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UNUSUAL GEOMETRY OF AZIDO GROUP AND *SYN* CONFORMATION IN TRANS-DIAZIDOBIS(2,2-DIMETHYL-1,3-PROPANEDIAMINE)CHROMIUM(III) MOIETY

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ABSTRACT

A new complex **1**, *trans*-*syn*-$[Cr(Me_2tn)_2(N_3)_{0.8}Cl_{1.2}]ClO_4$ (Me_2tn = 2,2-dimethyl-1,3-propanediamine) was prepared and its structure was determined from synchrotron radiation data at 95 K. The complex crystallized in the space group *Pbca* of the orthorhombic system with eight mononuclear formula units in a cell of dimensions a = 12.559(3), b = 15.078(3), and c = 20.726(4) Å. The chromium ion was in a distorted octahedral coordination with four N atoms of two chelating Me_2tn ligands and two mixed Cl/N atoms in the *trans* axial position. The two six-membered rings in the complex cation adopted only *syn* chair-chair conformations with respect to each other. The mean Cr-N(Me_2tn) and Cr-N(azido) bond lengths were 2.084 (9) and 1.815 (8) Å, respectively. Unusually short inner N_α-N_β bond distances of azido groups resulted from the crystallographic disorder between the N_β atom and chloride. The crystal lattice was stabilized by hydrogen bonding interactions among the oxygens of ClO_4^-, nitrogens of N_3^-, and NH groups of the Me_2tn ligand.

Key words: Crystallographic disorder, *Syn*-Conformer, Chromium(III) complex, Synchrotron radiation, Spectral properties.

INTRODUCTION

The study on geometry and conformation of chelating ligands in the metal complexes are very important in the medical application, and likely to be a major factor in determining the antiviral activity and its side-effect.[1-3] 2,2-Dimethyl-1,3-propanediamine (Me_2tn) is a bidentate ligand that can coordinate to the central metal ion by forming a six-membered chelate ring with a chair conformation.[4] The $[Cr(Me_2tn)_2X_2]^{n+}$ (X = monodentate)

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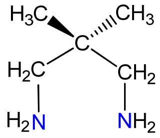
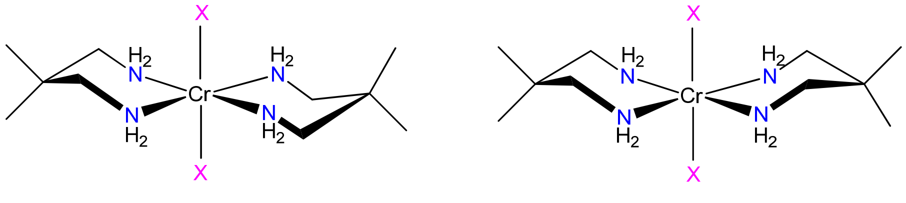
cation can adopt either the *trans* or the *cis* geometry. In addition, two different kinds of conformation with respect to the chelate rings of Me_2tn are seen in the *trans* isomer (Fig. 1).



Me_2tn = 2,2-dimethyl-1,3-propanediamine



anti conformer *syn* conformer

Fig. 1: Structure of ligand Me_2tn and two possible conformational isomers of *trans*-$[Cr(Me_2tn)_2X_2]^+$

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*-$[Cr(Me_2tn)_2Cl_2]Cl$, *trans-anti/syn*-$[Cr(Me_2tn)_2Br_2]Br$ and *trans-anti/syn*-$[Cr(Me_2tn)_2Br_2]_2Br_2{\cdot}HClO_4{\cdot}H_2O$, crystallographically independent *syn* and *anti* conformational isomers were found within the same crystals.[5-7] However, structural analyses of *trans-anti*-$[Cr(Me_2tn)_2(NCS)_2]NCS{\cdot}0.5H_2O$, *trans-anti*-$[Cr(Me_2tn)_2Cl_2]ClO_4$, *anti*-$[Cr(Me_2tn)_2Br_2]$ ClO_4 and *trans-anti*-$[Cr(Me_2tn)_2Cl_2]_2ZnCl_4$ indicated that two chelate rings of the Me_2tn ligands are only in the *anti* chair-chair conformation.[8-11] The different arrangements of the two six-membered chelate rings of Me_2tn ligands may be dependent on the crystallographic disorder, packing forces, hydrated molecules and counter anions in the crystal structure. The factors that determine the stability of these geometric conformations are subtle, and complicated.[5-11] 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 azide ion (N_3^-) 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. As part of a continuing investigation of chromium(III) complexes with mixed ligands, we describe here the preparation, X-ray crystal structure and physical properties of the complex **1** in order to determine the bonding mode of the azido ligand, to confirm crystallographic disorder and to obtain definite information on the conformation including the position of the carbon atoms of the Me_2tn chelate rings with respect to the equatorial coordination plane.

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.

Materials and synthesis

The free ligand 2,2-dimethyl-1,3-propanediamine was obtained from Aldrich Chemical Co. and used as supplied. All the chemicals were reagent-grade and used without further purification. The starting material *trans*-$[Cr(Me_2tn)_2Cl_2]Cl$ was prepared as described previously.[4] Sodium azide (0.5 g, 7.69 mmol) was added to an aqueous suspension (5 mL) of *trans*-$[Cr(Me_2tn)_2Cl_2]Cl$ (0.5 g, 1.38 mmol) and the mixture was heated at 323 K for 5 min. Sodium perchlorate (1.0 g, 8.17 mmol) was then added and heating was continued for a further 90 min to obtain a violet solution. The solution was allowed to cool overnight, during which time purple crystals were observed to form. These crystals were collected by filtration, washed with 2-propanol and air dried. Yield: 0.40g (65%). Anal. Found: C, 26.34; H, 6.33; N, 20.40; O, 14.05%. Calc. for $CrC_{10}H_{28}N_{6.4}Cl_{1.2}O_4$: C, 27.81; H, 6.53; N, 20.75; O, 14.82%. Visible spectral data for an aqueous solution, λ_{max} in nm (ε in M^{-1} cm^{-1}): 395 (57.5), 550 (78.3). IR spectrum (KBr, cm^{-1}): 3270 vs and 3226 s (ν NH), 3108 vs (ν CH), 2964 vs and 2876 s (ν CH), 2065 vs (ν_{as} N_3), 1590 vs (δ NH_2), 1476 vs (δ CH_2), 1418 s, 1358 m (ν_s N_3), 1344 m, 1277 m, 1223 s, 1142 vs, 1120 vs (ν CN), 1089 vs (ν_{as} ClO), 1040 s, 987 vs, 896 s and 778 s (ρ CH_2 and ρ NH_2), 636 s, 627 vs (δ OClO), 554 s, 445 s & 417 vs (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, N and O were performed on a Carlo Erba 1108 Elemental Vario EL analyzer.

Crystal structure analysis

A plate-shaped purple crystal of complex **1** with approximate dimensions 0.02 × 0.02 × 0.01 mm^3 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 (0.90001 Å) at the Pohang Accelerator Laboratory, Korea and a nitrogen cold stream (95 K). The ADSC Quantum-210 ADX program[15] was used for data collection, and HKL2000 (Ver. 0.98.699)[16] was used for cell refinement, reduction, and absorption correction. The structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS (Ver. 6.14) software 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 $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl groups, and C–H = 0.99 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ for methylene groups. The crystallographic experimental data and refinement parameters are summarized in Table 1.

Table 1: Crystallographic data for complex 1

Chemical formula	**$[Cr(C_5H_{14}N_2)_2(N_3)_{0.8}Cl_{1.2}]ClO_4$**
M_r (g mol^{-1})	431.98
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	95 (2)
a, *b*, *c* (Å)	12.559(3), 15.078(3), 20.726(4)
V (Å^3)	3924.8(14)
Z	8
Radiation type, λ (Å)	Synchrotron, 0.90001
μ (mm^{-1})	1.816
Crystal size (mm^3)	0.02 × 0.02 × 0.01
Data collection	ADSC Q210 CCD area detector diffractometer

Cont…

Chemical formula	**$[Cr(C_5H_{14}N_2)_2(N_3)_{0.8}Cl_{1.2}]ClO_4$**
T_{min}, T_{max}	0.982, 0.965
No. of independent reflections	2641
R_{int}	0.1013
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.1176, 0.2766, 1.050
No. of reflections	2789
No. of parameters	240
No. of restraints	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.563, -0.624

RESULTS AND DISCUSSION

Crystallography

The single-crystal X-ray structure analysis indicated that complex **1** consisted of a $[Cr(Me_2tn)_2(N_3)_{0.8}Cl_{1.2}]^+$ cation and one perchlorate anion, with orthorhombic space group of *Pbca* with $Z = 8$. Selected bond lengths and angles are given in Table 2. An ellipsoid plot of the complex molecule together with atomic numbering is illustrated in Fig. 1. Hydrogen atoms are shown as circles of arbitrary radii. The disordered and mixed Cl components of N6 and N9 atoms are omitted for clarity.

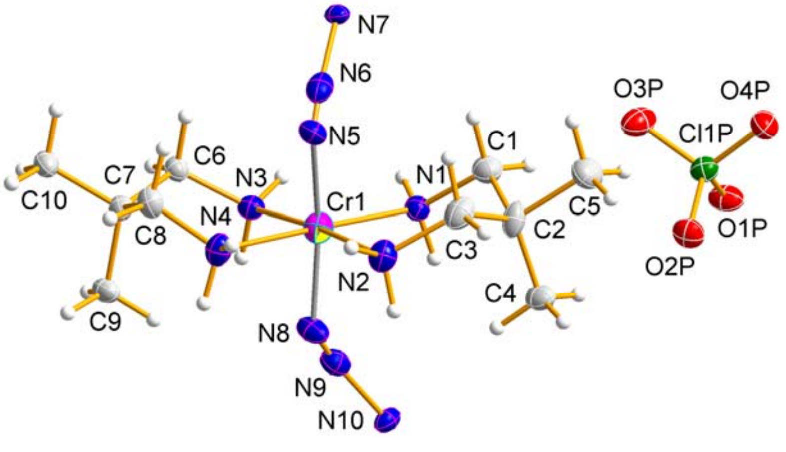


Fig. 1: A perspective view (50% probability level) of complex 1 with the atom-numbering scheme

Table 2: Selected bond distances (Å) and angles (°) for complex 1

Cr1–N1	2.077 (6)	Cr1–N2	2.065 (7)
Cr1–N3	2.081 (6)	Cr1–N4	2.113 (8)
Cr1–N5	1.81 (2)	Cr1–N8	1.82 (2)
N5–N6	0.874 (17)	N8–N9	0.90 (2)
N6–N7	1.526 (14)	N9–N10	1.535 (15)
N1–C1	1.545 (12)	N2–C3	1.559 (12)
N3–C6	1.479 (9)	N4–C8	1.466 (12)
C1–C2	1.570 (13)	C2–C3	1.455 (13)
C2–C4	1.496 (13)	C2–C5	1.581 (14)
C6–C7	1.541 (11)	C7–C8	1.519 (12)
C7–C9	1.531 (11)	C7–C10	1.521 (11)
Cl1P–O1P	1.432 (6)	Cl1P–O2P	1.432 (6)
Cl1P–O3P	1.439 (7)	Cl1P–O4P	1.433 (7)
N1–Cr1–N2	90.3 (3)	N1–Cr1–N3	91.1 (3)
N1–Cr1–N4	178.8 (3)	N1–Cr1–N5	95.4 (7)
N2–Cr1–N3	175.8 (3)	N2–Cr1–N4	89.2 (3)
N2–Cr1–N5	87.2 (8)	N2–Cr1–N8	83.8 (8)
N1–Cr1–N8	98.1 (7)	N3–Cr1–N4	89.2 (3)
N3–Cr1–N5	96.7 (7)	N3–Cr1–N8	92.1 (8)
N4–Cr1–N5	85.7 (7)	N4–Cr1–N8	80.8 (8)
N5–Cr1–N8	163.8 (10)	C1–N1–Cr1	121.0 (5)
C3–N2–Cr1	117.6 (6)	C6–N3–Cr1	119.7 (4)
C8–N4–Cr1	118.9 (6)	N6–N5–Cr1	132 (2)
N9–N8–Cr1	132.7 (19)	N1–C1–C2	108.4 (8)
C2–C3–N2	115.4 (8)	N3–C6–C7	115.1 (6)
N4–C8–C7	113.4 (7)	N5–N6–N7	172.9 (19)
N8–N9–N10	166.2 (19)	C3–C2–C1	110.2 (8)
C4–C2–C1	114.8 (8)	C1–C2–C5	100.2 (9)
C3–C2–C4	117.0 (9)	C3–C2–C5	106.2 (9)

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C4–C2–C5	106.6 (8)	C8–C7–C6	110.5 (6)
C9–C7–C6	110.7 (6)	C10–C7–C6	107.4 (7)
C8–C7–C9	111.7 (7)	C10–C7–C9	109.1 (6)
C8–C7–C10	107.3 (7)	O1P–Cl1P–O2P	107.9 (4)
O1P–Cl1P–O4P	111.2 (5)	O2P–Cl1P–O4P	109.3 (4)
O1P–Cl1P–O3P	108.6 (5)	O2P–Cl1P–O3P	111.3 (5)
O4P–Cl1P–O3P	108.6 (4)	Cr1–N1–C1–C2	59.6 (9)

Results of X-ray structure indicated that the chromium (III) is essentially coplanar with the four N atoms and adopts an octahedral geometry, where four N atoms of two bidentate Me_2tn ligands occupy the equatorial sites. The two end-on azido nitrogen (N5 and N8)/Cl atoms coordinate to the Cr metal center in the *trans* arrangement. The two chelate rings of Me_2tn ligands in complex **1** are only in the *syn* chair-chair conformation. The *syn* conformational arrangement differs from the *anti* conformation found in *trans-anti*-$[Cr(Me_2tn)_2(NCS)_2]NCS\cdot1/2H_2O$, *trans-anti*-$[Cr(Me_2tn)_2Cl_2]ClO_4$ and *trans-anti*-$[Cr(Me_2tn)_2Cl_2]_2ZnCl_4$.[8-11] However, the *syn* conformational arrangement is consistent with the partial *syn* conformation observed in *trans-anti/syn*-$[Cr(Me_2tn)_2Cl_2]Cl$, *trans-anti/syn*-$[Cr(Me_2tn)_2Br_2]Br$ and *trans-anti/syn*-$[Cr(Me_2tn)_2Br_2]_2Br_2\cdot HClO_4\cdot H_2O$, which contains the two types conformers.[5-7] The difference in the conformations of the two chelate rings appeared to be responsible for the differences in the packing forces and hydrogen-bonding networks among the auxiliary ligand, solvent molecule, complex cation and anion in the complexes. The Cr–N bond distances for the Me_2tn were observed to be 2.065 (7) – 2.113 (8) Å which are good in agreement with those observed in *trans-anti*-$[Cr(Me_2tn)_2 (NCS)_2]$ $NCS\cdot1/2H_2O$, *trans-anti*-$[Cr(Me_2tn)_2Cl_2]ClO_4$, *trans-anti/syn*-$[Cr(Me_2tn)_2Br_2]Br$, *trans-anti*-$[Cr(Me_2tn)_2Cl_2]_2ZnCl_4$, *trans-anti*-$[Cr(tn)_2Cl_2]ClO_4$, *trans-anti*-$[Cr(tn)_2Br_2]ClO_4$, *trans*-$[Cr(en)_2Br_2]ClO_4$, *cis*-β-[Cr(2,2,3-tet)$Cl_2$]$ClO_4$, [Cr(cyclam)ox] ClO_4, *trans*-[Cr(cyclam) (nic-*O*)$_2$]ClO_4, *trans*-[Cr(15aneN_4)F_2]ClO_4, and [Cr(edda)(acac)] [6-10, 18-24].[5-11,19-25] The average Cr-N(azido)/Cl bond of 1.815 (8) Å is slightly shorter than the distances of 1.941 (7), 1.954 (3), 1.977 (4), 2.021 (7), and 2.001 (3) Å in *trans*-[Fe(cyclam)$(N_3)_2$]ClO_4, *trans*-[Co(3,2,3-tet)$(N_3)_2$]ClO_4, *trans*-[Cr(cyclam)$(N_3)_2$]BPh_4 and *cis*-β-[Cr(2,2,3-tet)$(N_3)_2$]Br, respectively.[26-29] The Cr1-N5-N6 and Cr1-N8-N9 bond angles were similar at 132.0 and 132.7°, respectively.

Recently, we have reported on the preparation and full characterization of complex **2**, *trans-anti*-$[Cr(Me_2tn)_2(N_3)_2]ClO_4\cdot2H_2O$.[30] The structure analysis of complex **2** indicates the monoclinic space group *C*2/*c* with four mononuclear formula units in a cell of dimensions *a*

= 16.60 (3), *b* = 7.709 (2), *c* = 16.865 (3) Å, and β = 99.07 (3)°. The mean Cr-N(azide) and Cr-N(Me_2tn) are 2.007 and 2.081 Å, respectively. N_α-N_β-N_γ (azide) and Cr-N_α-N_β bond angles are 1.170 and 138.77°. The N_α-N_β-N_γ bond angle value of the azide group is 176.9° and nearly linear. However, azido ligands observed in the complex **1** were bent with an N8–N9–N10 angle of 162°, which differs also from the N5-N6-N7 angle of 172.9°. The inner N_α-N_β bond distances, too, were significantly shorter than the terminal N_β-N_γ bond lengths. The unusual geometry of the end-on azido groups may be due to the disorder in the structurally non-equivalent atoms at a single crystallographic site. Crystallographic disorder in single crystals, in which a site is partially occupied by different atoms, is well known.[31] The composition of the crystal as determined by refining azide and chloride site occupancies is *trans*-*syn*-$[Cr(Me_2tn)_2(N_3)_{0.8}Cl_{1.2}]ClO_4$, in agreement with result of the elemental analysis. The Cr1-N6/Cl and Cr1-N9/Cl bond lengths of 2.524 (7) and 2.482 (7) Å are slightly longer than pure Cr-Cl bond lengths found in *trans*-*anti*-$[Cr(Me_2tn)_2Cl_2]ClO_4$ [2.3246 (9) Å][11] and *trans*-*anti*-$[CrCl_2(Me_2tn)_2]Cl$ [2.3253 (7) Å][5], respectively. The origin of the unusually short inner N_α-N_β bond distances in the complex **1** was probably the compositional disorder from the chloride impurity. The terminal N_β-N_γ bond lengths (1.526 and 1.535 Å) were longer than that for the pure complex **2** (1.156 Å). The overall distance between N_α and N_γ of the azido nitrogen atoms (2.435 Å) was similar to that observed in complex **2** (2.340 Å). Thus, the presence of the chloride impurity appears to shift the N_β atom away from N_γ and toward the N_α atom, there by shortening the inner N_α-N_β bond distance. The disordered chlorine also moves the N_α nitrogen toward the chromium(III) center, resulting in an decrease in the Cr-N (azide) bond length (1.815 Å) can be compared with the distance of 2.007 Å observed in complex **2**. The longer terminal N–N bond lengths, too, may be attributed to the hydrogen bonding of azido N7 and N10 atoms with the N-H groups of Me_2tn ligand. The two six-membered rings are in stable chair conformations with N1-Cr1-N2 and N3-Cr1-N4 angles of 90.3 (2)° and 89.2 (3)°. The average Cr–N–C and N–C–C bond angles in the six-membered chair rings are 119.3 (5) and 113.1 (9)°, 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 Me_2tn ligand are comparable to those observed in similar *trans*-$[Cr(Me_2tn)X_2]^+$ (X = Cl, Br, NCS) complexes.[5-11] The uncoordinated ClO_4^- anions remain outside the coordination sphere. The perchlorate anion shows a distorted tetrahedral arrangement of oxygen atoms around the central chloride atom with Cl-O distances of 1.432 (6) - 1.439 (7) Å and O-Cl-O angles ranging from 107.9 (4)° to 111.3 (5)°. In complex **1**, the crystal lattice is stabilized by hydrogen bonding interactions (Table 3) between the NH groups of the Me_2tn ligand and the oxygens of the ClO_4^- anion. Consideration of the crystal packing diagram shows that the N-H…N(azide) hydrogen bonds are present (Fig. 2). Thus, the $[Cr(Me_2tn)_2(N_3)_{0.8}Cl_{1.2}]^+$ cation, N atoms of the N_3^- ligand and the ClO_4^- are linked together by a network of hydrogen bonds.

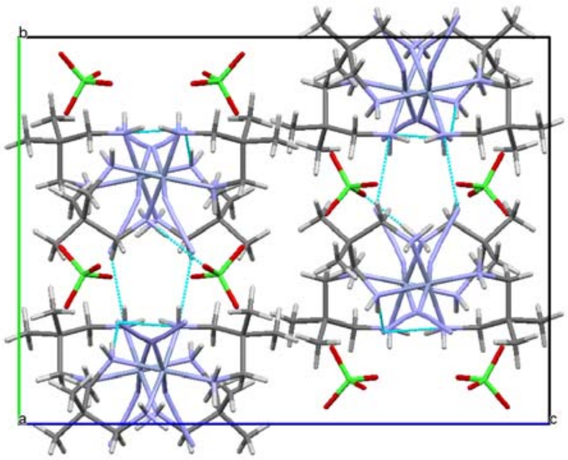

Fig. 2: Hydrogen-bonded thick sheet structure of complex 1 viewed along the *a* axis. Hydrogen bonding is denoted by dashed lines

The differences found in the conformations of the two six-membered chelate rings may well be attributed to the crystallographic disorder and difference in the hydrogen bonding networks including crystal packing forces between the chromium (III) complex cation and the counter anion present in the lattice.

Table 3: Hydrogen-bonding geometry (Å, °) for complex 1

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N1–H1*A*···N9	0.99	2.60	3.080 (7)	110
N3–H3*A*···O1*P*^{i}	0.99	1.95	2.932 (9)	172
N1–H1*B*···O1*P*^{i}	0.99	2.18	3.150 (10)	166
N2–H2*A*···N9^{ii}	0.99	2.68	3.520 (8)	142
N2–H2*A*···N10^{ii}	0.99	2.13	3.092 (17)	164
N4–H4*B*···N10^{ii}	0.99	1.90	2.871 (17)	167
N2–H2*B*···N7^{iii}	0.99	2.29	2.973 (16)	125
N3–H3*B*···N5^{iv}	0.99	2.72	3.69 (2)	166
N3–H3*B*···N6^{iv}	0.99	2.47	3.397 (7)	155
N4–H4*A*···O2*P*^{v}	0.99	2.24	3.149 (11)	153

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

Infrared spectroscopy

Infrared (IR) spectroscopy can be used to determine the configuration of the *cis* and *trans* isomers of diacidobis(diamine) type complexes, and to distinguish between monodentate azido and bridging azido complexes.[32,33] The IR absorption spectrum of the *trans* isomer reveals a simpler pattern than that of the *cis* isomer, and this pattern may be rationalized on the basis of the higher symmetry of the *trans* isomer. The FT-IR spectra of (a) *trans*-$[Cr(Me_2tn)_2Cl_2]Cl$ and (b) complex **1** were compared (Fig. 3) and the resulting wavenumbers, intensities and assignments of the principal IR bands are summarized in Table 4. The assignments were made according to the literature data.[8,9,12,33]

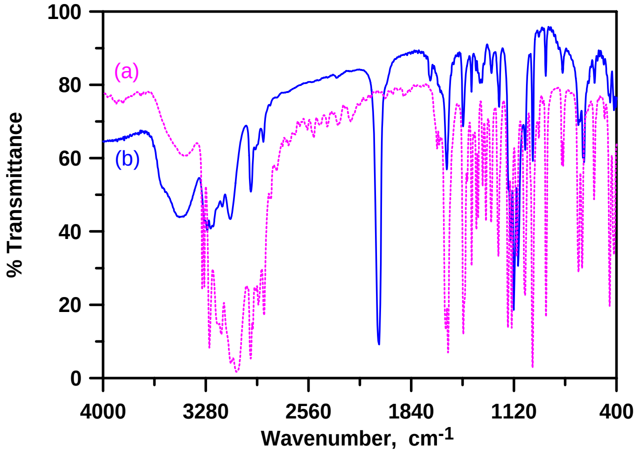

Fig. 3: FT-infrared spectra of (a) *trans*-$[Cr(Me_2tn)_2Cl_2]Cl$ and (b) complex 1

Table 4: Assignments of the selected bands occurring in the IR spectrum of complex 1

Frequencies (cm^{-1})	Assignment	Frequencies (cm^{-1})	Assignment
3466 vs	ν(OH)	1158 sh	$\gamma(NH_2)$
3270 vs	ν(NH)	1142 vs	$\gamma(NH_2)$
3108 vs	ν(NH)	1120 vs	ν(CN)
2964 vs	ν(CH)	1089 vs	ν_{as}(Cl-O)
2876 s	ν(CH)	1040 s	$\gamma(CH_2)$, ν(CN)
2065 vs	$\nu_{as}(N_3)$	987 vs	ν(CC)
1705 w		896 s	$\rho(NH_2)$

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Frequencies (cm^{-1})	**Assignment**	**Frequencies (cm^{-1})**	**Assignment**
1590 vs	$\delta(NH_2)$	778 vs	$\rho(CH_2)$
1476 vs	$\delta(CH_2)$	667 s	
1418 s	$\delta(CH_2)$	636 vs	δ(O-Cl-O)
1358 m	$\nu_s(N_3)$	627 vs	δ(O-Cl-O)
1344 m	$\omega(NH_2)$	554 s	δ(CCC)
1277 m		445 s	ν(Cr-N)
1223 m		417 vs	ν(Cr-N)

The broad O-H stretching absorption near 3473 cm^{-1} indicated that hydrogen bonds were present in complex **1**. Strong bands in the region 3100 - 3300 cm^{-1} and 2800-3000 cm^{-1} were observed and these were attributed to the symmetric and antisymmetric N-H and C-H stretching modes, respectively. The single strong absorption band at 2065 cm^{-1} was attributed to the asymmetric stretching frequency of the azido ligand, thus confirming the *trans* geometry. The medium absorption at 1358 cm^{-1} was assigned to the $\nu_s(N_3)$ frequency.[12,33] It is known that the *cis* isomer exhibits at least three bands in the 830 - 890 cm^{-1} region due to the NH_2 rocking mode while the methylene vibration splits into two peaks in the 760 - 830 cm^{-1} region. However, the *trans* isomer shows two groups of bands: one band near 890 cm^{-1}, arising from the amine vibration and a doublet near 800 cm^{-1}, due mainly to the methylene vibration.[21,22] The complex **1** exhibited one band at 896 cm^{-1} in the NH_2 rocking frequency region. CH_2 rocking bands at 778 cm^{-1} also were observed. The absorption positions of bending (δ), wagging (ω), twisting (γ) and rocking (ρ) bands of NH_2 and CH_2 deformations are not significantly affected by differing counter anions.[5,7,8] The very strong absorptions at 1089 cm^{-1} and 627 cm^{-1} were assigned to $\delta(ClO_4^-)$ and $\nu_{as}(ClO)$ of the ionic perchlorate.[12] The broadening or splitting of the perchlorate peaks resulted from the reduction in the symmetry of the ClO_4^- ion to C_{3v} or C_{2v} due to its interaction with the amine hydrogen atoms and the formation of partial H-bonding. The positions of the $\nu_{as}(N_3^-)$, $\nu_s(N_3^-)$, $\delta(ClO_4^-)$ and $\nu_{as}(ClO)$ modes could be also determined, by comparing which the bands are absent in the IR spectrum of the *trans*-$[Cr(Me_2tn)_2Cl_2]Cl$ (Fig. 3a). The metal-ligand stretching and ring-deformation bands appear in the far infrared range. The two strong peaks at 445 and 417 cm^{-1} were assigned to the Cr-N stretching modes. The IR spectral properties supported the assignment of the *trans* configurational geometry, but no evidence of *syn* or *anti* conformation of the two six-membered chelate rings in complex **1** was observed in the spectroscopic data.

Electronic absorption spectroscopy

Inspection of the *d-d* absorption spectra of some chromium (III) complexes with mixed ligands may allow for assignment of the geometrical configuration.[34-37] The position of the spin-allowed transitions in the electronic spectra, the number of bands, and their extinction coefficients can be reliable indicators for distinguishing between the *trans* and *cis* isomers. Electronic absorption spectroscopy of tetragonally distorted chromium (III) complexes reveals significant splitting under the $^4A_{2g} \rightarrow {}^4T_{2g}$ envelope for the *trans* geometrical isomers, whereas small or undetected splitting is 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 complex **1** in aqueous solution at room temperature is presented in Fig. 4.

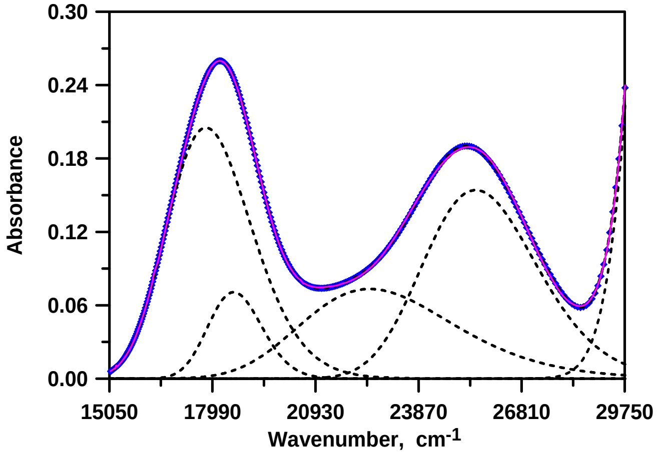

Fig. 4: Visible absorption spectrum (solid line) of complex 1 and the resolved overlapping peaks (dotted curves)

It exhibited two main bands at 18 180 cm^{-1} (ν_1) and 25 315 cm^{-1} (ν_2), which were assigned to the $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$ (O_h) transitions, respectively. The $^4A_{2g}\rightarrow{}^4T_{1g}$ (^4P) transition corresponds to a higher energy range and hence could not be observed under our experimental conditions. The third band (ν_3) may be obscured by the charge-transfer and ligand-specific transition bands. The first quartet absorption band $^4A_{2g}\rightarrow{}^4T_{2g}$ tends to show a shoulder or splitting in the case of the *trans* form of dihalogenobis(diamine)chromium(III) complexes, but no shoulder was apparent in the electronic spectrum of complex **1** in the current work. However, two bands had slightly asymmetric profile. The band profiles were fitted through the use of four Gaussian curves to provide a point of reference for the splitting of the bands (Fig. 4). A deconvolution procedure on the experimental band pattern yielded maxima at 17 795, 18 585, 22 470 and 25 510 cm^{-1} for the non-cubic (D_{4h}) split levels (${}^4E^{a}_{g}+{}^4B^{2g}$ and ${}^4A^{2g}+{}^4E^{b}_{g}$) of ${}^4T_{2g}$ and ${}^4T_{1g}$ (O_h), respectively. The deconvoluted band positions can be used as the observed spin-allowed transition energies in the ligand field calculation to derive the AOM parameters.[8,9,20,38]

In conclusion, the IR and electronic spectroscopic properties of a newly prepared complex were in agreement with the X-ray crystallography results. The chromium atom was in a distorted octahedral environment with four N atoms of two bidentate, 2,2-dimethyl-1,3-diaminopropane ligands in equatorial positions and two azido ligands in *trans* positions. The average Cr-N(Me_2tn) and Cr-N(azido) bond lengths were observed to be 2.084 (9) and 1.815 (8) Å, respectively. The carbon atoms of the two chelate rings in complex 1 were on same sides (*syn* conformation) with respect to the Me_2tn coordination plane and did not adopt *anti* conformation. The unusually short inner N_α-N_β bond distance and distortion of azido groups were attributed to the crystallographic mixed disorder with chloride. The compositional disorder, crystal-packing force, hydrogen-bonding type, and counter anion dimensions were probably responsible for the observed difference in the unique *syn* conformation.

Supplementary material

Crystallographic data, tables of atomic coordinates and thermal parameters, and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC 891187. Copies of this information may be obtained free of charge from The Director, CCDC, 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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