Acta Cryst. (1978). B**34**, 3367–3369

(±)-Tris(ethylenediamine)chromium(III) Iodide Monohydrate at −155°C

By N. W. Alcock, P. de Meester and T. J. Kemp

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, England

(*Received* 16 *June* 1978; *accepted* 18 *July* 1978)

Abstract. $C_6H_{26}CrI_3N_6O$, FW 631·0, orthorhombic, *Pbca*. At −155°C, a = 23·198 (5), b = 11·624 (2), c = 13·508 (3) Å, V = 3642·5 Å^3, Z = 8, D_c = 2·301 g cm^{-3}, μ(Mo $K\alpha$) = 56·5 cm^{-1}. Final R = 0·035. The Cr atom is octahedrally bonded to six N atoms with an average Cr—N distance of 2·081 (5) Å and *cis* angles at the metal ranging from 81·9 (2) to 94·7 (2)°. The water molecule is disordered and distributed in two sites of occupancy $\frac{2}{3}$ and $\frac{1}{3}$. There are several hydrogen bonds of the type N—H···O, N—H···I and O—H···I.

Introduction. Sartori, Castelli & Cervone (1971) have reported that, in the solid state, $Cr(en)_3I_3$ undergoes a thermally reversible photoreaction at liquid-nitrogen temperature, involving the breaking of a Cr—N bond followed by insertion of an iodide anion in the metal coordination sphere. In an attempt to characterize by X-ray methods the compound formed after irradiation, a single crystal of the title complex was mounted on a Syntex $P2_1$ diffractometer and its temperature lowered to −155°C, the minimum temperature accessible to our LT-1 low-temperature attachment. X-ray rotation photographs were taken at regular intervals during a period of *ca* 48 hours of irradiation with a xenon lamp. We have not been able to see any difference between the photographs taken before and after irradiation, although the colour of the crystal changes from yellow-orange to reddish, apparently due to a film on the crystal surface. Since the title complex is not isostructural with its chloride analogue (Whuler, Brouty, Spinat & Herpin, 1975), we undertook its crystal structure determination.

The complex was prepared according to the method of Rollinson & Bailar (1946). Photographs indicate the orthorhombic space group *Pbca*, with systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$ and $hk0$, $h = 2n + 1$. A crystal bounded by faces {100} and {211} was held at −155°C. The cell constants were obtained by a least-squares procedure. With Mo $K\alpha$ and a graphite monochromator, data were collected to $2\theta = 55°$ by the θ–2θ technique, the peaks being scanned from −0·65° in 2θ below $K\alpha_1$ to 0·65° above $K\alpha_2$, at scan rates between 2·0 and 29·3° min^{-1}, depending on the intensity of a 2 s pre-scan. Three standard reflections were used; these showed no

Table 1. *Fractional coordinates with e.s.d.'s in parentheses*

(*a*) Non-hydrogen atoms

	x	y	z
Cr	0·13609 (4)	0·46961 (8)	0·30689 (7)
N(1)	0·0688 (2)	0·3507 (5)	0·2995 (4)
N(2)	0·1823 (2)	0·3243 (4)	0·3469 (4)
N(3)	0·2051 (2)	0·5778 (4)	0·3314 (4)
N(4)	0·1177 (2)	0·5096 (4)	0·4543 (4)
N(5)	0·0849 (2)	0·6017 (5)	0·2492 (4)
N(6)	0·1591 (3)	0·4523 (5)	0·1585 (4)
C(1)	0·0924 (3)	0·2316 (5)	0·3008 (5)
C(2)	0·1425 (3)	0·2276 (5)	0·3711 (5)
C(3)	0·2131 (3)	0·5954 (5)	0·4405 (5)
C(4)	0·1546 (3)	0·6072 (5)	0·4874 (5)
C(5)	0·1025 (3)	0·6264 (6)	0·1444 (5)
C(6)	0·1161 (3)	0·5134 (6)	0·0951 (5)
I(1)	0·21957 (2)	0·16764 (3)	0·11131 (3)
I(2)	0·00988 (2)	0·02375 (4)	0·04941 (3)
I(3)	0·33410 (2)	0·38373 (3)	0·30910 (3)
O(1)*	0·4800 (4)	0·4655 (8)	0·3266 (8)
O(2)†	0·4679 (7)	0·4844 (14)	0·2217 (15)

(*b*) Hydrogen atoms

	Attached to	x	y	z
H(1)	N(1)	0·040	0·353	0·351
H(2)	N(1)	0·042	0·368	0·250
H(3)	C(1)	0·056	0·174	0·306
H(4)	C(1)	0·113	0·219	0·226
H(5)	C(2)	0·133	0·239	0·432
H(6)	C(2)	0·156	0·155	0·379
H(7)	N(2)	0·208	0·335	0·395
H(8)	N(2)	0·214	0·294	0·303
H(9)	N(3)	0·245	0·545	0·313
H(10)	N(3)	0·202	0·647	0·311
H(11)	C(3)	0·237	0·523	0·470
H(12)	C(3)	0·239	0·665	0·457
H(13)	C(4)	0·153	0·595	0·572
H(14)	C(4)	0·134	0·682	0·466
H(15)	N(4)	0·131	0·440	0·500
H(16)	N(4)	0·081	0·515	0·449
H(17)	N(5)	0·039	0·565	0·246
H(18)	N(5)	0·087	0·667	0·295
H(19)	C(5)	0·064	0·665	0·113
H(20)	C(5)	0·136	0·678	0·152
H(21)	C(6)	0·081	0·461	0·093
H(22)	C(6)	0·132	0·530	0·036
H(23)	N(6)	0·158	0·376	0·127
H(24)	N(6)	0·191	0·470	0·151

* Occupancy $\frac{2}{3}$.
† Occupancy $\frac{1}{3}$.

significant change in intensity. The data were corrected for Lorentz–polarization effects, and for absorption (transmission coefficient range on F: 0·644 to 0·917). 3504 independent reflections had $I > 3\sigma(I)$ and were used in the subsequent structure analysis. XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used for the calculation. Full-matrix least-squares refinement was used throughout and the function minimized was $\sum w(F_o - F_c)^2$. Scattering factors were from Cromer & Mann (1968) and the real and imaginary parts of the anomalous dispersion for Cr and I from Cromer & Liberman (1970). The structure was solved by the heavy-atom method. The correct location of two I atoms allowed us to recognize all remaining non-hydrogen atoms on a subsequent difference map. Refinement with the Cr and I atoms anisotropic, and all other atoms isotropic, including one water O(1) with occupancy of 1·0, gave R = 0·052. At this stage it was clear that the water was disordered, with two sites O(1) and O(2) of respective occupancies $\frac{2}{3}$ and $\frac{1}{3}$. All H atoms, except those belonging to the two water molecules, could be located and were included as fixed atoms with B = 4·5 Å^2. A refinement with all non-hydrogen atoms anisotropic and $w^{-1} = 1 + [(F_o - B)/A]^2$, where A = 180 and B = 70, gave the final R = 0·035 and R_w = 0·042. The fractional coordinates of the non-hydrogen atoms are presented in Table 1(*a*), and those of the H atoms in Table 1(*b*).*

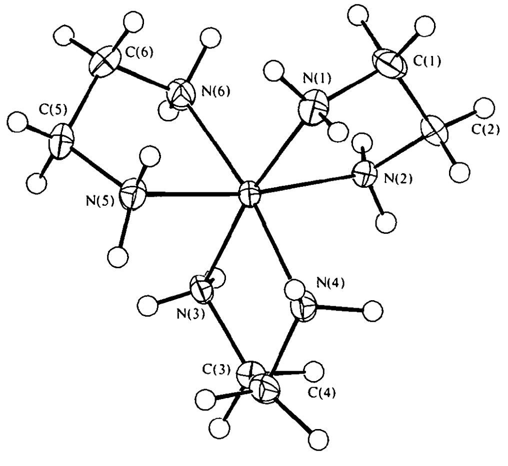

Fig. 1. View of the complex cation Cr(en)$_3^{3+}$. Thermal ellipsoids are scaled at the 50% probability level. Hydrogen atoms are represented by circles of arbitrary size.

Discussion. The complex cation is shown in Fig. 1. The configuration about the Cr atom presented here is Λ (IUPAC, 1970), with one of the ligands, N(3), C(3), C(4), N(4), present in the δ conformation so that the C(3)—C(4) vector is nearly parallel to the pseudo threefold axis of the cation. The two other rings are present as λ, with their C—C bonds forming an oblique angle with the pseudo threefold axis of the cation. The interatomic distances and angles of interest are presented in Table 2. The mean Cr—N distance of 2·081 (5) Å is very similar to the mean of 2·076 (4) Å found in Cr(en)$_3$(SCN)$_3$ (Brouty, Spinat, Whuler & Herpin, 1977) and an average value of 2·096 (3) Å in Cr[NH$_2$—(CH$_2$)$_3$—NH$_2$]$_3$ (Jurnak & Raymond, 1974). The other distances and angles in the ligands appear normal. There is an

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cr—N(1)	2·088 (6)	Cr—N(4)	2·088 (5)
Cr—N(2)	2·072 (5)	Cr—N(5)	2·091 (6)
Cr—N(3)	2·063 (5)	Cr—N(6)	2·084 (5)
N(1)—C(1)	1·489 (9)	C(4)—N(4)	1·490 (8)
C(1)—C(2)	1·502 (9)	N(5)—C(5)	1·501 (8)
C(2)—N(2)	1·489 (8)	C(5)—C(6)	1·506 (10)
N(3)—C(3)	1·498 (8)	C(6)—N(6)	1·495 (9)
C(3)—C(4)	1·504 (10)		
N(1)—Cr—N(2)	81·9 (2)	N(2)—Cr—N(6)	92·3 (2)
N(1)—Cr—N(3)	172·7 (2)	N(3)—Cr—N(4)	82·5 (2)
N(1)—Cr—N(4)	92·3 (2)	N(3)—Cr—N(5)	93·0 (2)
N(1)—Cr—N(5)	92·5 (2)	N(3)—Cr—N(6)	90·8 (2)
N(1)—Cr—N(6)	94·7 (2)	N(4)—Cr—N(5)	94·3 (2)
N(2)—Cr—N(3)	93·1 (1)	N(4)—Cr—N(6)	172·2 (2)
N(2)—Cr—N(4)	92·2 (2)	N(5)—Cr—N(6)	81·9 (2)
N(2)—Cr—N(5)	171·6 (2)		
Cr—N(1)—C(1)	109·9 (4)	Cr—N(4)—C(4)	109·8 (4)
Cr—N(2)—C(2)	110·6 (4)	Cr—N(5)—C(5)	109·8 (4)
Cr—N(3)—C(3)	109·7 (4)	Cr—N(6)—C(6)	109·5 (4)
N(1)—C(1)—C(2)	108·7 (5)	C(3)—C(4)—N(4)	108·8 (5)
C(1)—C(2)—N(2)	108·5 (5)	N(5)—C(5)—C(6)	107·8 (5)
N(3)—C(3)—C(4)	108·4 (5)	C(5)—C(6)—N(6)	107·6 (5)

Hydrogen-bonding distances

$A—B\cdots C$	$A\cdots C$	$B\cdots C$	$A—B—C$ (°)
N(1)—H(1)···I(2^{i})	3·696 (6)	2·847	147
N(1)—H(2)···O(1^{ii})	2·989 (10)	2·104	157
N(2)—H(7)···I(1^{i})	3·676 (5)	2·934	142
N(3)—H(10)···I(3^{iii})	3·682 (5)	2·877	158
N(4)—H(15)···I(1^{i})	3·786 (5)	2·837	149
N(4)—H(16)···I(2^{iv})	3·722 (5)	3·043	138
N(5)—H(17)···O(1^{ii})	3·080 (10)	2·044	148
N(5)—H(17)···O(2^{ii})	3·063 (17)	1·947	163
N(6)—H(24)···I(1^{iii})	3·820 (6)	3·142	148
O(1)···I(3)	3·522 (9)		
O(1)···I(2^{v})	3·542 (9)		
O(2)···I(3)	3·521 (17)		
O(2)···I(2^{iv})	3·490 (19)		

Roman superscripts refer to atom in the following positions:
(i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, z$; (iv) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $\frac{1}{2} + x, y, \frac{1}{2} - z$.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33789 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

extensive network of hydrogen bonds. The N—H···I hydrogen bonds range from 3·676 to 3·820 Å and O—H···I from 3·490 to 3·522 Å. These distances are close to the sums of the van der Waals radii (Pauling, 1960): 3·65 and 3·55 Å for I···N and I···O, respectively. The N—H···O hydrogen bonds range from 2·989 to 3·080 Å.

References

Brouty, C., Spinat, P., Whuler, A. & Herpin, P. (1977). *Acta Cryst.* **B33**, 1920–1926.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

IUPAC (1970). *Inorg. Chem.* **9**, 1–5.

Jurnak, F. A. & Raymond, K. N. (1974). *Inorg. Chem.* **13**, 2387–2397.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ Press.

Rollinson, C. L. & Bailar, J. C. (1946). *Inorg. Synth.* **2**, 196–200.

Sartori, G., Castelli, F. & Cervone, E. (1971). *Gazz. Chim. Ital.* **101**, 32–40.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192, Computer Science Center, University of Maryland, College Park, Maryland, USA.

Whuler, A., Brouty, C., Spinat, P. & Herpin, P. (1975). *Acta Cryst.* **B31**, 2069–2076.

Acta Cryst. (1978). B**34**, 3369–3372

Refinement of the Structure of the Costunolide–Silver Nitrate Complex

By A. Línek and C. Novák

Institute of Solid State Physics, Czechoslovak Academy of Sciences, Cukrovarnická 10, 162 53 *Praha* 6, *Czechoslovakia*

(*Received* 21 *March* 1978; *accepted* 18 *July* 1978)

Abstract. The structure [Šorm, Suchý, Holub, Línek, Hadinec & Novák (1970). *Tetrahedron Lett.* pp. 1893–1896] of $C_{15}H_{20}O_2.2AgNO_3$, $M_r = 572{\cdot}1$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}495\ (2)$, $b = 11{\cdot}411\ (3)$, $c = 21{\cdot}436\ (3)$ Å, $Z = 4$, was refined to $R = 0{\cdot}043$. The coordinated C=C double bonds in the *trans,trans*-cyclodeca-1,5-diene ring of the complex are significantly longer than the C=C bonds in the uncomplexed molecule [Bovill, Cox, Cradwick, Guy, Sim & White (1976). *Acta Cryst.* **B32**, 3203–3209].

Introduction. Counter data were collected on a Hilger & Watts tape-controlled diffractometer, using Mo $K\alpha$ radiation. 2183 independent reflexions were obtained (each of them measured four times including left and right background) with an ω–2θ step scan for 2θ up to 60°. Very strong reflexions (more than 15 thousand counts s^{-1} in the peak) were remeasured with attenuators. One standard reflexion was measured after each 12 measurements. The specimen appeared to be stable to air, light and X-rays. Corrections were made for background (linear), standard-reflexion level and Lp. No absorption correction (for a needle-shaped specimen supposed to be cylindrical, $\mu R < 0{\cdot}6$) or extinction correction was made.

A local version (Novák, 1973) of *ORFLS* (Busing, Martin & Levy, 1962), allowing the use of anomalous-

Table 1. *Fractional coordinates of non-hydrogen atoms* ($\times 10^4$; *for* Ag *atoms* $\times 10^5$)

E.s.d.'s (in parentheses) refer to the last decimal place.

	x	*y*	*z*
Ag(1)	38894 (10)	79603 (6)	69744 (3)
Ag(2)	93357 (10)	5331 (5)	42840 (2)
N(1)	6118 (9)	2851 (6)	6691 (3)
N(2)	6382 (9)	6311 (6)	6438 (3)
O(1)	9366 (8)	2459 (4)	5206 (2)
O(2)	9551 (8)	4405 (5)	5100 (3)
O(3)	5327 (9)	3633 (5)	6983 (3)
O(4)	7032 (9)	2113 (6)	6977 (3)
O(5)	6013 (10)	2804 (6)	6104 (2)
O(6)	4741 (8)	6203 (5)	6343 (3)
O(7)	7447 (10)	5669 (7)	6177 (4)
O(8)	6870 (9)	7107 (5)	6787 (3)
C(1)	2280 (11)	8805 (6)	6167 (3)
C(2)	1149 (12)	7861 (6)	5874 (3)
C(3)	324 (13)	8318 (6)	5249 (3)
C(4)	9347 (10)	9447 (6)	5387 (3)
C(5)	304 (10)	472 (6)	5359 (3)
C(6)	9850 (10)	1584 (5)	5678 (3)
C(7)	1453 (10)	2123 (6)	6028 (3)
C(8)	1761 (12)	1723 (6)	6705 (3)
C(9)	2816 (10)	594 (6)	6797 (3)
C(10)	1823 (11)	9490 (6)	6665 (3)
C(11)	1056 (11)	3423 (6)	5942 (3)
C(12)	9930 (10)	3534 (7)	5388 (3)
C(13)	1414 (10)	4331 (6)	6310 (3)
C(14)	7545 (11)	9318 (7)	5660 (5)
C(15)	234 (13)	9291 (7)	7057 (4)