metal-organic compounds

4-(Dimethylamino)pyridinium *trans*-diaquabis[oxalato(2−)-$\kappa^2 O^1,O^2$]-chromate(III)

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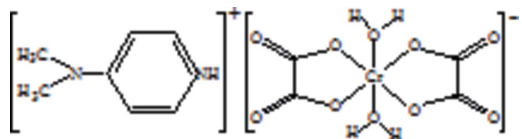Correspondence e-mail: jnenwa@yahoo.fr

In the title salt, $(C_7H_{11}N_2)[Cr(C_2O_4)_2(H_2O)_2]$, the asymmetric unit contains one half-cation and one half-anion. The Cr atom, the C and N atoms involved in C—N(exocyclic) bonding and the N and H atoms of N—H groups lie on twofold rotation axis. The Cr^{III} atom of the complex anion is six-coordinated in a distorted (4 + 2) octahedral geometry with four equatorial O atoms of two nearly coplanar oxalate and two quasi-axial aqua O atoms. In the crystal, the protonated N atoms of the pyridine rings are hydrogen bonded to the carbonyl O atoms of the anions, forming chains along [010]. These chains are connected by lateral O—H···O hydrogen bonds, stabilizing the structure.

Related literature

For general background to the coordination chemistry of oxalate, see: Martin *et al.* (2007). For related structures, see: Bélombé *et al.* (2009); Ghouili *et al.* (2010).

Experimental

Crystal data

$(C_7H_{11}N_2)[Cr(C_2O_4)_2(H_2O)_2]$	a = 11.524 (4) Å
M_r = 387.25	b = 20.372 (8) Å
Monoclinic, $C2/c$	c = 7.355 (2) Å
β = 120.626 (6)°	μ = 0.83 mm⁻¹
V = 1485.9 (9) Å³	T = 293 K
Z = 4	$0.20 \times 0.20 \times 0.10$ mm
Mo $K\alpha$ radiation	

Data collection

Bruker APEX CCD area-detector diffractometer	10203 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	1857 independent reflections
T_{min} = 0.895, T_{max} = 0.910	1739 reflections with $I > 2\sigma(I)$
	R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.089	
S = 1.16	
1857 reflections	$\Delta\rho_{max}$ = 0.37 e Å⁻³
127 parameters	$\Delta\rho_{min}$ = −0.38 e Å⁻³
2 restraints	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O4ⁱ	0.82 (1)	1.91 (1)	2.719 (2)	171 (2)
O1—H1B···O5ⁱⁱ	0.80 (1)	1.91 (1)	2.680 (2)	160 (2)
N12—H12···O4ⁱⁱⁱ	0.86	2.19	2.906 (3)	141
N12—H12···O4ⁱᵛ	0.86	2.19	2.906 (3)	141

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2312).

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supporting information

4-(Dimethylamino)pyridinium *trans*-diaquabis[oxalato(2−)-$\kappa^2 O^1,O^2$]chromate(III)

Justin Nenwa, Michel M. Belombe, Jean Ngoune and Boniface P. T. Fokwa

S1. Comment

The coordination chemistry of oxalate ($C_2O_4^{2-}$) continues receiving considerable attention, due to the ability of this ion to act as a remarkably flexible ligand system in complexations with a wide range of metal ions [Martin *et al.*,2007]. Recently, we published the structure of an organic-inorganic hybrid salt involving the quinolinium cation, $[C_9H_8N]^+$ and complex anion, $[Cr(H_2O)_2(C_2O_4)_2]^-$ (Bélombé *et al.*, 2009). We report here the crystal structure of a homologous salt, with 4-Dimethylaminopyridinium as the organic cation. The Fig. 1 shows the 4-dimethylaminopyridinium cation, $[C_7H_{11}N_2]^+$, and the complex anion, $[Cr(H_2O)_2(C_2O_4)_2]^-$. The asymmetric unit is formed by one-half cation and one-half anion. The geometrical parameters of the $[C_7H_{11}N_2]^+$ cation are in agreement with those found in salts with the same cationic entity (Ghouili *et al.*, 2010). The Cr^{III} ion of the complex anion adopts a distorted (4 + 2) octahedral coordination involving four equatorial O atoms (O2, O2^i, O3, O3^i) of two nearly coplanar oxalate and two quasi axial O atoms (O1, O1^i) of water ligands (Fig. 1). The equatorial Cr–O distances are 1.9706 (13) Å (Cr–O(2), Cr–O(2^i)) and 1.9468 (13) Å (Cr–O(3), Cr–O(3^i)) respectively, and are significantly shorter than the axial Cr–O distance of 2.0055 (14)Å (Cr–O(1), Cr–O(1^i)). The bond distances in the complex anion are comparable with those reported for the quinolinium compound (Bélombé *et al.*, 2009).In the crystal structure, intermolecular N–H⋯O(carbonyl) hydrogen bonds connect the ionic entities, generating layers parallel to [010]. These layers are further connected by lateral O–H⋯O hydrogen bonds,stabilizing the structure (Table 1, Fig. 2)

S2. Experimental

A mixture of 4-dimethylaminopyridine (1 mmol, 122.2 mg) and oxalic acid (2.2 mmol, 277.2 mg) was dissolved in 30 ml of water. The filtered solution was stirred at 328 K and an aqueous solution (20 ml) of CrCl$_3$.6H$_2$O (1 mmol, 266.5 mg) was added in successive small portions and stirred for 2 h continuously. The final red-violet solution obtained was left at room temperature and brown plate-like crystals suitable for X-ray diffraction were obtained after a few days.

S3. Refinement

The H atoms were positioned geometrically, with C—H, N—H distances of 0.96 and 0.86 Å respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5Ueq(C) and 1.2Ueq(N). The water H atoms were first located in a difference Fourier map and refined with distance restraints of d(O–H1) = 0.81 (1) with all U_{iso}(H) refined freely.
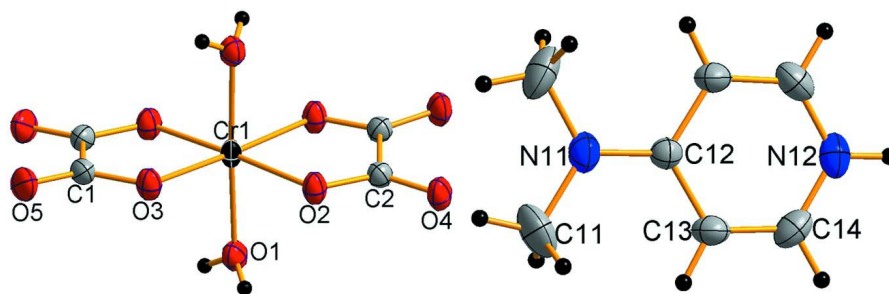
Figure 1

A view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related two labeled atoms by the symmetry code for cation and anion are: 1-x,y,1/2-z; -x,y,1/2-z
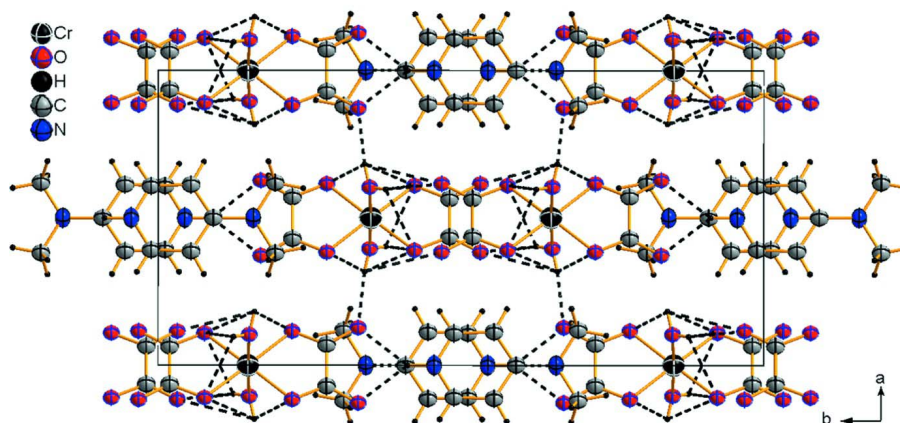

Figure 2

Packing diagram of the title compound. Dotted lines show hydrogen bonding.

4-(Dimethylamino)pyridinium *trans*-diaquabis[oxalato(2-)-κ^2O^1,O^2]chromate(III)

Crystal data

$(C_7H_{11}N_2)[Cr(C_2O_4)_2(H_2O)_2]$	$F(000) = 796$
$M_r = 387.25$	$D_x = 1.731$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1857 reflections
$a = 11.524$ (4) Å	$\theta = 2.0–28.3°$
$b = 20.372$ (8) Å	$\mu = 0.83$ mm^{-1}
$c = 7.355$ (2) Å	$T = 293$ K
$\beta = 120.626$ (6)°	Prism, dark-violet
$V = 1485.9$ (9) Å^3	$0.20 \times 0.20 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker APEX CCD area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
Radiation source: fine-focus sealed tube	$T_{min} = 0.895$, $T_{max} = 0.910$
Graphite monochromator	10203 measured reflections
integration method scans	1857 independent reflections
	1739 reflections with $I > 2\sigma(I)$

$R_{int} = 0.046$
$\theta_{max} = 28.3°, \theta_{min} = 2.0°$
$h = -15 \rightarrow 15$

$k = -27 \rightarrow 27$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.033$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.089$	
$S = 1.16$	$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 1.1284P]$
1857 reflections	where $P = (F_o^2 + 2F_c^2)/3$
127 parameters	$(\Delta/\sigma)_{max} < 0.001$
2 restraints	$\Delta\rho_{max} = 0.37$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.38$ e Å^{-3}
Secondary atom site location: difference Fourier map	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
	Extinction coefficient: 0.0065 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Cr1	0.0000	0.148676 (17)	0.2500	0.02141 (14)
O1	0.10432 (13)	0.15066 (6)	0.5670 (2)	0.0278 (3)
H1A	0.1841 (11)	0.1603 (11)	0.618 (4)	0.038 (6)*
H1B	0.097 (2)	0.1194 (8)	0.626 (3)	0.039 (6)*
O2	0.11598 (12)	0.22143 (6)	0.2606 (2)	0.0273 (3)
O3	0.10971 (12)	0.07688 (6)	0.2448 (2)	0.0275 (3)
O4	0.12757 (13)	0.33040 (6)	0.2756 (2)	0.0324 (3)
O5	0.11585 (14)	−0.03196 (7)	0.2324 (2)	0.0394 (4)
C1	0.06468 (17)	0.01913 (8)	0.2430 (3)	0.0259 (4)
C2	0.07080 (16)	0.27821 (8)	0.2608 (3)	0.0236 (3)
N11	0.5000	0.15711 (11)	0.2500	0.0374 (5)
N12	0.5000	−0.04417 (12)	0.2500	0.0393 (6)
H12	0.5000	−0.0864	0.2500	0.096 (17)*
C11	0.3808 (3)	0.19340 (12)	0.2074 (5)	0.0594 (7)
H11C	0.3998	0.2396	0.2191	0.121 (15)*
H11D	0.3548	0.1811	0.3077	0.088 (11)*
H11E	0.3087	0.1836	0.0671	0.077 (10)*
C12	0.5000	0.09124 (12)	0.2500	0.0263 (5)
C13	0.38704 (18)	0.05453 (10)	0.2186 (3)	0.0341 (4)
H13	0.3097	0.0760	0.1967	0.049 (7)*

C14	0.3915 (2)	−0.01145 (10)	0.2204 (3)	0.0394 (5)
H14	0.3167	−0.0349	0.2005	0.070 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.0191 (2)	0.0153 (2)	0.0318 (2)	0.000	0.01434 (16)	0.000
O1	0.0272 (7)	0.0222 (6)	0.0332 (7)	−0.0025 (5)	0.0147 (6)	0.0010 (5)
O2	0.0237 (6)	0.0200 (6)	0.0417 (7)	−0.0003 (4)	0.0192 (6)	0.0007 (5)
O3	0.0236 (6)	0.0222 (6)	0.0400 (7)	0.0021 (5)	0.0186 (5)	−0.0004 (5)
O4	0.0275 (6)	0.0205 (6)	0.0477 (8)	−0.0031 (5)	0.0180 (6)	0.0019 (5)
O5	0.0379 (8)	0.0254 (7)	0.0459 (8)	0.0093 (5)	0.0148 (6)	−0.0056 (6)
C1	0.0242 (8)	0.0219 (8)	0.0252 (8)	0.0029 (6)	0.0080 (7)	−0.0011 (6)
C2	0.0216 (8)	0.0216 (8)	0.0258 (8)	0.0007 (6)	0.0110 (6)	0.0014 (6)
N11	0.0452 (14)	0.0244 (11)	0.0443 (14)	0.000	0.0240 (12)	0.000
N12	0.0497 (15)	0.0244 (12)	0.0397 (13)	0.000	0.0198 (11)	0.000
C11	0.0716 (18)	0.0393 (13)	0.0646 (16)	0.0220 (12)	0.0327 (15)	−0.0016 (11)
C12	0.0265 (12)	0.0271 (12)	0.0259 (11)	0.000	0.0138 (10)	0.000
C13	0.0248 (9)	0.0395 (10)	0.0398 (10)	−0.0006 (7)	0.0178 (8)	−0.0021 (8)
C14	0.0376 (11)	0.0398 (11)	0.0399 (11)	−0.0139 (8)	0.0190 (9)	−0.0035 (8)

Geometric parameters (Å, º)

Cr1—O3ⁱ	1.9466 (13)	N11—C12	1.342 (3)
Cr1—O3	1.9466 (13)	N11—C11ⁱⁱ	1.447 (3)
Cr1—O2	1.9706 (13)	N11—C11	1.447 (3)
Cr1—O2ⁱ	1.9706 (13)	N12—C14ⁱⁱ	1.333 (3)
Cr1—O1ⁱ	2.0067 (14)	N12—C14	1.333 (3)
Cr1—O1	2.0067 (14)	N12—H12	0.8600
O1—H1A	0.821 (10)	C11—H11C	0.9600
O1—H1B	0.802 (10)	C11—H11D	0.9600
O2—C2	1.269 (2)	C11—H11E	0.9600
O3—C1	1.283 (2)	C12—C13	1.414 (2)
O4—C2	1.224 (2)	C12—C13ⁱⁱ	1.414 (2)
O5—C1	1.218 (2)	C13—C14	1.345 (3)
C1—C1ⁱ	1.546 (4)	C13—H13	0.9300
C2—C2ⁱ	1.557 (3)	C14—H14	0.9300
O3ⁱ—Cr1—O3	82.57 (8)	O4—C2—C2ⁱ	119.61 (10)
O3ⁱ—Cr1—O2	177.08 (5)	O2—C2—C2ⁱ	114.16 (9)
O3—Cr1—O2	97.57 (6)	C12—N11—C11ⁱⁱ	120.73 (15)
O3ⁱ—Cr1—O2ⁱ	97.57 (6)	C12—N11—C11	120.73 (15)
O3—Cr1—O2ⁱ	177.08 (5)	C11ⁱⁱ—N11—C11	118.5 (3)
O2—Cr1—O2ⁱ	82.45 (7)	C14ⁱⁱ—N12—C14	120.0 (3)
O3ⁱ—Cr1—O1ⁱ	91.57 (5)	C14ⁱⁱ—N12—H12	120.0
O3—Cr1—O1ⁱ	90.16 (5)	C14—N12—H12	120.0
O2—Cr1—O1ⁱ	91.35 (5)	N11—C11—H11C	109.5
O2ⁱ—Cr1—O1ⁱ	86.91 (5)	N11—C11—H11D	109.5

O3^i—Cr1—O1	90.16 (5)	H11C—C11—H11D	109.5
O3—Cr1—O1	91.57 (5)	N11—C11—H11E	109.5
O2—Cr1—O1	86.91 (5)	H11C—C11—H11E	109.5
O2^i—Cr1—O1	91.35 (5)	H11D—C11—H11E	109.5
O1^i—Cr1—O1	177.70 (7)	N11—C12—C13	121.92 (12)
Cr1—O1—H1A	114.1 (17)	N11—C12—C13^{ii}	121.92 (12)
Cr1—O1—H1B	116.7 (17)	C13—C12—C13^{ii}	116.2 (2)
H1A—O1—H1B	110 (2)	C14—C13—C12	119.97 (19)
C2—O2—Cr1	114.53 (11)	C14—C13—H13	120.0
C1—O3—Cr1	115.20 (11)	C12—C13—H13	120.0
O5—C1—O3	125.28 (17)	N12—C14—C13	121.95 (19)
O5—C1—C1^i	121.26 (11)	N12—C14—H14	119.0
O3—C1—C1^i	113.46 (9)	C13—C14—H14	119.0
O4—C2—O2	126.23 (15)		

O3^i—Cr1—O2—C2	−89.0 (10)	Cr1—O3—C1—C1^i	−3.0 (2)
O3—Cr1—O2—C2	178.46 (12)	Cr1—O2—C2—O4	176.72 (14)
O2^i—Cr1—O2—C2	1.40 (9)	Cr1—O2—C2—C2^i	−3.4 (2)
O1^i—Cr1—O2—C2	88.11 (12)	C11^{ii}—N11—C12—C13	177.00 (16)
O1—Cr1—O2—C2	−90.37 (12)	C11—N11—C12—C13	−3.00 (16)
O3^i—Cr1—O3—C1	1.22 (9)	C11^{ii}—N11—C12—C13^{ii}	−3.00 (16)
O2—Cr1—O3—C1	178.27 (12)	C11—N11—C12—C13^{ii}	177.00 (16)
O2^i—Cr1—O3—C1	−91.7 (10)	N11—C12—C13—C14	−179.79 (14)
O1^i—Cr1—O3—C1	−90.34 (12)	C13^{ii}—C12—C13—C14	0.21 (14)
O1—Cr1—O3—C1	91.18 (12)	C14^{ii}—N12—C14—C13	0.22 (15)
Cr1—O3—C1—O5	177.34 (15)	C12—C13—C14—N12	−0.4 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O4^{iii}	0.82 (1)	1.91 (1)	2.719 (2)	171 (2)
O1—H1*B*···O5^{iv}	0.80 (1)	1.91 (1)	2.680 (2)	160 (2)
N12—H12···O4^v	0.86	2.19	2.906 (3)	141
N12—H12···O4^{vi}	0.86	2.19	2.906 (3)	141

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