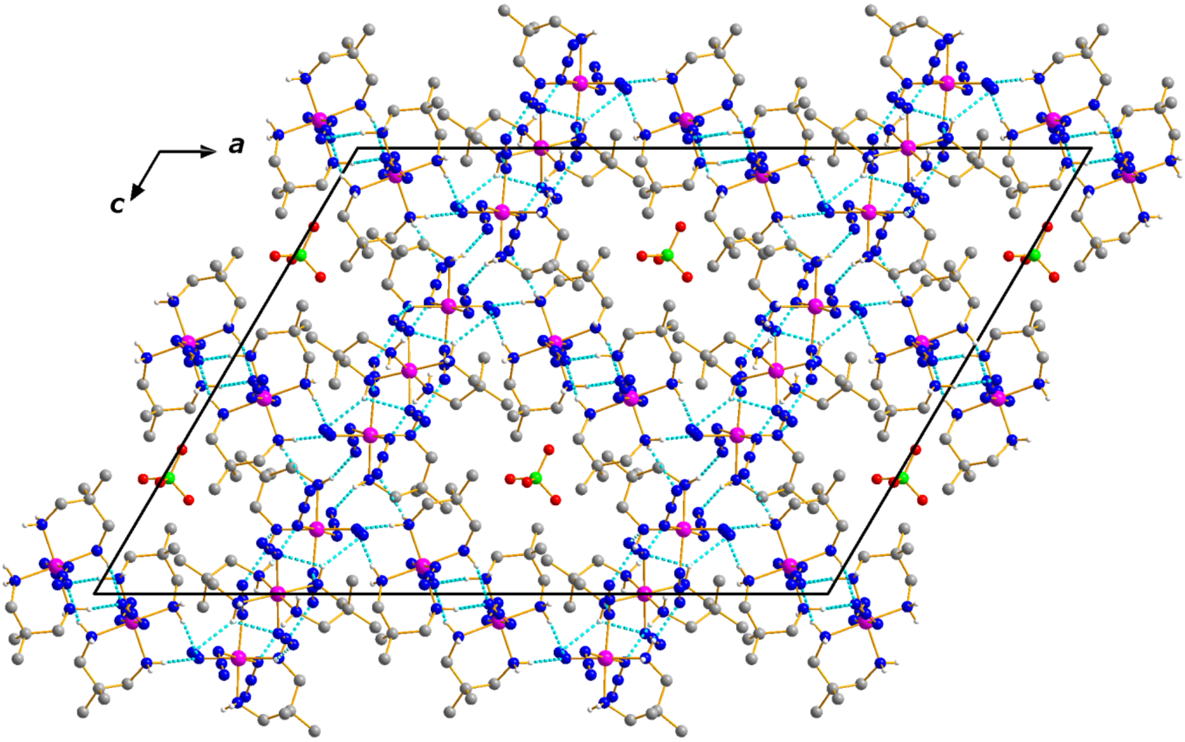


**Fig. 8**. Crystal packing diagram of [*trans*-$Cr(N_3)_2(Me_2tn)_2]_3[Cr(N_3)_4(Me_2tn)]_2ClO_4$. The view is perpendicular to the *ac* plane. Dashed lines represent N–H···N hydrogen-bonding interactions. The C–bound H atoms are omitted for clarity

## 4. Concluding remarks

A newly prepared double complex has been characterized using UV-visible and spectroscopy, elemental analysis, and single-crystal X-ray diffraction analysis. The asymmetric unit contains one half of a *trans*-*anti*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cation, one independent *trans*-*syn*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cation, one $[Cr(N_3)_4(Me_2tn)]^-$ anion, and one half of a perchlorate anion. In two complex cations, the $Cr^{III}$ ions are each coordinated by four N atoms of two chelating

$Me_2tn$ and two N atoms of the azido group in a distorted octahedral geometry, whereas the $Cr^{III}$ ion in $[Cr(N_3)_4(Me_2tn)]^-$ anion has a distorted octahedral coordination with two N atoms of one $Me_2tn$ and four N atoms of the azido group. The two six-membered rings in two *trans*-$[Cr(N_3)_2(Me_2tn)_2]^+$ cations in the same crystal adopt both *anti* and *syn* chair-chair conformations with each other. The Cr–N($Me_2tn$) bond lengths vary from 2.0556 (15) to 2.0992 (19) Å, whereas the Cr–N(azido) bond lengths are within the range of 2.0205(16) to 2.0428 (16) Å. The perchlorate anion is disordered over two sets of sites, and has a distorted tetrahedral geometry. The crystal lattice is stabilized by hydrogen bonding interactions between the nitrogen of $N_3^-$ and the NH groups of the $Me_2tn$ ligand. The crystal-packing and hydrogen-bonding forces are probably responsible for the different conformations observed.

## Supplementary material

CCDC 1859055 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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## Highlights

. Synthesis of a new double chromium(III) complex with azido groups.

. Structural determination from synchrotron X-ray radiation data.

. Description of spectral properties by IR and electronic absorption spectroscopy.