

Ethylenediammonium bis{bis[*N*-(2-aminoethyl)glycinato- κ^3 N,N',O]-chromium(III)} tetrachloride dihydrate at 293 and 100 K

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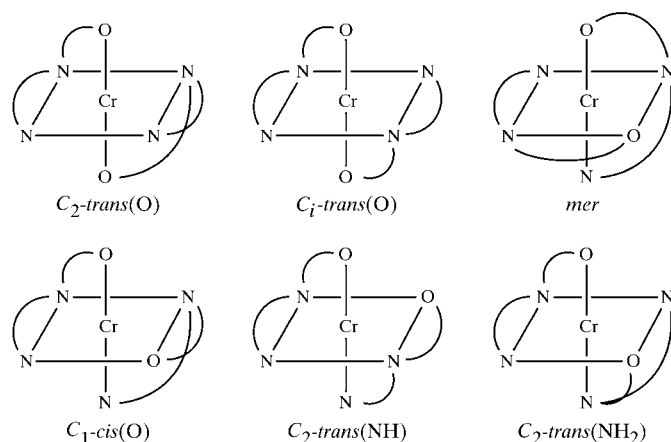
The crystal structure of the title compound, $(C_2H_{10}N_2)[Cr(C_4H_9N_2O_2)_2]_2Cl_4 \cdot 2H_2O$, has been determined by single-crystal X-ray diffraction studies at 293 and 100 K. The analyses demonstrated that the crystal consists of ethylenediammonium dications (which lie about inversion centres), bis[*N*-(2-aminoethyl)glycinato]chromium(III) monocations, Cl^- anions and hydrate water molecules, in a molecular ratio of 1:2:4:2. The complex cation unit has a slightly distorted octahedrally coordinated Cr atom, with two Cr–O and four Cr–N bonds in the ranges 1.951 (1)–1.953 (1) and 2.054 (1)–2.089 (2) Å, respectively, at 293 K. The geometry of the bis[*N*-(2-aminoethyl)glycinato]chromium(III) moiety was found to be *trans,cis,cis* with respect to the carboxylate O atom and the primary and secondary amine N atoms. The two analyses, at 293 and 100 K, exhibited no remarkable structural differences, although the colour of the crystals did differ, being red at 293 K and orange at 100 K.

Comment

N-(2-Aminoethyl)glycinate [ethylenediaminemonoacetate or 4-amino-2-azabutanecarboxylate (edma)] has one acetate group and two amino groups, and can act as a tridentate ligand in complexation with cobalt(III) or chromium(III) ions (Fujii *et al.*, 1970; Battaglia *et al.*, 1974; Ama *et al.*, 1985; Okamoto *et al.*, 1991; Yasui *et al.*, 1994). On the basis of elemental analysis and visible absorption, ¹³C NMR and circular dichroism spectra, the molecular structure of the cobalt(III) complex with the edma ligand has been determined (Igi & Douglas, 1974; Yasui *et al.*, 1983).

A tridentate ligand can take on various coordination forms in an octahedral environment, depending on the steric

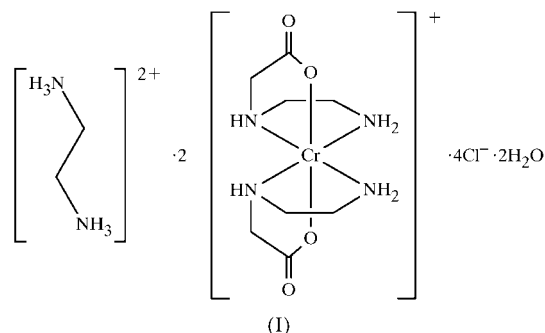
requirements of the ligand and the character of the central metal ion. There are six possible geometric diastereomers of the bis[*N*-(2-aminoethyl)glycinato]chromium(III) moiety, as shown in the *Scheme* below. These may be further identified as (i) C_2 -*trans*(O), (ii) C_1 -*trans*(O), (iii) *mer*, (iv) C_1 -*cis*(O), (v) C_2 - C_2 -*trans*(NH₂) and (vi) C_2 -*trans*(NH), where O, NH₂ and NH refer to the carboxylate O atom and the primary and secondary amine N atoms, respectively. Of these, only a *trans* form with respect to the coordinated carboxylate O atoms has been isolated and its spectroscopic properties reported (Fujii *et al.*, 1970; Yuen, 1981). However, two configurations are possible for a *trans*(O)-type complex, namely, the chiral configuration C_2 -*trans*(O) and the achiral configuration C_1 -*trans*(O). The choice of *cis* or *trans* configuration with respect to the primary and secondary amine N atoms is not clear.



Electronic absorption and IR spectra can be used diagnostically to identify the geometric isomers of chromium(III) complexes with tridentate ligands (Choi & Hoggard, 1992). However, it should be noted that the assignments based on spectroscopic investigations are not always conclusive (Stearns & Armstrong, 1992). Recently, we have been interested in the emission and excitation spectroscopic measurements of chromium(III) complexes at low temperature (Choi, 2000*a,b*). A notable feature is that, on cooling single crystals of the title complex, (I), to liquid-nitrogen temperature, their colour changed from bright red to orange–yellow. The colour change is reversible on warming back to room temperature. A similar thermochromism was also observed for *trans*- and *cis*-[Cr(NCS)₂(cyclam)](ClO₄) (cyclam is 1,4,8,11-tetraazacyclotetradecane; Friesen *et al.*, 1997). In order to establish the details of the coordination, to verify the spectroscopic structural assignment previously described, and to help in studying the temperature-dependent occurrence of geometric isomerism, an X-ray crystal analysis of the title chromium(III) complex with edma has been undertaken at room (293 K) and low (100 K) temperatures. We used the same single crystal for both measurements. The colour of the crystal was red at room temperature and orange at 100 K.

The structural analysis indicated that the crystal of (I) consists of ethylenediammonium dications (H_2en^{2+}), bis[*N*-(2-aminoethyl)glycinato]chromium(III) monocations, Cl^- anions

and hydrated water molecules, in a molecular ratio of 1:2:4:2, so that it can be formulated as $(\text{H}_2\text{en})[\text{Cr}(\text{edma})_2]_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. This is in agreement with the elemental analysis. The chemical formula is different from that previously suggested by Fujii *et al.* (1970).



The $[\text{Cr}(\text{edma})_2]^+$ moiety has a *trans,cis,cis* configuration with respect to the carboxylate O atom and the primary and secondary amine N atoms (Fig. 1). At 293 K, the Cr—O bond length of 1.953 (1) Å is relatively short, and can be compared with the distance of 1.972 (5) Å found in $[\text{Cr}(\text{dpt})(\text{glygly})]^+$ [dpt is bis(3-aminopropyl)amine and H_2glygly is glycylglycine; Choi *et al.*, 1995]. The Cr—N bond lengths are in the range 2.054 (1)–2.089 (1) Å, and the O—Cr—O angle is 176.36 (4)° (Table 1). Both ethylenediamine rings have λ conformations for the Δ stereoisomer (two acetate chelates are used to determine the absolute configuration around Cr) and δ conformations for the Λ stereoisomer.

The ethylenediammonium dication has a centre of symmetry. In the crystal of (I), there are hydrogen bonds between ethylenediammonium dications, bis[*N*-(2-aminoethyl)glycinato]chromium(III) monocations, Cl^- anions and hydrate water molecules, forming a three-dimensional hydrogen-bonding network (Fig. 2 and Table 2). There are no remarkable differences between the 293 and 100 K structures, either in the molecular structure of the complex cation or in

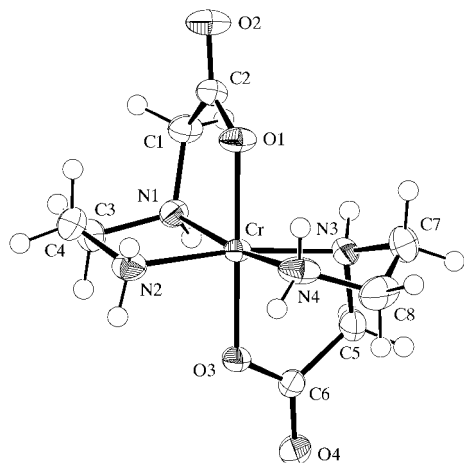


Figure 1
A perspective view of the complex cation in (I) at 293 K. Displacement ellipsoids are drawn at the 50% probability level.

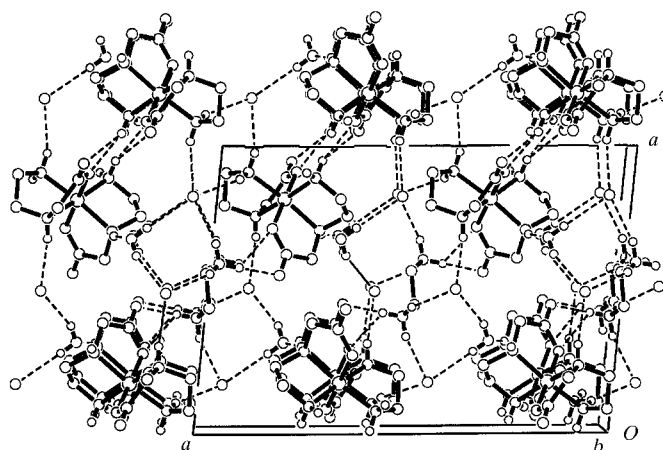


Figure 2
A packing diagram (viewed along the *b* axis) showing the hydrogen-bonding interactions between the ethylenediammonium dications, bis[*N*-(2-aminoethyl)glycinato]chromium(III) monocations, Cl^- anions and hydrate water molecules of (I) at 293 K.

the crystal packing, although the cell lengths and volume are slightly reduced in the 293 K structure compared to the 100 K structure.

This crystallographic study indicates that the observed colour change of the crystal does not originate from a structural change of the complex.

Experimental

The ligand Hedma-2HCl·H₂O and the title complex were prepared according to the literature method of Fujii *et al.* (1970). Recrystallization of the complex from 10% ethanol solution gave bright-red crystals of (I) suitable for crystallographic analysis. Analysis found: C 26.52, H 6.21, N 17.21%; calculated for $\text{C}_{18}\text{H}_{50}\text{Cl}_4\text{Cr}_2\text{N}_{10}\text{O}_{10}$: C 26.61, H 6.20, N 17.24%.

Compound (I) at 293 K

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Cr}(\text{C}_4\text{H}_9\text{N}_2\text{O}_2)_2]_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$
 $M_r = 812.48$
 Monoclinic, $P2_1/c$
 $a = 12.5921$ (3) Å
 $b = 7.5227$ (1) Å
 $c = 18.2511$ (4) Å
 $\beta = 95.915$ (1)°
 $V = 1719.66$ (6) Å³
 $Z = 2$

$D_x = 1.569$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 12 402 reflections
 $\theta = 2.7$ – 27.4 °
 $\mu = 1.00$ mm⁻¹
 $T = 293$ (2) K
 Hexagonal column, red
 0.22 × 0.22 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
 ω scans
 Absorption correction: multi-scan (Higashi, 1995)
 $T_{\text{min}} = 0.725$, $T_{\text{max}} = 0.835$
 16 059 measured reflections

3932 independent reflections
 3482 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5$ °
 $h = -16 \rightarrow 16$
 $k = -9 \rightarrow 9$
 $l = -23 \rightarrow 23$

Table 1
Selected geometric parameters (Å, °) for (I) at 293 K.

Cr—O1	1.9529 (10)	Cr—N2	2.0633 (13)
Cr—O3	1.9506 (10)	Cr—N3	2.0777 (13)
Cr—N1	2.0885 (12)	Cr—N4	2.0541 (13)
O1—Cr—O3	176.36 (4)	O3—Cr—N4	93.48 (5)
O1—Cr—N1	82.19 (4)	N1—Cr—N2	84.21 (5)
O1—Cr—N2	92.79 (5)	N1—Cr—N3	97.09 (5)
O1—Cr—N3	95.56 (5)	N1—Cr—N4	171.86 (5)
O1—Cr—N4	89.69 (5)	N2—Cr—N3	171.65 (5)
O3—Cr—N1	94.66 (5)	N2—Cr—N4	95.81 (6)
O3—Cr—N2	88.68 (5)	N3—Cr—N4	84.08 (6)
O3—Cr—N3	83.00 (4)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I) at 293 K.

<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—H01...Cl1 ⁱ	0.91	2.29	3.195 (1)	171
N2—H02A...Cl2 ⁱⁱ	0.90	2.57	3.391 (1)	153
N2—H02B...Cl2 ⁱⁱⁱ	0.90	2.40	3.253 (1)	157
N3—H03...O6 ^{iv}	0.91	2.04	2.920 (2)	161
N4—H04A...O2 ^v	0.90	2.21	3.030 (2)	152
N4—H04B...O2 ^{vi}	0.90	2.03	2.919 (2)	170
N5—H05A...Cl2 ^{vii}	0.89	2.31	3.142 (1)	157
N5—H05B...O4 ^{viii}	0.89	1.95	2.791 (2)	156
N5—H05C...Cl1	0.89	2.33	3.134 (1)	151
O6—H06A...Cl2	0.84 (2)	2.42 (2)	3.255 (2)	177 (2)
O6—H06B...Cl1 ^{vii}	0.87 (2)	2.69 (2)	3.509 (2)	159 (2)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.070$
 $S = 1.01$
 3932 reflections
 206 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.4474P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{Å}^{-3}$

Compound (I) at 100 K

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)[\text{Cr}(\text{C}_4\text{H}_9\text{N}_2\text{O}_2)_2]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$
 $M_r = 812.48$
 Monoclinic, $P2_1/c$
 $a = 12.5546 (4) \text{ Å}$
 $b = 7.4907 (1) \text{ Å}$
 $c = 18.1157 (4) \text{ Å}$
 $\beta = 95.939 (1)^\circ$
 $V = 1694.51 (7) \text{ Å}^3$
 $Z = 2$

$D_x = 1.592 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 12 063 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 1.02 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Hexagonal column, orange
 $0.22 \times 0.22 \times 0.18 \text{ mm}$

Data collection

Rigaku R-Axis RAPID imaging-plate diffractometer
 ω scans
 Absorption correction: multi-scan (Higashi, 1995)
 $T_{\min} = 0.733, T_{\max} = 0.832$
 15 950 measured reflections

3894 independent reflections
 3514 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 27.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -9 \rightarrow 9$
 $l = -23 \rightarrow 23$

Table 3
Selected geometric parameters (Å, °) for (I) at 100 K.

Cr—O1	1.9552 (9)	Cr—N2	2.0649 (11)
Cr—O3	1.9505 (9)	Cr—N3	2.0807 (11)
Cr—N1	2.0904 (11)	Cr—N4	2.0511 (11)
O1—Cr—O3	176.77 (4)	O3—Cr—N4	93.51 (4)
O1—Cr—N1	82.23 (4)	N1—Cr—N2	84.33 (4)
O1—Cr—N2	92.70 (4)	N1—Cr—N3	96.89 (4)
O1—Cr—N3	95.82 (4)	N1—Cr—N4	171.70 (4)
O1—Cr—N4	89.48 (4)	N2—Cr—N3	171.48 (4)
O3—Cr—N1	94.79 (4)	N2—Cr—N4	95.65 (5)
O3—Cr—N2	88.21 (4)	N3—Cr—N4	84.35 (5)
O3—Cr—N3	83.29 (4)		

Table 4
Hydrogen-bonding geometry (Å, °) for (I) at 100 K.

<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—H01...Cl1 ⁱ	0.93	2.27	3.193 (1)	172
N2—H02A...Cl2 ⁱⁱ	0.92	2.53	3.368 (1)	152
N2—H02B...Cl2 ⁱⁱⁱ	0.92	2.38	3.240 (1)	156
N3—H03...O6 ^{iv}	0.93	2.02	2.911 (2)	160
N4—H04A...O2 ^v	0.92	2.15	3.001 (2)	153
N4—H04A...O1 ^v	0.92	2.65	3.193 (1)	118
N4—H04B...O2 ^{vi}	0.92	2.00	2.913 (1)	172
N5—H05A...Cl1	0.91	2.30	3.116 (1)	149
N5—H05B...Cl2 ^{vii}	0.91	2.29	3.139 (1)	155
N5—H05C...O4 ^{viii}	0.91	1.90	2.765 (1)	157
O6—H06A...Cl2	0.879 (12)	2.349 (11)	3.223 (1)	173.3 (5)
O6—H06B...Cl1 ^{vii}	0.851 (14)	2.628 (10)	3.438 (1)	160 (1)

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

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.059$
 $S = 1.06$
 3894 reflections
 202 parameters
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0350P)^2 + 0.5214P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$

The H atoms of the hydrate water molecules were located from difference Fourier syntheses and their positions were refined. The other H atoms were placed geometrically, with N—H distances in the range 0.89–0.93 Å and C—H distances in the range 0.97–0.99 Å, and these atoms were refined using a riding model. For all H atoms, $U_{\text{iso}}(\text{H})$ was set to be 0.041 (for the 293 K determination) or 0.017 Å² (for the 100 K determination).

For both compounds, data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1970); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1068). Services for accessing these data are described at the back of the journal.

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