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Piperazinium chromate(VI)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.026
wR factor = 0.082
Data-to-parameter ratio = 23.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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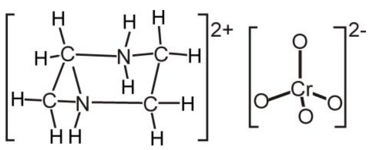
The structure of the title complex, $(C_4H_{12}N_2)[CrO_4]$, consists of tetrahedral $[CrO_4]^{2-}$ dianions which are connected to the cyclic organic piperazinium dications *via* hydrogen bonding. All the atoms are located in general positions.

Comment

The present structural description of piperazinium chromate constitutes a part of our ongoing investigations of compounds resulting from the interaction of organic diamines with group 6 oxo- and thiometalates. Among the investigated complexes we have previously described the structures of ethylenediammonium tetrathiomolybdate (Srinivasan *et al.*, 2001), ethylenediamonium tetrathiotungstate (Srinivasan *et al.*, 2002), 1,3-propanediammonium tetrathiotungstate, *N,N,*-*N′,N′*-tetramethylethylenediammonium tetrathiotungstate (Srinivasan *et al.*, 2003*a*) and ethylenediammonium chromate (Srinivasan *et al.*, 2003*b*). Some examples of chromates bound to organic cations, such as 2,2-dimethyl-1,3-propanediammonium chromate (Chebbi *et al.*, 2000), 4-ammonio-2,2,6,6,-tetramethylpiperidinium chromate (Chebbi & Driss, 2001), 1,4-butanediammonium chromate (Chebbi & Driss, 2002*a*) and bis(2-methyl-2-propanammonium) chromate (Chebbi & Driss, 2002*b*), have also been reported in the recent literature. The extensive use of Cr^{VI} compounds in combination with organic amines in organic synthesis is one reason for the continued interest in this field. The base-promoted cation exchange reactions developed by us for the synthesis of the sulfide complexes of Mo and W mentioned above can also be used for the synthesis of oxochromates. Thus the title complex, (I), was obtained in good yields by reacting the cyclic diamine piperazine with ammonium chromate.



(I)

The structure of (I) consists of tetrahedral $[CrO_4]^{2-}$ dianions and piperazinium dications (Fig. 1). As expected, the piperazinium dication adopts the chair conformation, with internal bond lengths and bond angles (Table 1) in the ranges usually observed in this form (Tran Qui & Palacios, 1990; Tyrselová *et al.*, 1996). The CrO_4 tetrahedron in (I) is distorted, with O—Cr—O angles ranging from 107.07 (6) to 111.27 (8)° (Table 1). The Cr—O bond distances vary from

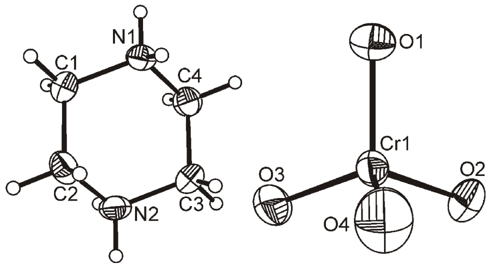


Figure 1
The crystal structure of piperazinium chromate, with the atom labelling scheme and displacement ellipsoids drawn at the 50% probability level.

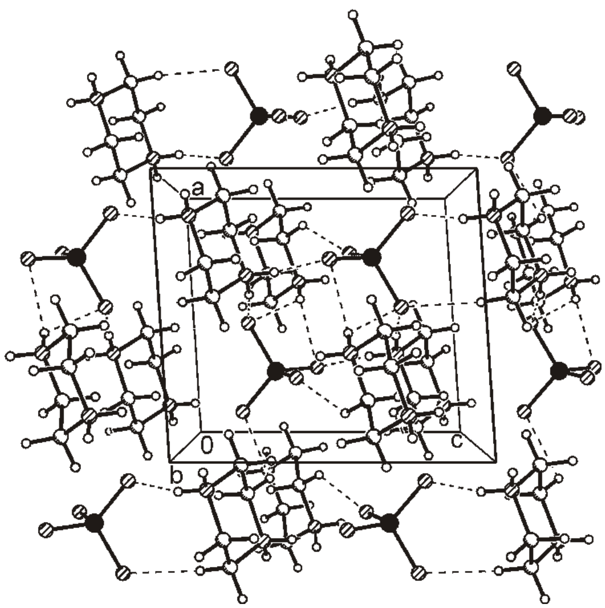


Figure 2
The crystal structure of piperazinium chromate, viewed along the *b* axis (intermolecular hydrogen bonding is shown as dashed lines).

1.6176 (14) to 1.6631 (12) Å, with a mean Cr—O bond length of 1.6468 Å. This value is generally observed for this type of tetrahedron (Bars *et al.*, 1977; Brauer *et al.*, 1991; Chebbi *et al.*, 2000; Chebbi & Driss, 2002*a*). The maximum difference in O···O distances in (I) is 0.034 Å. This value is of the same order as that observed in $(NaNH_4)[CrO_4]$ (0.030 Å; Khan & Baur, 1972), in $(C_4H_{14}N_2)[CrO_4]$ (0.037 Å; Chebbi & Driss, 2002*a*) and in $(CH_6N_3)_2[CrO_4]$ (0.040 Å; Cygler *et al.*, 1976).

In the crystal structure, the anions and cations are connected *via* N—H···O hydrogen bonding between the O atoms of the chromate dianions and the H atoms of the N atoms. Each chromate is connected to five piperazinium cations, forming a three-dimensional hydrogen-bonding network (Fig. 2). The deformation of the chromate tetrahedron in (I) is related to the hydrogen bonding interactions. A dependence of the Cr—O distances upon the strength of hydrogen bonds formed has been found in the title complex, with short hydrogen-bonding contacts ranging from 1.78 to 2.22 Å (Table 2). Atom O1, which forms two short hydrogen bonds with an average N···O distance of 2.785 Å, corresponds to the longest Cr—O distance [1.6631 (12) Å], while atom O4, which is not involved in any hydrogen bonding, shows the shortest Cr—O bond length [1.6176 (14) Å]. Intermediate Cr—O distances of 1.6451 (12) and 1.6617 (12) Å, respectively, are found for O3, which has a single H···O contact, and O2, which makes two contacts with an average N···O distance of 2.807 Å. In chromates bound to acyclic organic diammonium cations such as 1,4-butanediammonium, 2,2-dimethyl-1,3-propanediammonium and ethylenediammonium, longer Cr—O distances than in (I) have been reported.

Experimental

$(NH_4)_2[CrO_4]$ (5 mmol) was dissolved in 10 ml distilled water and anhydrous piperazine (5 mmol) was added. The solution was stirred well and filtered. The clear yellow filtrate was left undisturbed. After a few days, yellow blocks of the title compound crystallized. The crystals were washed with ice-cold water (1 ml), and dried in air. Yield 70% based on Cr. The crystals are stable in air. Analysis calculated for $C_4H_{12}CrN_2O_4$: C 23.53, H 5.94, N 13.72%; found: C 23.58, H 5.94, N 13.59%.

Crystal data

$C_4H_{12}N_2^{2+}\cdot O_4Cr^{2-}$
$M_r = 204.16$
Monoclinic, $P2_1/n$
$a = 7.6651$ (9) Å
$b = 12.3726$ (18) Å
$c = 8.4886$ (10) Å
$\beta = 93.766$ (12)°
$V = 803.30$ (18) Å^3
$Z = 4$
$D_x = 1.688$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 105 reflections
$\theta = 16$–20°
$\mu = 1.40$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.18 × 0.12 × 0.08 mm

Data collection

Stoe AED-II four-circle diffractometer
ω scans
Absorption correction: numerical (*X-SHAPE* and *X-RED*; Stoe & Cie, 1998)
$T_{min} = 0.810$, $T_{max} = 0.894$
4578 measured reflections
2350 independent reflections
2034 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 30.0°$
$h = -10 \rightarrow 1$
$k = -17 \rightarrow 9$
$l = -11 \rightarrow 11$
4 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.082$
$S = 1.06$
2350 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.3211P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.105 (5)

Table 1
Selected geometric parameters (Å, °).

Cr1—O4	1.6176 (14)	N1—C1	1.490 (2)
Cr1—O3	1.6451 (12)	C1—C2	1.503 (2)
Cr1—O2	1.6617 (12)	C2—N2	1.486 (2)
Cr1—O1	1.6631 (12)	N2—C3	1.486 (2)
N1—C4	1.476 (2)	C3—C4	1.508 (2)
O4—Cr1—O3	111.27 (8)	C4—N1—C1	112.01 (12)
O4—Cr1—O2	109.97 (7)	N1—C1—C2	109.36 (13)
O3—Cr1—O2	109.96 (7)	N2—C2—C1	110.52 (14)
O4—Cr1—O1	109.23 (8)	C2—N2—C3	111.48 (12)
O3—Cr1—O1	109.25 (6)	N2—C3—C4	109.94 (13)
O2—Cr1—O1	107.07 (6)	N1—C4—C3	110.10 (14)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N1···O1^{i}	0.90	1.78	2.6697 (18)	169
N1—H2N1···O2^{ii}	0.90	1.81	2.7009 (18)	173
N2—H1N2···O3	0.90	1.83	2.709 (2)	164
N2—H2N2···O2^{iii}	0.90	2.19	2.9133 (19)	137
N2—H2N2···O1^{iii}	0.90	2.22	2.9014 (19)	132

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

The H atoms on C and N atoms were positioned with idealized geometry (C—H = 0.97 Å and N—H = 0.90 Å) and refined with fixed isotropic displacement parameters according to a riding model [U_{iso}(H) = 1.2U_{eq}($C_{methylene}$/N—H)].

Data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

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References

Bars, O., Le Marouille, J. Y. & Grandjean, D. (1977). *Acta Cryst.* B**33**, 3751–3755.
Brauer, C., Jannin, M., Puget, R. & Perret, R. (1991). *Acta Cryst.* C**47**, 2231–2232.
Bruker (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Chebbi, H. & Driss, A. (2001). *Acta Cryst.* C**57**, 1369–1370.
Chebbi, H. & Driss, A. (2002*a*). *Acta Cryst.* E**58**, m147–m149.
Chebbi, H. & Driss, A. (2002*b*). *Acta Cryst.* E**58**, m494–m496.
Chebbi, H., Hajem, A. A. & Driss, A. (2000). *Acta Cryst.* C**56**, e333–e334.
Cygler, M., Grabowski, M. J., Stepien, A. & Wajsman, E. (1976). *Acta Cryst.* B**32**, 2391–2395.
Khan, A. A. & Baur, W. H. (1972). *Acta Cryst.* B**28**, 683–693.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2002). *Acta Cryst.* E**58**, m622–m624.
Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2003*a*). *Acta Cryst.* C**59**, m124–m127.
Srinivasan, B. R., Dhuri, S. N., Näther, C. & Bensch, W. (2003*b*). *Indian J. Chem. Sect. A*. In the press.
Srinivasan, B. R., Vernekar, B. K. & Nagarajan, K. (2001). *Indian J. Chem. Sect. A*, **40**, 563–567.
Stoe & Cie (1992). *DIF*4 (Version 7.09X/DOS) and *REDU*4 (Version 7.03). Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1998). *X-SHAPE* and *X-RED*. Version 1.03. Stoe & Cie, Darmstadt, Germany.
Tran Qui, D. & Palacios, E. (1990). *Acta Cryst.* C**46**, 1212–1215.
Tyrselová, J., Kuchta, L. & Pavelcik, F. (1996). *Acta Cryst.* C**52**, 17–19.