

Crystal Structure and Spectroscopic Properties of *cis-β*-[CrCl₂(1,4,8,11-tetrazaundecane)chromium(III) Perchlorate

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Linear flexible 1,4,8,11-tetrazaundecane (2,3,2-tet) (Fig. 1) provide a rich field of geometrical and conformational isomerism in octahedral transition metal complexes.^{1,2} The 2,3,2-tet ligand is a structural isomer of 1,4,7,11-tetrazaundecane (2,2,3-tet). The linear tetradentate with four nitrogen atoms as donors can adopt three different configurations in chromium(III) complexes with two chloro ligands as shown in Figure 1. Generally, the chromium(III) tetradentate complexes have been shown to have a diverse stereochemistry. It is not possible from the CD spectrum to assign the *cis-α* or *cis-β* configuration. The electronic absorption and infrared spectra often can be used diagnostically to identify the geometric isomers of chromium(III) complexes.³⁻⁹ However, it is also not easy to determine the geometric configurations of *cis-α* and *β* forms because their UV-visible and IR spectra have very similar patterns. In addition to, it should be noted that the assignments based on spectroscopic investigations are not always conclusive.¹⁰

Both *trans* and *cis* isomers of [CrCl₂(2,3,2-tet)]ClO₄ have been isolated. The synthesis, optical activity and hydrolysis kinetics of the dichlorochromium(III) complexes containing the 2,3,2-tet as a tetradentate ligand have been reported, but

have not been structurally characterized.¹¹

In this paper, we present the results on the structural and spectroscopic properties of [CrCl₂(2,3,2-tet)]ClO₄.

The crystal data and details of data collection together with the refinement procedure of *cis-β*-[CrCl₂(2,3,2-tet)]ClO₄ at 150 K are given in Table 1.

A perspective drawing of the molecular structure together with the atomic labeling is depicted in Figure 2, and selected bond lengths and angles are presented in Tables 2 and 3.

The structural analysis showed the space group *P*2₁ of the monoclinic system with a cell of dimensions *a* = 6.4764(13), *b* = 11.801(2), *c* = 9.778(2) Å, β = 93.79(3)° and *Z* = 2. The compound consists of isolated complex cation [CrCl₂(2,3,2-tet)]⁺ and ClO₄ counter anion. The Cr-N(2,3,2-tet) bond lengths are in the range 2.076(10)-2.112(8) Å, and the Cl-Cr-Cl angle is 90.97(11)°. The Cr-Cl bond lengths are 2.328(3) and 2.360(3) Å, and can be compared to distances of

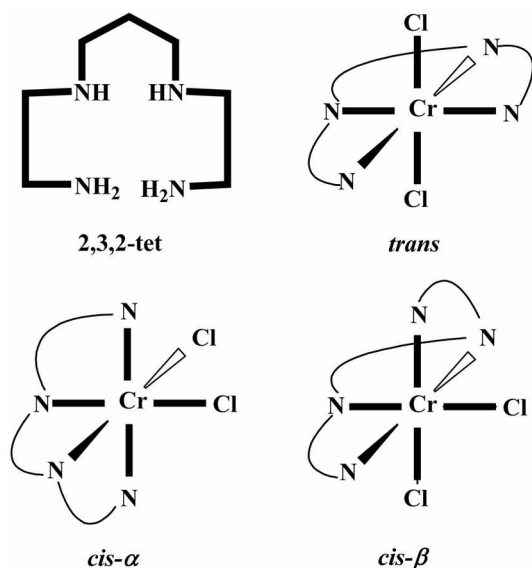


Figure 1. The structure of 2,3,2-tet and three possible geometric isomers of [CrCl₂(2,3,2-tet)]⁺.

Table 1. Crystal data and structure refinement for *cis-β*-[CrCl₂(2,3,2-tet)]ClO₄

Empirical formula	C ₇ H ₂₀ Cl ₃ CrN ₄ O ₄
Formula weight	382.62
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2(1)
Unit cell dimensions	<i>a</i> = 6.4704(13) Å <i>b</i> = 11.801(2) Å <i>c</i> = 9.778(2) Å β = 93.79(3)°
Volume	745.0(3) Å ³
<i>Z</i>	2
Density (calculated)	1.706 Mg/m ³
Absorption coefficient	1.320 mm ⁻¹
<i>F</i> (000)	394
Crystal size	0.325 × 0.264 × 0.260 mm ³
θ range for data collection	4.04 to 27.50°
Index ranges	-8 ≤ <i>h</i> ≤ 8, -15 ≤ <i>k</i> ≤ 15, 0 ≤ <i>l</i> ≤ 12
Reflections collected	3278
Completeness to θ = 27.50°	99.6%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3278 / 1 / 173
Goodness-of-fit on <i>F</i> ²	1.192
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0920, <i>wR</i> ₂ = 0.2757

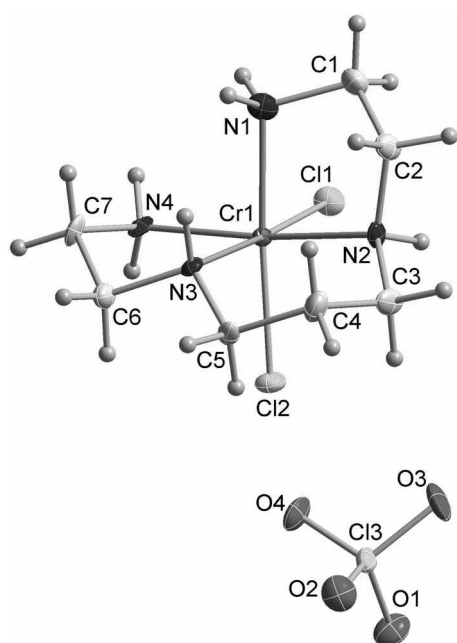


Figure 2. Perspective view of *cis*- β -[CrCl₂(2,3,2-tet)]ClO₄ at 150 K.

Table 2. Selected bond distances (Å) and angles (°) for *cis*- β -[CrCl₂(2,3,2-tet)]ClO₄

Cr(1)-N(4)	2.077(9)	Cr(1)-N(1)	2.076(10)
Cr(1)-N(3)	2.085(9)	Cr(1)-N(2)	2.112(8)
Cr(1)-Cl(2)	2.328(3)	Cr(1)-Cl(1)	2.360(3)
N(4)-Cr(1)-N(1)	90.7(4)	N(4)-Cr(1)-N(3)	82.6(4)
N(1)-Cr(1)-N(3)	92.9(4)	N(4)-Cr(1)-N(2)	169.7(3)
N(1)-Cr(1)-N(2)	82.4(4)	N(3)-Cr(1)-N(2)	90.2(3)
N(4)-Cr(1)-Cl(2)	92.1(3)	N(1)-Cr(1)-Cl(2)	176.5(3)
N(3)-Cr(1)-Cl(2)	89.5(3)	N(2)-Cr(1)-Cl(2)	95.1(3)
N(4)-Cr(1)-Cl(1)	92.0(3)	N(1)-Cr(1)-Cl(1)	86.8(3)
N(3)-Cr(1)-Cl(1)	174.6(3)	N(2)-Cr(1)-Cl(1)	95.1(3)
Cl(2)-Cr(1)-Cl(1)	90.97(11)	C(1)-N(1)-Cr(1)	107.3(7)

Symmetry transformations used to generate equivalent atoms.

Table 3. Hydrogen-bonding geometry (Å, °) for *cis*- β -[CrCl₂(2,3,2-tet)]ClO₄

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1C...O1 ⁱ	0.92	2.47	3.16(1)	132
N1-H1D...Cl1 ⁱⁱ	0.92	2.65	3.57(1)	174
N2-H2...O3 ⁱⁱⁱ	0.93	2.11	2.99(1)	156
N3-H3...Cl1 ^{iv}	0.93	2.56	3.468(9)	166
N4-H4C...Cl2 ^v	0.92	2.49	3.36(1)	159
N4-H4D...O1 ^{vi}	0.92	2.57	3.33(1)	141
N4-H4D...O4 ^{vii}	0.92	2.15	3.00(1)	153

Symmetry codes: i) $x, y-1, z$; ii) $1-x, y, z$; iii) $-x, -0.5+y, 1-z$; iv) $-x, -0.5-y, -z$.

2.3071(7) and 2.3243(7) Å of *cis*- β -[CrCl₂(2,2,3-tet)]ClO₄.¹² The Cr-N1 and Cr-N4 bond lengths of 2.076(10) and 2.077(9) Å of primary amines are slightly shorter than Cr-N2 and Cr-N3 distances of 2.112(8) and 2.085(9) Å of secondary amines. The mean Cr-N bond length of 2.088(8)

Å is normal, agreeing with many literature values, e.g. for [Cr(cyclam)(ox)]ClO₄ (cyclam = 1,4,8,11-tetraazacyclotetradecane), *cis*-[Cr(cyclam)(ONO)₂]NO₂, *mer*-[Cr(dpt)(glygly)]ClO₄ (dpt = di(3-aminopropyl)amine; glygly = glycyglycinate), [Cr(edma)₂]⁺ (edma = ethylenediaminemonoacetate), [Cr₂(μ -OH)₂(nta)₂]⁻ (nta = nitrilotriacetate), *trans*-[Cr(15aneN₄)F₂]ClO₄ (15aneN₄ = 1,4,8,12-tetraazacyclopentadecane), *trans*-[Cr(Me₂tn)₂Cl₂]Cl (Me₂tn = 2,2-dimethyl-1,3-diaminopropane) and *cis*- β -[CrCl₂(2,2,3-tet)]ClO₄ (2,2,3-tet = 1,4,7,11-tetraazaundecane).¹³⁻¹⁹

As usually observed, the five-membered chelate rings adopt a *gauche*, and six-membered rings are in the chair conformations.^{13,14,19} The average bond angles of five- and six-membered chelate rings around chromium(III) are the 82.5(4) and 90.2(3)°, respectively. The mean C-N (1.494 Å) and C-C (1.523 Å) distances in 2,3,2-tet ligand are typical for tetramine chromium(III) complexes. The C-N-C and C-C-N angles are also typical. However, the N-C distances (1.473(14)-1.513(15) Å) involved in the coordinated nitrogen atoms is slightly longer than the corresponding N-C distances (1.463(3)-1.474(3) Å) of the free ligand.²⁰

The uncoordinated ClO₄⁻ anions remain outside the coordination sphere. The perchlorate group has close to the tetrahedral geometry with Cl-O lengths in the range 1.437(8)-1.458(10) Å and the O-Cl-O angle ranging from 108.6(6) to 110.6(6)°. The crystals are held together by hydrogen bonds between primary NH₂ groups, secondary NH groups, chloro ligands and perchlorate anions. Table 3 contains the distances and angles of hydrogen bonds. These hydrogen-bonded networks help to stabilize the crystal structure. Within the unit cell of the title complex there are only two molecules while the *cis*- β -[CrCl₂(2,2,3-tet)]ClO₄ in the space group of *Pbca* of the orthorhombic system with four molecules of the Λ -(R,S)-cation and four molecules of the molecules of the enantiomeric Δ -(S,R)-cation in a cell of dimensions $a = 6.4764(13)$, $b = 11.801(2)$, $c = 9.778(2)$ Å and $\beta = 93.79(3)$ °. The differences in the numbers of molecules and diastereomers within unit cell may be concerned the sharp-line electronic transition splitting pattern of chromium(III) complex.¹²

The assignment of geometrical configuration can be suggested by inspection of the *d-d* absorption spectra.²¹ The position of the spin-allowed transitions in the electronic spectra, the number of bands and their 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 ⁴A_{2g} → ⁴T_{2g} envelope occurring for the *trans* geometrical isomers, but small or undetected splitting observed the *cis* isomers. In general, the more symmetrical *trans* chromium(III) complexes with two chloro and flexible tetradentate 2,3,2-tet ligand 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 of [CrCl₂(2,3,2-tet)]⁺ in aqueous solution exhibits two main bands, one at 18940 cm⁻¹ (ν_1),

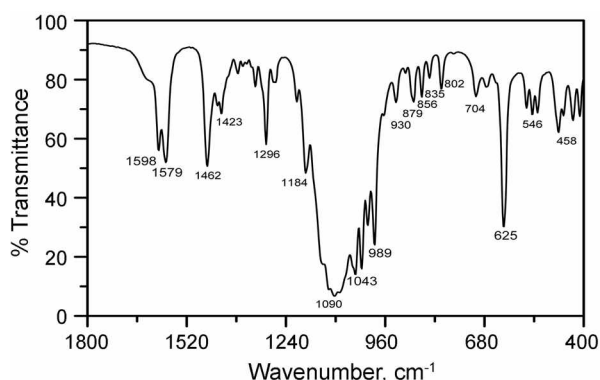


Figure 3. The mid-infrared spectrum of *cis-β*-[CrCl₂(2,3,2-tet)]ClO₄ at 298 K.

and the other at 24810 cm⁻¹ (ν_2), corresponding to the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(O_h)$ transitions, respectively. The electronic spectrum is fully consistent with the *cis* stereochemistry. Although the absorption spectrum confirms the *cis* assignments, it does not establish whether a complex is *cis-α* or *cis-β* configuration.

The infrared spectroscopy is one of the useful tool in the configuration assignment of two *cis* and one *trans* isomers of dichlorochromium(III) complexes with tetradentate ligand.²² It is immediately obviously that the *cis-α* form has two identically positioned Cl atoms, while in the *cis-β* geometry they are differently disposed with respect to the rest of the molecule. The mid-infrared spectrum of *cis*-[CrCl₂(2,3,2-tet)]ClO₄ in the frequency range of 1800-400 cm⁻¹ is presented in Figure 3.

The strong peaks at 1579 and 1598 cm⁻¹ are due to the NH₂ asymmetric deformation mode. The deformation mode at about 1600 cm⁻¹ give one main absorption for *cis-α* and *trans* isomers whereas *cis-β* isomer gives two peaks with lower-energy absorption. The rather weak CH₂ deformation peaks are observed in the region 1470-1420 cm⁻¹. Medium to weak absorptions in the region 1330-1290 cm⁻¹ can be assigned to the symmetric NH₂ deformation. The C-N stretching frequency occurs as a weak band at 1375 cm⁻¹. The four strong absorptions at 989, 1009, 1043 and 1090 cm⁻¹ are appeared in the CH₂ twisting region. It is well known that the *cis-β* isomer exhibits four bands in the 920 to 860 cm⁻¹ while the *cis-α* isomer and *trans* isomer show only two strong bands and one weak absorption, respectively.²² The four absorption peaks at 902, 879, 856 and 835 cm⁻¹ are observed due to the CH₂ rocking vibrational frequencies. The very strong absorptions at 1090, 930, 625 and 458 cm⁻¹ are assigned to ionic perchlorate. Metal-ligand stretching bands occur in the far infrared range.²² The broadening or the split of the perchlorate peak in the studied complexes results from the reduction in the symmetry of the ClO₄⁻ ion to C_{3v} or C_{2v} due to its interaction with the amine hydrogen atoms and to the formation of partial or strong H-bonding.

The peaks in the range 490-410 cm⁻¹ can be assigned to the Cr-N stretching mode.^{23,27} The Cr-N and Cr-Cl stretching bands in the far-infrared spectrum to which we have assigned a *cis* dichloro geometric configuration exhibit

splitting, whereas the *trans* isomer shows no splitting of these bands, as would be expected from the lower symmetry of the Cr-N skeleton in the *cis* complex. For the *cis*-[CrCl₂N₄]⁺ complex with C_{2v} symmetry, the group theoretical analysis predicts four Cr-N and two Cr-Cl infrared-active stretching vibrations, respectively. The peaks in the range 480-410 cm⁻¹ can be assigned to the Cr-N(2,3,2-tet) stretching modes. Typically, all chloro chromium(III) complexes exhibit absorption bands in the 370-320 cm⁻¹ region due to the $\nu(\text{Cr-Cl})$.¹ The absorption at 329 cm⁻¹ is assigned to the Cr-Cl stretching modes.^{12,28} A number of absorption bands below 300 cm⁻¹ arise from the skeletal bending and lattice vibration modes.

In conclusion, it is found that the title complex crystallizes in the space group *P*2₁ of the monoclinic system with two mononuclear formula units in a cell. The complex cation unit has its central Cr atom in a distorted octahedral coordination with four nitrogen atoms of the 2,3,2-tet ligand and two chlorine atoms in a *cis-β* position. The IR and visible absorption spectral properties are in agreement with the result of structural analysis.

Experimental Section

The free ligand 1,4,8,11-tetrazaundecane was prepared using previously described procedure²⁵ or can be purchased from Strem Chemical Company, USA. All other chemicals were of reagent grade or better quality and used without further purification. The complex of *cis-β*-[CrCl₂(2,3,2-tet)]ClO₄ was prepared by the method of House and Yang.¹¹ The crude product was then dissolved in a minimum amount of water and followed by precipitation with a saturated solution of sodium perchlorate. Recrystallization from aqueous solution afforded dark violet crystals suitable for crystallographic analysis.

The far-infrared spectrum in the region 600-50 cm⁻¹ was recorded with a Bruker 113v spectrometer in Nujol mull sandwiched between polyethylene plates. The mid-infrared spectrum was obtained with a Mattson Infinities series FT-IR spectrometer using a KBr pellet. The UV-visible absorption spectrum was recorded with a HP 8453 diode array spectrophotometer.

Single-crystal X-ray diffraction data were collected on a Bruker SMART 1 K CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell parameters were determined using SMART³⁰ and refined based on the positions of all strong reflections using SAINT.³⁰ Absorption correction was by SADABS³¹ based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods using SIR97³² and refined by full-matrix least-squares on F^2 using SHELXTL.³³ Molecular graphics were produced using DIAMOND-3.³⁴ Non-hydrogen atoms were refined anisotropically; hydrogen atoms were first located in a difference map; N-H hydrogen atoms were freely refined and C-H hydrogen atoms were constrained to ride on the parent carbon atom, with C-H = 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene groups.

Supplementary Material. Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 679242. 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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