

1,4-Butanediammonium chromate

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.024

wR factor = 0.075

Data-to-parameter ratio = 15.8

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

The title compound, $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+} \cdot \text{CrO}_4^{2-}$, is a new chromate associated with the diprotonated 1,4-butanediamine molecule. The structure can be described as a succession of inorganic and organic layers parallel to the (010) plane. The structural cohesion is established by a three-dimensional network of $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds.

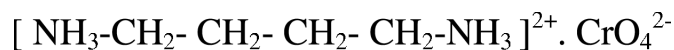
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Comment

Although the number of known inorganic cation chromate structures keeps growing, the number of organic cations remains limited. Up to now, the atomic arrangements are known for only a few organic chromates: $2\text{CN}_3\text{H}_6^+ \cdot \text{CrO}_4^{2-}$ (Cygler *et al.*, 1976), $2[(\text{CH}_3)_4\text{N}]^+ \cdot \text{CrO}_4^{2-} \cdot x\text{H}_2\text{O}$ ($x = 0.5$ or 2 ; Sorehkin *et al.*, 1978), 2,2-dimethyl-1,3-propanediammonium chromate (Chebbi *et al.*, 2000) and 4-ammonio-2,2,6,6-tetramethylpiperidinium chromate dihydrate (Chebbi & Driss, 2001). In this work, we report the structural investigation of a new chromate associated with the diprotonated 1,4-butanediamine molecule, also called putrescine (Takusagawa & Koetzle, 1978). This organic molecule is a linear diamine which plays an important role as a diprotonated cation in biological systems. It interacts with nucleic acids through hydrogen bonds.



(I)

Two components, inorganic CrO_4^{2-} and organic $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$, constitute the molecular arrangement $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{CrO}_4$, (I) (Fig. 1). The structure of (I) consists of organic cations stacked in layers parallel to the (010) plane, separated by layers of inorganic chromate anions. Protonation of 1,4-butanediamine leads to 1,4-butanediammonium cations, where the two terminal N atoms are positively charged. These cations are arranged in layers parallel to the (010) plane. The $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]^{2+}$ cations in this layer have no local symmetry and possess a *trans* configuration identical to that observed in $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{Cl}_2$ (Chandrasekhar & Pattabhi, 1980). The organic groups are anchored on two inorganic layers through multiple hydrogen bonds involving the H atoms of the NH_3 groups, with $\text{H} \cdots \text{O}$ distances between 1.91 and 2.55 Å (Fig. 2). The N–C and C–C distances and the C–C–N and C–C–C angles in the organic cation are comparable with those observed for other compounds containing the same cation: $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (Kamoun & Jouini, 1990) and $[\text{NH}_3(\text{CH}_2)_4\text{NH}_3]_2\text{P}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ (Soumhi *et al.*, 1998).

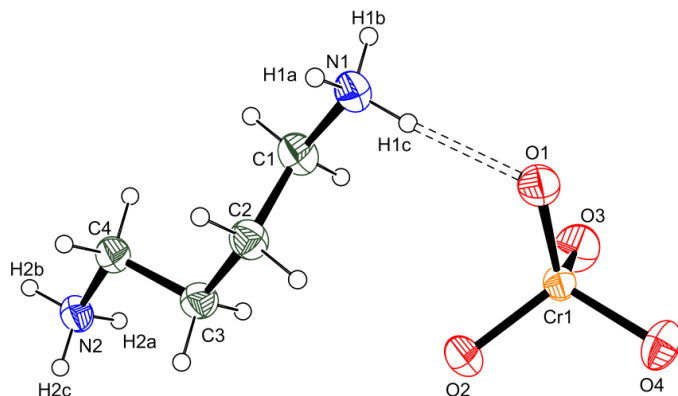


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

The chromate ion is a distorted tetrahedron with a mean Cr–O bond distance of 1.652 (6) Å. This value is generally observed for this type of tetrahedron (Stephens & Cruickshank, 1970; Bars *et al.*, 1977; Gerault *et al.*, 1987; Brauer *et al.*, 1991). The maximum difference in O···O distances is 0.037 Å. This value is of the same order as that observed in NaNH₄CrO₄ (0.030 Å; Khan & Baur, 1972) and in (CH₆N₃)₂CrO₄ (0.040 Å; Cygler *et al.*, 1976). The deformation of the chromate tetrahedron in [NH₃(CH₂)₄NH₃]CrO₄ is probably related to a highly specific hydrogen-bond system. A dependence of the Cr–O distance upon the strength of hydrogen bonds formed by different O atoms has been found in this structure. The O3 atom, which forms two weak N–H···O hydrogen bonds (Table 2), with an average N···O distance of 3.028 (2) Å, corresponds to the shortest Cr–O distance [1.620 (1) Å], while the O1 atom, which forms two strong N–H···O hydrogen bonds (Table 2), with a mean N···O distance of 2.830 (2) Å, corresponds to the longest Cr–O distance [1.667 (1) Å]. Atoms O2 and O4, which have the same Cr–O distance [1.662 (1) Å], form N–H···O hydrogen bonds (Table 2) with an average N···O distance of 2.835 (2) Å.

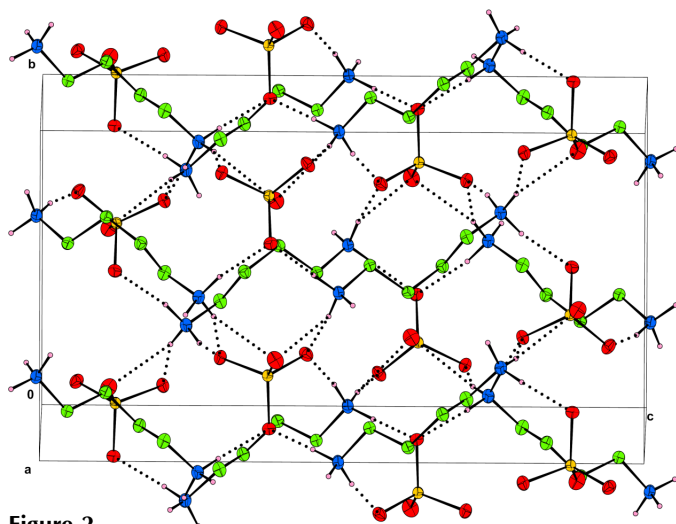


Figure 2
Projection of the crystal structure of [NH₃(CH₂)₄NH₃]CrO₄ along the *a* axis, showing the hydrogen bonds. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compound was prepared from a 1:1:100 mixture of CrO₃ (2 g), C₄H₁₂N₂ (1.76 g) and H₂O (36 g). Good quality yellow single crystals of prismatic habit were grown by slow evaporation of the solvent at room temperature; one of the crystals was selected and used for the X-ray analysis.

Crystal data

(C₄H₁₄N₂)[CrO₄]
M_r = 206.17
 Orthorhombic, *Pbca*
a = 8.824 (1) Å
b = 10.547 (1) Å
c = 18.928 (2) Å
V = 1761.6 (3) Å³
Z = 8
D_x = 1.555 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 11–14°
 μ = 1.27 mm⁻¹
T = 293 (2) K
 Prism, yellow
 0.6 × 0.2 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.713, *T_{max}* = 0.880
 1917 measured reflections
 1917 independent reflections

1619 reflections with *I* > 2σ(*I*)
 θ_{\max} = 27.0°
h = 0 → 11
k = 0 → 13
l = 0 → 24
 2 standard reflections
 frequency: 120 min
 intensity decay: 0.4%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.075
S = 1.08
 1917 reflections
 121 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.8354P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0152 (8)

Table 1

Selected geometric parameters (Å, °).

Cr–O3	1.6199 (14)	N2–C4	1.490 (2)
Cr–O2	1.6620 (12)	C1–C2	1.516 (2)
Cr–O4	1.6624 (12)	C2–C3	1.531 (2)
Cr–O1	1.6666 (14)	C3–C4	1.525 (2)
N1–C1	1.490 (2)		
O3–Cr–O2	107.54 (8)	O4–Cr–O1	110.63 (7)
O3–Cr–O4	107.44 (7)	N1–C1–C2	111.59 (15)
O2–Cr–O4	110.30 (7)	C1–C2–C3	112.39 (15)
O3–Cr–O1	110.54 (8)	C4–C3–C2	113.06 (15)
O2–Cr–O1	110.30 (6)	N2–C4–C3	109.68 (14)

Table 2

Hydrogen-bonding geometry (Å, °).

<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>
N2–H6···O1 ⁱ	0.85 (2)	1.97 (2)	2.815 (2)	173 (2)
N1–H3···O1	0.82 (2)	2.03 (2)	2.845 (2)	169 (2)
N2–H5···O4 ⁱⁱ	0.90	1.92	2.811 (2)	171
N1–H2···O2 ⁱⁱⁱ	0.88	1.96	2.822 (2)	166
N1–H2···O3 ⁱⁱⁱ	0.88	2.55	3.110 (2)	122
N1–H1···O2 ^{iv}	0.85	1.91	2.761 (2)	177
N2–H4···O3 ^v	0.88	2.44	2.947 (2)	117
N2–H4···O4 ^v	0.88	2.03	2.885 (2)	166

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

H atoms of CH₂ groups were placed at calculated positions and refined as riding, with C–H = 0.97 Å. H atoms bonded to N atoms were located in calculated positions. H1, H2, H4 and H5 were not refined, but H3 and H6 were refined with distance restraints: N1–H3 = 0.87 (2) Å and N2–H6 = 0.87 (2) Å

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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