C(1)	0.3211 (5)	−0.1079 (6)	0.8114 (2)	2.4 (2)
C(2)	0.4357 (5)	−0.1862 (6)	0.7957 (2)	3.1 (2)
C(3)	0.5633 (5)	−0.1674 (7)	0.8265 (2)	3.1 (2)
C(4)	0.5793 (5)	−0.0738 (6)	0.8716 (2)	2.8 (2)
C(5)	0.4602 (5)	−0.0022 (6)	0.8853 (2)	2.3 (2)
C(6)	0.4492 (5)	0.0996 (6)	0.9310 (2)	2.3 (2)
C(7)	0.4965 (5)	0.2507 (6)	1.0015 (2)	2.4 (2)
C(8)	0.3518 (5)	0.2476 (6)	0.9841 (2)	2.5 (2)
C(9)	0.2606 (5)	0.3363 (7)	1.0105 (2)	3.0 (2)
C(10)	0.3201 (6)	0.4249 (6)	1.0535 (2)	3.4 (2)
C(11)	0.4648 (6)	0.4264 (6)	1.0702 (2)	3.3 (2)
C(12)	0.5555 (5)	0.3383 (6)	1.0453 (2)	3.0 (2)
C(13)	0.1773 (5)	−0.1055 (6)	0.7844 (2)	2.4 (2)
C(14)	−0.0076 (5)	−0.1235 (6)	0.7283 (2)	2.5 (2)
C(15)	−0.0371 (5)	−0.0329 (6)	0.7719 (2)	2.4 (2)
C(16)	−0.1698 (5)	0.0335 (6)	0.7731 (2)	3.0 (2)
C(17)	−0.2694 (5)	0.0076 (7)	0.7298 (2)	3.2 (2)
C(18)	−0.2399 (5)	−0.0816 (7)	0.6863 (2)	3.4 (2)
C(19)	−0.1106 (6)	−0.1480 (7)	0.6851 (2)	3.2 (2)
C(21)	0.1714 (6)	0.4478 (7)	0.8479 (2)	4.3 (3)
C(31)	0.0043 (7)	−0.2211 (8)	0.9064 (3)	4.8 (3)

Table 2. *Selected geometric parameters* (Å, °)

Ni—N(1)	2.028 (4)	Ni—O(21)	2.074 (3)
Ni—N(2)	2.061 (4)	Ni—N(3)	2.114 (4)
Ni—N(11)	2.063 (4)	Ni—O(31)	2.151 (3)
N(1)—Ni—N(2)	78.0 (1)	N(2)—Ni—O(31)	91.0 (1)
N(1)—Ni—N(11)	177.3 (2)	N(11)—Ni—O(21)	91.0 (2)
N(1)—Ni—O(21)	89.6 (1)	N(11)—Ni—N(3)	100.0 (2)
N(1)—Ni—N(3)	77.4 (1)	N(11)—Ni—O(31)	88.9 (2)
N(1)—Ni—O(31)	90.4 (1)	O(21)—Ni—N(3)	89.1 (2)
N(2)—Ni—N(11)	104.6 (2)	O(21)—Ni—O(31)	178.1 (1)
N(2)—Ni—O(21)	90.9 (2)	N(3)—Ni—O(31)	89.1 (1)
N(2)—Ni—N(3)	155.3 (1)	N(12)—N(11)—Ni	131.9 (4)

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1983) and refined by full-matrix least-squares methods. All non-H atoms were located in successive $\Delta\rho$ maps and refined with anisotropic displacement parameters. All H atoms were located geometrically and included with isotropic displacement parameters in the structure-factor calculations, but not refined.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and complete geometry have been deposited with the IUCr (Reference: AB1196). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Addison, A. W. & Burke, P. J. (1981). *J. Heterocycl. Chem.* **18**, 803–805.

Alagna, L., Hasnain, S. S., Piggott, B. & Williams, D. J. (1984). *Biochem. J.* **220**, 591–595.

Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data.* Univ. of Glasgow, Scotland.

Sundberg, R. J. & Martin, R. B. (1974). *Chem. Rev.* **74**, 471–517.

Wang, S., Luo, Q., Zhou, X. & Zeng, Z. (1993). *Polyhedron*, **12**, 1939–1945.

Wang, S., Zhu, Y., Zhang, F., Wang, Q. & Wang, L. (1992). *Polyhedron*, **11**, 1909–1915.

Ethylenediaminium Dichromate

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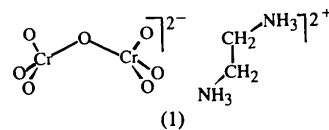
Abstract

The synthesis, characterization, and crystal and molecular structures of $C_2H_{10}N_2^{2+}.Cr_2O_7^{2-}$ are described. The structure of this compound was determined by X-ray crystallography and showed that the $C_2H_{10}N_2^{2+}$ organic cations are bound to the $Cr_2O_7^{2-}$ anions by N—H⋯O hydrogen-bonding interactions [2.988 (3) Å and 92.30 (17)°].

Comment

To our knowledge, no fluoropolychromates(VI) have been reported previously. We attempted to prepare an organic fluoropolychromate(VI) from organic base, chromium(VI) trioxide and HF in aqueous medium, but obtained instead an organic dichromate(VI). We describe here the preparation, characterization, and molecular and crystal structures of ethylenediaminium dichromate, (1).

(1)

A view of the molecule is shown in Fig. 1, with the unit-cell packing in Fig. 2. The structure consists of discrete dinegative dichromate anions hydrogen bonded to

dipositive ethylenediaminium cations. The Cr—O bond distances are close to the expected values for the dichromate anion (1.60 Å) (Martín-Zarza, Gili, Rodríguez-Romero, Ruiz-Pérez & Solans, 1994; Pressprich, Willet, Sheets, Paudler & Gard, 1990), with the exception of the Cr(1)—O(4) distance [1.6300 (11) Å] which may be attributed to the N—H···O hydrogen bond. The angles around Cr(1) are nearly tetrahedral [107.59 (6)–110.94 (8)°]. The most important hydrogen bonds are N(1)—H(1)···O(4) [2.988 (3) Å and 92.30 (17)°], N(1)—H(1)···O(4^i) [2.812 (3) Å and 161.83 (19)°; symmetry code: (i) $\frac{3}{2}-x$, $\frac{1}{2}-y$, $1-z$], N(1)—H(2)···O(3^{ii})

[2.914 (3) Å and 147.52 (19)°; symmetry code: (ii) x, $1-y$, $z-\frac{1}{2}$] and N(1)—H(2)···O(4) [2.988 (3) Å and 116.81 (16)°]. All these hydrogen bonds are bifurcated.

Experimental

The IR spectrum of the compound shows bands at 3100 cm^{-1} corresponding to the stretching vibrations of NH_3^+ of the ethylenediaminium cation when an intermolecular hydrogen bond exists (Bellamy, 1975). The bands at 948 and 878 cm^{-1} are assigned to the symmetric and asymmetric Cr—O stretching vibrations of the terminal bonds (ν_1 frequency, symmetry A) (Martín-Zarza, Gili, Rodríguez-Romero, Ruiz-Pérez & Solans, 1994). The IR spectrum was obtained with a Nicolet 710FT-IR spectrophotometer in the 4000–250 cm^{-1} range using KBr pellets.

The electronic spectrum of the title compound presents bands at 440, 360–370 and 274 nm. The assignments are 440 ($^1A_1 \rightarrow ^1E^a$), 360–370 ($^1A_1 \rightarrow ^1A_1$ and $^1E^b$ or $t_1^6 \rightarrow t_1^5e^1$) and 274 nm ($^1A_1 \rightarrow ^1E^c$ or $t_1^6 \rightarrow t_1^5t_2^1$) (Ciéslak-Golonka, 1991). The electronic spectrum as diffuse reflectance was recorded on a Perkin-Elmer 550S spectrophotometer dispersing all samples in $BaSO_4$.
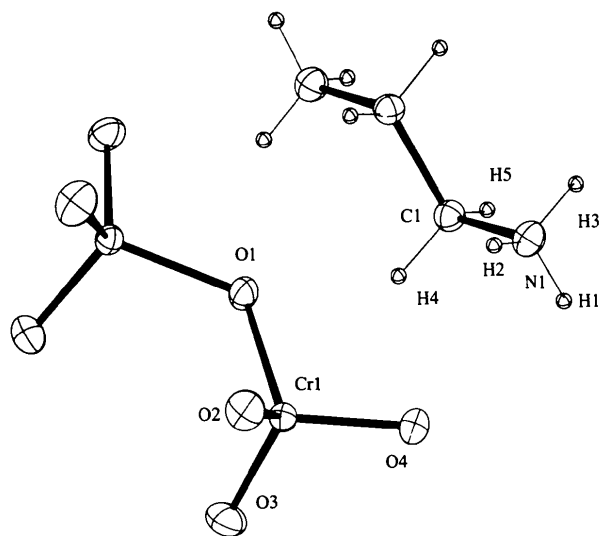

Fig. 1. Structure of the title compound showing the atom numbering. Displacement ellipsoids are plotted at the 50% probability level.
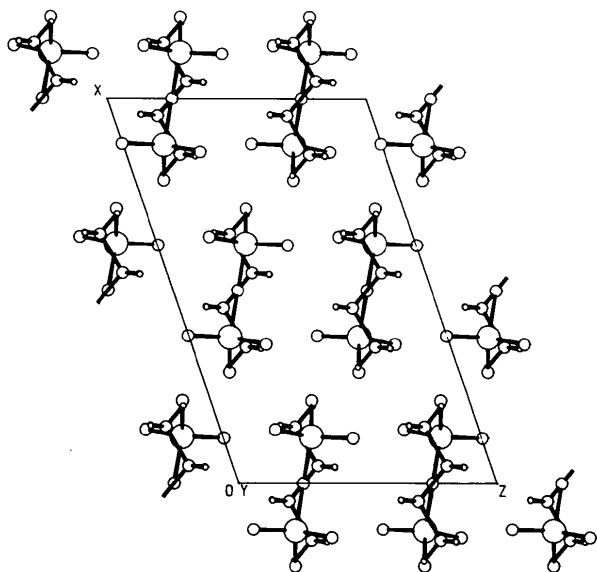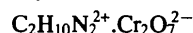

Fig. 2. Packing diagram of the unit cell.

Crystal data

$C_2H_{10}N_2^{2+}.Cr_2O_7^{2-}$	Mo $K\alpha$ radiation
$M_r = 278.12$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$C2/c$	reflections
$a = 13.526$ (7) Å	$\theta = 10$–$25°$
$b = 7.801$ (7) Å	$\mu = 2.515$ mm^{-1}
$c = 8.706$ (11) Å	$T = 293$ K
$\beta = 109.14$ (5)°	Hexagonal prismatic
$V = 867.8$ (11) Å^3	0.8 × 0.4 × 0.4 mm
$Z = 4$	Red–orange
$D_x = 2.129$ Mg m^{-3}	

Data collection

Stoe Siemens AED-2 diffractometer	1676 observed reflections $[F_o > 4\sigma(F_o)]$
$\theta/2\theta$ scans	$\theta_{max} = 34.98°$
Absorption correction:	$h = -21 \rightarrow 19$
ψ scan (Stoe & Cie, 1987a)	$k = 0 \rightarrow 12$
	$l = 0 \rightarrow 13$
$T_{min} = 0.4526$, $T_{max} = 0.5652$	2 standard reflections frequency: 60 min
1898 measured reflections	intensity decay: <3%
1898 independent reflections	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.390$ e Å^{-3}
$R(F) = 0.0223$	$\Delta\rho_{min} = -0.450$ e Å^{-3}

$wR(F^2) = 0.0733$
$S = 0.837$
1676 reflections
63 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 1.12P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.064 (2)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Stoe & Cie (1987a). *DIF4. Data Collection Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1987b). *REDU4. Data Reduction Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cr(1)	0.6215 (1)	0.5992 (1)	0.3424 (1)	0.023 (1)
N(1)	0.6467 (1)	0.0935 (2)	0.2932 (2)	0.031 (1)
C(1)	0.5460 (1)	0.0954 (2)	0.3288 (2)	0.026 (1)
O(1)	1/2	0.4925 (2)	1/4	0.030 (1)
O(2)	0.6398 (1)	0.7336 (2)	0.2116 (2)	0.039 (1)
O(3)	0.6179 (1)	0.7009 (2)	0.5023 (2)	0.043 (1)
O(4)	0.7132 (1)	0.4539 (2)	0.3900 (1)	0.034 (1)

Table 2. *Selected geometric parameters (Å, °)*

Cr(1)—O(3)	1.617 (2)	N(1)—C(1)	1.494 (2)
Cr(1)—O(2)	1.625 (2)	C(1)—C(1^i)	1.520 (3)
Cr(1)—O(4)	1.6300 (11)	O(1)—Cr(1^i)	1.7818 (10)
Cr(1)—O(1)	1.7818 (10)		
O(3)—Cr(1)—O(2)	109.96 (9)	O(2)—Cr(1)—O(1)	108.37 (7)
O(3)—Cr(1)—O(4)	110.94 (8)	O(4)—Cr(1)—O(1)	107.59 (6)
O(2)—Cr(1)—O(4)	110.42 (7)	N(1)—C(1)—C(1^i)	110.15 (14)
O(3)—Cr(1)—O(1)	109.49 (6)	Cr(1)—O(1)—Cr(1^i)	124.27 (8)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Data collection and lattice-constant refinement used *DIF4* (Stoe & Cie, 1987a). Lorentz and polarization corrections were applied (*REDU4*; Stoe & Cie, 1987b). The structure was solved by the Patterson method using *SHELXS86* (Sheldrick, 1990). All non-H atoms were refined anisotropically with *SHELXL93* (Sheldrick, 1993). H atoms were refined with restraints: distances N—H and C—H = 1.08 Å; isotropic displacement factors = 0.043 and 0.033 Å² for H atoms bonded to N and C, respectively. Molecular graphics were produced using *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SH1107). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bellamy, L. J. (1975). *The Infrared Spectra of Complex Molecules,* Vol. 1, 3rd ed., pp. 289–290. London: Chapman & Hall.
Ciéslak-Golonka, M. (1991). *Coord. Chem. Rev.* **109**, 223–249.
Johnson, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Martín-Zarza, P., Gili, P., Rodríguez-Romero, F. V., Ruiz-Pérez, C. & Solans, X. (1994). *Polyhedron.* In the press.
Pressprich, M. R., Willet, R. D., Sheets, R. M., Paudler, W. W. & Gard, G. L. (1990). *Acta Cryst.* C**46**, 1635–1637.

A Chelate-Stabilized Molybdenum–Imido–Alkylidene Complex, [TpMo{CHC(Me)₂Ph}(NAr)(OTf)]

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Abstract

The title compound, (2,6-diisopropylphenylimido)[hydrotris(1-pyrazolyl-N^3)borato](2-methyl-2-phenylpropylidene)(trifluoromethanesulfonato)molybdenum(VI), [Mo(CF₃O₃S)(C₁₀H₁₂)(C₁₂H₁₇N)(C₉H₁₀BN₆)], has been synthesized and its crystal structure determined. The geometry around the Mo atom, imposed by the tridentate tris(pyrazolyl)borate ligand, is that of a distorted octahedron. There appears to be significant interaction between the ligands and the transition metal center. Principal distances include Mo—N(imido) 1.753 (8), Mo—C(propylidene) 1.949 (10), Mo—O(trifluoromethanesulfonate) 2.121 (7) and Mo—N(pyrazolyl) 2.167 (8)–2.311 (9) Å.

Comment

The chemistry of high-oxidation-state metal–alkylidene complexes is of particular interest because of their role in olefin metathesis reactions and polymerizations (Nugent & Mayer, 1988; Schrock, 1986). Our efforts have focused on employing ancillary chelating ligands to form metal–alkylidene complexes of increased thermal stability (Blosch, Gamble, Abboud & Boncella, 1992; Gamble & Boncella, 1993). As part of our investigation of the use of hydrotris(pyrazolyl)borate (Tp) ligands (Trofimenko, 1971) in the stablization of metal–alkylidene complexes, we have determined the structure of the title compound