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Synthesis, Crystal Structure and Hirshfeld Surface Analysis of N,N,N',N'-Tetramethylethylenediammonium Dichromate $(C_6H_{18}N_2)[Cr_2O_7]$

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Abstract

In the title salt, $C_6H_{18}N_2^{2+}.Cr_2O_7^{2-}$, (I), one dication is organized around an inversion centre located at the centre of the $-CH_2-CH_2-$ bridge and the two dimethylamine groups are anti with respect to one another. One dichromate anion in (I) also exhibits inversion symmetry. In the crystal, the cations and anions form a layered arrangement parallel to (110) plane. Normal and bifurcated N-H…O hydrogen bonds between the cations and anions and additional weak C-H…O interactions lead to the formation of a three-dimensional network structure. The three-dimensional Hirshfeld surfaces (3D-HS) analysis shows closely similar Hirschfeld surface shapes for the two dications in the salt, reflecting similar intermolecular contacts and similar conformations. The two-dimensional fingerprint plots (2D-FP) are quite asymmetric, due to the presence of more than one component (cation and anion). 3D-HS and 2D-FP reveal that the structure is dominated by H…O (63%) and H…H (37%) contacts.

Keywords: Crystal structure; N,N,N',N'-Tetramethylethylenediammonium; Dichromate; Hirshfeld surface analysis; Fingerprint plots

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Introduction

In the last three decades, chromium(VI) reagents in combination with amines have been widely used for the oxidation of alcohols to the corresponding carbonyl compounds **[1].** It has been shown that the nature of the amine determines the oxidizing power of the dichromate anion and this is inversely related to the donor strength of the associated amine ligand **[1,2].** As part of an ongoing research program, our group has been involved in the synthesis and structural characterization of new organic dichromates over several years, which can be used for oxidation of organic substrates **[3-7]**.As a continuation of our studies in this area, we report here the synthesis of a new organic dichromat salt, $(C_6H_{18}N_2)[Cr_2O_7]$, (I). The chemical composition and crystal structure were determined by energy-dispersive X-ray spectroscopy (EDX) analysis **(Figure 1)** and single-crystal X-ray diffraction; the proposed structural model is supported by validation tools by means of bond-valence-sum (BVS) calculations for chromium and oxygen atoms **[8,9].** In order to evaluate the nature and energetic associated with intermolecular interactions in the crystal packing, the detailed analyses of Hirshfeld surface and fingerprint plots calculations were performed **[10-13].**

Experimental

Synthesis and crystallization of $(C_6H_{18}N_2)[Cr_2O_7]$

The title compound was prepared by dissolving 10 mmol of chromium trioxyde (1 g, purity 99.99%, Sigma-Aldrich) in 20 ml of distilled water and 10 mmol of *N*,*N*,*N*',*N*'-tetramethylethylenediamine (1,5 ml, purity 99.0%, Merck) in 15 ml of ethanol (96%) with a molar ratio of 1:1. The mixture was stirred for 20 minutes and the solution is allowed to stand at room temperature. Brown single crystals of suitable dimensions for crystallographic study were formed in the reactionnel middle after 5 days of slow evaporation of the solvent. The reactional mechanism is as follows :

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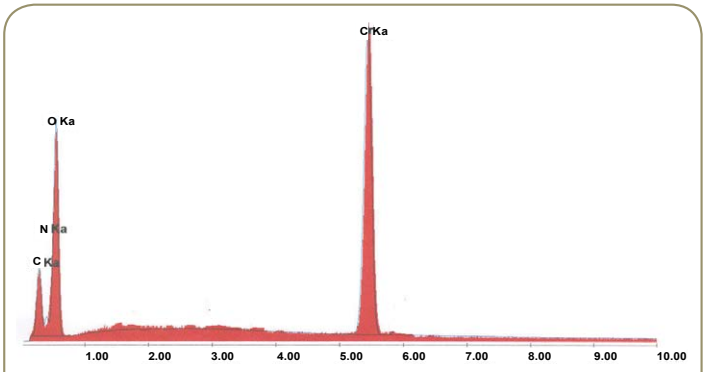

Figure 1 The EDX spectrum of (I).

First step : dissolution of CrO_3

$CrO_3 + H_2O \rightarrow H_2CrO_4$

$H_2CrO_4 + H_2O = HCrO_4^- + H_3O^+$ pka_1 =1, 14

Second step : condensation of $HCrO_4^-$

$2\ HCrO_4^- = Cr_2O_7^{2-} + 2\ H_2O$ 2<pH<6

Third step : protonation of base

$C_6H_{16}N_2 + 2\ H_3O^+ \rightarrow C_6H_{18}N_2^{2+} + 2\ H_2O$

Fourth step : formation of compound

$C_6H_{18}N_2^{2+} + Cr_2O_7^{2-} \rightarrow (C_6H_{18}N_2)[Cr_2O_7]$

X-ray structure determination

Single crystal X-ray diffraction data for the compound at room temperature was collected on a CAD-4 Enraf-Nonius diffractometer equipped with graphite monochromated MoKα radiation (λ=0.71073 Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections. The cell parameters were then refined using the full set of collected reflections in the range 2°<2θ<44°. The half sphere of data was collected at 293 K giving rise to 2392 unique reflections, of which 1626 were observed with I/σ(I)>2. The linear absorption coefficient for MoKα is 1.68 mm^{-1}. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and successive Fourier difference syntheses and refined on (F^2) by full-matrix least-squares methods respectively with the SHELXS-97 and SHELXL-97 programs **[14]** All non-H atoms were refined anisotropically H atoms attached to CH_3, CH_2 and N_1 atoms were placed geometrically and refined using a riding model: C-H=0.96 Å for CH_3 group with U_{iso}(H)=1.5U_{eq}(C); C-H=0.97 Å of CH_2 group with *Uiso*(H)=1.2 U_{eq}(N); N_1-H=0.98 Å with *Uiso*(H) = 1.2 *Ueq*(N_1). The positions of H atoms attached to N_2 and N_3 atoms were localized in difference Fourier maps, the distances were restrained with N-H=0.86 Å and the hydrogen atom were refined isotropically with U_{iso}(H)=1.2 U_{eq} of parent atom. The final cycle of full-matrix least-squares refinement was based on 1626 observed reflections [I>2.00σ(I)] and 242 variable parameters and converged with agreement factors of R (F^2>2σ(F^2))=0.079 and wR(F^2)=0.219 (All data). The structure graphics were drawn with Diamond Version 3.2e supplied by Crystal Impact **[15]** The crystal data and refinement details are summarized in **(Table 1).** Atomic coordinates with equivalent isotropic displacement parameters for non-hydrogen atoms are given in **(Table 2).** Selected bond distances and angles are listed in **(Table 3)** Hydrogen bond scheme and C-H···O interactions are described in **(Table 4).** Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-1491800. Copies of this information may be obtained free of charge from web: www.ccdc.cam.ac.uk

Results and discussion

Crystal structure of $(C_6H_{18}N_2)[Cr_2O_7]$

The molecular structure of (I) is shown in **Figure 2** In this structure, the asymmetric unit is composed of one and half of a dichromate anions and one and half of a *N*,*N*,*N*′,*N*′-tetramethylethylenediammonium dications. One dication is organized around an inversion centre located at the centre of the $–CH_2$-$CH_2–$ bridge and the two dimethylamine groups are anti with respect to one another.

Table 1 Crystal data, data collection and refinement details of (I).

Crystal data	
$(C_6H_{18}N_2)[Cr_2O_7]$	Z=3
Mr=334.22 g.mol^{-1}	F(000)=516
Triclinic, P1	Dx=1.692 Mg m^{-3}
a=3.189 (6) Å	M_o *Kα* radiation λ=0.71073 Å
b=14.172 (4) Å	Cell parameters from 25 reflections
c=5.729 (3) Å	ϑ=8.0–14.8°
α=81.71 (3)°	μ=1.68 mm^{-1}
β=97.45 (5)°	T=293 K
γ=111.30 (3)°	Parallelepiped, brown
V=983.8 (8) A^3	0.15 × 0.12 × 0.11 mm
Data collection	
Enraf-Nonius CAD-4	R_{int}=0.034
diffractometer	ϑ_{max}=22.0°, ϑ_{min} = 2.6°
Radiation source: fine-focus sealed tube	h=−13→13
Graphite monochromator	k=−14→14
$\omega/2\vartheta$ scans	l=0→6
2688 measured reflections	2 standard reflections every 400 reflections
2392 independent reflections	intensity decay: 1%
1626 reflections with I >2σ(I)	
Refinement	
Least-squares matrix: full	
R [F_2 > 2σ(F_2)]=0.079	H atoms treated by a mixture of independent and constrained refinement
$wR(F_2)$=0.219	w=1/ [$\sigma^2(F_o^2)$ + (0.1354P) ^{2}]
S=1.03	where P = (F_o^2 + 2F_c^2)/3
2392 reflections	Δ/σ_{max} < 0.001
242 parameters	Δ/ρ_{max}=0.91 e Å^{-3}
2 restraints	Δ/ρ_{min}=−1.41 e Å^{-3}
Hydrogen site location: mixed	

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) of (I).

Atome	x	y	z	Uiso/Ueq	OCC.<1
Cr_1	−0.26645(12)	0.45453(12)	0.0702(3)	0.0289(6)	
Cr_2	−0.40446(13)	0.21332(12)	0.0226(3)	0.0323(6)	
Cr_3	0.07748(13)	0.11740(12)	0.0885(3)	0.0331(6)	
O_1	−0.1493(6)	0.4484(6)	0.0571(15)	0.052(2)	
O_2	−0.2832(7)	0.4577(7)	0.3380(13)	0.058(2)	
O_3	−0.2797(7)	0.5545(6)	−0.0894(15)	0.057(2)	
O_4	−0.3722(6)	0.3474(5)	−0.0427(13)	0.045(2)	
O_5	−0.3118(7)	0.1790(7)	−0.0462(16)	0.065(3)	
O_6	−0.5193(7)	0.1620(6)	−0.1200(18)	0.075(3)	
O_7	−0.4105(7)	0.1832(6)	0.3060(14)	0.059(2)	
O_8	0.0385(10)	0.2022(8)	−0.0620(17)	0.093(4)	
O_9	0.2027(7)	0.1385(9)	0.0584(18)	0.082(3)	
O_{10}	0.0639(8)	0.1206(8)	0.3613(15)	0.078(3)	
O_{11}	−0.0204(15)	0.0148(14)	−0.044(3)	0.58(5)*	O11.....0.5
N_1	0.7269(6)	0.0574(6)	0.4233(14)	0.031(2)	
H_1	0.6893	0.0962	0.3138	0.037*	
N_2	0.9684(6)	0.2976(6)	0.5332(14)	0.026(2)	
H_2	1.005(7)	0.27(7)	0.636(13)	0.031*	
N_3	0.3856(6)	0.3716(6)	0.4754(14)	0.026(2)	
H_3	0.354(7)	0.404(7)	0.374(13)	0.032*	
C_1	0.8165(8)	0.1308(7)	0.5583(17)	0.035(3)	
H_1A	0.8644	0.097	0.644	0.041*	
H_1B	0.7865	0.1552	0.673	0.041*	
C_2	0.8821(7)	0.2211(7)	0.3931(16)	0.024(2)	
H_2A	0.9158	0.1973	0.2844	0.029*	
H_2B	0.8336	0.2526	0.3009	0.029*	
C_3	0.7652(9)	0.0006(8)	0.281(2)	0.048(3)	
H_3A	0.804	−0.0371	0.3838	0.071*	
H_3B	0.813	0.0474	0.1702	0.071*	
H_3C	0.7037	−0.0456	0.1975	0.071*	
C_4	0.6451(9)	−0.0148(8)	0.586(2)	0.048(3)	
H_4A	0.6273	0.023	0.6907	0.072*	
H_4B	0.6757	−0.0619	0.6773	0.072*	
H_4C	0.5801	−0.0516	0.4941	0.072*	
C_5	0.9246(9)	0.3551(8)	0.6615(19)	0.040(3)	
H_5A	0.8716	0.3086	0.7629	0.060*	
H_5B	0.8907	0.3944	0.55	0.060*	
H_5C	0.983	0.4	0.7552	0.060*	
C_6	1.0550(8)	0.3685(8)	0.375(2)	0.040(3)	
H_6A	1.0215	0.4021	0.2475	0.060*	
H_6B	1.0893	0.3298	0.3106	0.060*	
H_6C	1.1089	0.4184	0.4654	0.060*	
C_7	0.4289(9)	0.3140(8)	0.343(2)	0.041(3)	
H_7A	0.4671	0.2779	0.4528	0.061*	
H_7B	0.4782	0.3605	0.2345	0.061*	
H_7C	0.3696	0.2664	0.2577	0.061*	
C_8	0.4741(8)	0.4554(7)	0.5916(16)	0.028(2)	
H_8A	0.5296	0.4299	0.6731	0.034*	
H_8B	0.4439	0.4788	0.708	0.034*	
C_9	0.3113(9)	0.3002(8)	0.6564(19)	0.040(3)	
H_9A	0.2902	0.3392	0.752	0.061*	
H_9B	0.3493	0.2609	0.7556	0.061*	
H_9C	0.2473	0.2552	0.5764	0.061*	

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Table 3 Geometric parameters (Å, °) of (I). Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Cr_1-O_2	1.58(8)	C_1-C_2	1.530(13)	N_3-C_8	1.496(12)
Cr_1-O_1	1.591(8)	C_1-H_1A	0.97	N_3-C_9	1.517(12)
Cr_1-O_3	1.625(8)	C_1-H_1B	0.97	N_3-H_3	0.86(2)
Cr_1-O_4	1.783(7)	C_2-H_2A	0.97		
Cr_2-O_5	1.580(9)	C_2-H_2B	0.97		
Cr_2-O_6	1.594(8)	C_3-H_3A	0.96		
Cr_2-O_7	1.623(8)	C_3-H_3B	0.96		
Cr_2-O_4	1.783(7)	C_3-H_3C	0.96		
Cr_3-O_8	1.577(9)	C_4-H_4A	0.96		
Cr_3-O_9	1.596(9)	C_4-H_4B	0.96		
Cr_3-O_{10}	1.605(9)	C_4-H_4C	0.96		
Cr_3-O11	1.747(19)	C_5-H_5A	0.96		
Cr_3-O_{11}^{i}	1.791(19)	C_5-H_5B	0.96		
O_{11}-O_{11}^{i}	0.86(3)	C_5-H_5C	0.96		
O_{11}-Cr_3^{i}	1.791(19)	C_6-H_6A	0.96		
N_1-C_3	1.468(14)	C_6-H_6B	0.96		
N_1-C_1	1.476(12)	C_6-H_6C	0.96		
N_1-C_4	1.505(12)	C_7-H_7A	0.96		
N_1-H_1	0.98	C_7-H_7B	0.96		
N_2-C_5	1.470(13)	C_7-H_7C	0.96		
N_2-C_2	1.495(11)	C_8-C_8^{ii}	1.530(18)		
N_2-C_6	1.520(13)	C_8-H_8A	0.97		
N_2-H_2	0.86(2)	C_8-H_8B	0.97		
N_3-C_7	1.480(13)	C_9-H_9A	0.96		
O_2-Cr_1-O_1	109.0(4)	H_1A-C_1-H_1B	108.1		
O_2-Cr_1-O_3	109.7(5)	N_2-C_2-C_1	110.3(7)		
O_1-Cr_1-O_3	111.5(4)	N_2-C_2-H_2A	109.6		
O_2-Cr_1-O_4	109.2(4)	C_1-C_2-H_2A	109.6		
O_1-Cr_1-O_4	111.2(4)	N_2-C_2-H_2B	109.6		
O_3-Cr_1-O_4	106.2(3)	C_1-C_2-H_2B	109.6		
O_5-Cr_2-O_6	112.6(5)	H_2A-C_2-H_2B	108.1		
O_5-Cr_2-O_7	106.0(5)	N_1-C_3-H_3B	109.5		
O_6-Cr_2-O_7	111.8(5)	H_3A-C_3-H_3B	109.5		
O_5-Cr_2-O_4	111.3(5)	N_1-C_3-H_3C	109.5		
O_6-Cr_2-O_4	105.8(4)	H_3A-C_3-H_3C	109.5		
O_7-Cr_2-O_4	109.3(4)	H_3B-C_3-H_3C	109.5		
O_8-Cr_3-O_9	110.9(6)	N_1-C_4-H_4A	109.5		
O_8-Cr_3-O_{10}	107.6(6)	N_1-C_4-H_4B	109.5		
O_9-Cr_3-O_{10}	109.0(5)	H_4A-C_4-H_4B	109.5		
O_8-Cr_3-O_{11}	95.9(6)	N_1-C_4-H_4C	109.5		
O_9-Cr_3-O_{11}	117.5(7)	H_4A-C_4-H_4C	109.5		
O_{10}-Cr_3-O_{11}	114.9(7)	N_2-C_5-H_5B	109.5		
O_{10}-Cr_3-O_{11}^{i}	104.9(7)	H_5A-C_5-H_5B	109.5		
O_{11}-Cr_3-O_{11}^{i}	28.3(9)	N_2-C_5-H_5C	109.5		
Cr_2-O_4-Cr_1	133.0(4)	H_5A-C_5-H_5C	109.5		
O_{11}i-O_{11}-Cr_3	79(2)	H_5B-C_5-H_5C	109.5		
O_{11}i-O_{11}-Cr_3^{i}	73(2)	N_2-C_6-H_6A	109.5		
Cr_3-O_{11}-Cr_3^{i}	151.7(9)	N_2-C_6-H_6B	109.5		
C_3-N_1-C_1	113.2(8)	H_6A-C_6-H_6B	109.5		
C_3-N_1-C_4	110.4(8)	N_2-C_6-H_6C	109.5		
C_1-N_1-C_4	110.6(8)	H_6A-C_6-H_6C	109.5		
C_3-N_1-H_1	107.5	H_6B-C_6-H_6C	109.5		
C_1-N_1-H_1	107.5	N_3-C_7-H_7A	109.5		
C_4-N_1-H_1	107.5	N_3-C_7-H_7B	109.5		

C_5-N_2-C_2	113.3(7)	H_7A-C_7-H_7B	109.5		
C_5-N_2-C_6	111.3(8)	N_3-C_7-H_7C	109.5		
C_2-N_2-C_6	110.2(7)	H_7A-C_7-H_7C	109.5		
C_5-N_2-H_2	107(7)	H_7B-C_7-H_7C	109.5		
C_2-N_2-H_2	112(7)	N_3-C_8-C_8^{ii}	110.8(9)		
C_6-N_2-H_2	103(7)	N_3-C_8-H_8A	109.5		
C_7-N_3-C_8	112.5(8)	C_8^{ii}-C_8-H_8A	109.5		
C_7-N_3-C_9	110.4(8)	N_3-C_8-H_8B	109.5		
C_8-N_3-C_9	110.5(7)	C_8^{ii}-C_8-H_8B	109.5		
C_7-N_3-H_3	108(7)	H_8A-C_8-H_8B	108.1		
C_8-N_3-H_3	102(7)	N_3-C_9-H_9A	109.5		
C_9-N_3-H_3	113(7)	N_3-C_9-H_9B	109.5		
N_1-C_1-C_2	110.8(8)	H_9A-C_9-H_9B	109.5		
N_1-C_1-H_1A	109.5	N_3-C_9-H_9C	109.5		
C_2-C_1-H_1A	109.5	H_9A-C_9-H_9C	109.5		
N_1-C_1-H_1B	109.5	H_9B-C_9-H_9C	109.5		
C_2-C_1-H_1B	109.5	N_1-C_3-H_3B	109.5		

Table 4 Hydrogen-bond geometry (Å, °) of (I). Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) *x*+1, *y*, *z*+1 v) −*x*, −*y*+1, −*z*; (vi) −*x*+1, −*y*, −*z*+1; (vii) −*x*, −*y*+1, −*z*+1.

D-H…A	D-H	H…A	D…A	D-H…A
N_1-H_1···$O5^{iii}$	0.98	2.22	3.068(12)	144
N_1-H_1···$O7^{iii}$	0.98	2.1	2.932(12)	142
N_2-H_2···$O8^{iv}$	0.86(2)	1.93(4)	2.74(12)	157(9)
N_3-H_3···$O3^{v}$	0.86(2)	1.92(4)	2.744(11)	162(10)
C_1-H_1B···$O3^{v}$	0.97	2.32	3.278(14)	168
C_2-H_2A···$O10^{iii}$	0.97	2.52	3.237(14)	130
C_3-H_3C···$O6^{i}$	0.96	2.42	3.330(13)	159
C_4-H_4B···$O9^{vi}$	0.96	2.49	3.423(16)	164
C_6-H_6C···$O2^{ii}$	0.96	2.57	3.512(12)	167
C_7-H_7C···O^{9}	0.96	2.55	3.503(14)	175
C_8-H_8A···$O4^{iv}$	0.97	2.39	3.328(13)	163
C_8-H_8B···$O2^{vii}$	0.97	2.56	3.268(14)	130
C_9-H_9B···$O6^{iv}$	0.96	2.57	3.490(15)	159

In the cations, the nitrogen atoms are protonated. Examination of the organic cations shows that the bond distances and angles have no significant differences from those in other compounds involving the same organic groups: organic acide base from *N*,*N*,*N*′,*N*′-tetramethylethylenediammonium **[16]** $(C_6H_{18}N_2)_3[Cr_2O_7]_2.H_2O$ and $(C_6H_{18}N_2)_3[C_2O_4][Cr_2O_7]_2.4H_2O$**[3,4]** $(C_6H_{18}N_2)[HPO_4]_2.4H_2O$**[17]**$(C_6H_{18}N_2)_2[P_4O_{12}].4H_2O$**[18]**and$C_6H_{18}N_2)[H_2P_2O_7].2H_2O$ **[19].**The $[Cr_2(3)O_7]^{2-}$ anion exhibits disorder of the bridging O_{11} oxygen atom around the inversion symmetry over two positions O_{11} and O_{11}(i) -*x*, −*y*, −*z*) in a ratio 0.5:0.5. Contrary to the quasi eclipse conformation generally encountered in alkali dichromates **[20,21]** this one exhibits a surprising staggered conformation: the tetrahedral twist about 60° away from the exactly eclipsed conformation. In dichromate anions, the Cr-O terminal bond lengths are in the range 1.577 (9)-1.625 (8) Å and the bridging Cr-O bonds are longer and in the range 1.783 (7)-1.791 (19) Å. Similar geometrical features have also been noticed in other crystal structures of organic dichromates **[3,4,6,7,22,26].** The terminal Cr_1-O_3 distance is considerably longer (1.625 (8) Å) than the other therminal Cr-O bond lengths. This lengthening can be explained on the basis of strenth of different O…H bonding interactions: The O_3 oxygen atom accepts one strong hydrogen bond of type N-H…O **[27,28].**

The bond-valence-sum (BVS) calculations for chromium (Cr_1, Cr_2, Cr_3) and oxygen (O_1, O_2, O_5, O_6, O_8, O_9) atoms are close to their oxidation states: Cr_1: 5.94, Cr_2: 5.96, Cr_3: 6.04, O_1: 1.84, O_2: 1.83., O_5: 1.93, O_6: 1.80, O_8: 1.94, O_9:1.83 v.u. (valence unit). The bond valence sum found for O_3, O_4, O_7, O_{10} and O_{11}differes significantly from the expected value of 2.0 vu: O_3: 1.78., O_4: 2.28, O_7: 1.77, O_{10}: 1.76, O (11 Indice): 2.33 v.u. This can be explained by strenth N-H…O bonds for O_3 and O_7, by the existence of a significant bond valence of H…O bond lengths of intermolecular C-H…O interactions that we did not calculated here, for O_4 and O_{10} and by the disorder for O_{11}.

The organic cations and inorganic anions are each arranged in columns parallel to *c* axis and alternate with each other along (1-10) direction, forming a layered arrangement parallel to (110) plane **(Figure 3).** Each organic dication, involving NH^+, CH_2 and CH_3 groups, is connected to six different dichromate anions *via* for N-H…O and nine C-H…O hydrogen bonds **(Table 4),** forming a three-dimensional supramolecular network. Only two of the N-H …O hydrogen bonds are considered as strong according to the Blessing and Brown criteria **[27,28].** A detailed packing analysis of the crystal structure of (I) revealed the formation of {$(C_6H_{18}N_2)$

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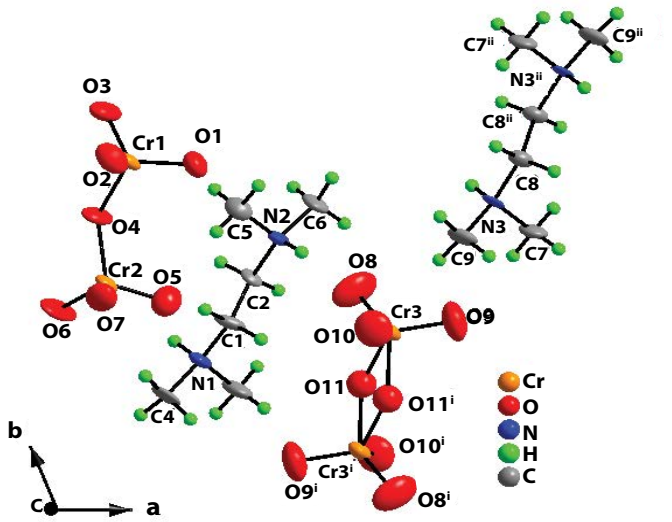

Figure 2 The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry-related atoms are generated by a crystallographic inversion centres. [Symmetry codes: (i) *x*,*y* + 1, *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*].

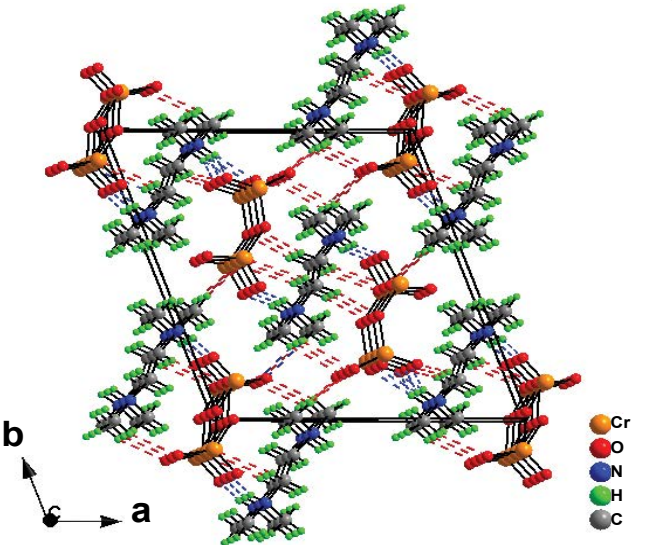

Figure 3 The packing of the molecular entities in the crystal structure of (I).

$[Cr_2O_7]\}_n$ infinite undulating chains lying parallel to the [1-10] direction, which generate $R2^2(12)$, $R2^2(8)$ and $R1^2$ (4) ring motifs [29,30](**Figure 4**). These one-dimensional chains extending on the (110) plane formed a layer.

Hirshfeld surface analysis

Organic small molecule crystal packings are often dominated by the hydrogen bonding patterns. However, a crystal structure is determined by a combination of many forces, and hence all of the intermolecular interaction of a structure should be taken into account. Visualization and exploration of intermolecular close contacts of a structure is invaluable, and this can be achieved using the Hirshfeld surface **[10,11].** A large range of properties can be visualized on the Hirshfeld surface with the program Crystal Explorer **[31]** including d_e and di (i : indice, di : italic), in which de and di(i : indice, di : italic), represent the distances from a point on the HS to the nearest atoms outside (external) and inside (interna) the surface, respectively. The intermolecular distance information on the surface can be condensed into a two-dimensional histogram of d_e and d_i, which is a unique identifier for molecules in a crystal structure, called a fingerprint plot **[12,13].** Instead of plotting d_e and d_i on the Hirshfeld surface, contact distances are normalized in CrystalExplorer using the van der Waals radius of the appropriate internal and external atom of the surface: $d_{norm} = (d_i - r_i^{vdw})/ r_i^{vdw} + (d_e - r_e^{vdw})/ r_e^{dw}$.

For the two dications of (I), the three-dimensional Hirshfeld surface (3D-HS) that has been mapped over d_{norm} is given in **Figure 5**. Contacts with distances equal to the sum of the van der Waals radii are shown in white (label 3), and contacts with distances shorter than or longer than the related sum values are shown in red (labels 1 and 2) (highlighted contacts) or blue, respectively. The interaction between N-H and oxygen atoms can be seen in the Hirshfeld surface as the bright-red area (label 1) **(Figure 5).** The light-red spots are due to C—H…O interactions (label 2). The shapes of the HSs of the two dications in the structure of (I) are similar, reflecting similar intermolecular contacts and similar conformations (anti conformation of the dimethylamine groups).

Figure 6 illustrates the analysis of the two-dimensional fingerprint plots (2D-FP) for the two dications of (I). 2D-FP are the two-dimensional representations of the information provided by visual inspection of the 3D-HS, which are plotted on an evenly spaced grid formed by (d_e, d_i) pairs. Each grid point is coloured according to the frequency of occurrence of the (d_e,d_i) pair on the 3D-HS, from blue for small contributions, through green to red for maximum contributions, if present. The 2D-FP in **Figure 6** are quite asymmetric; this is expected, since interactions occur between two different species (cation and anion) **[32].** For the

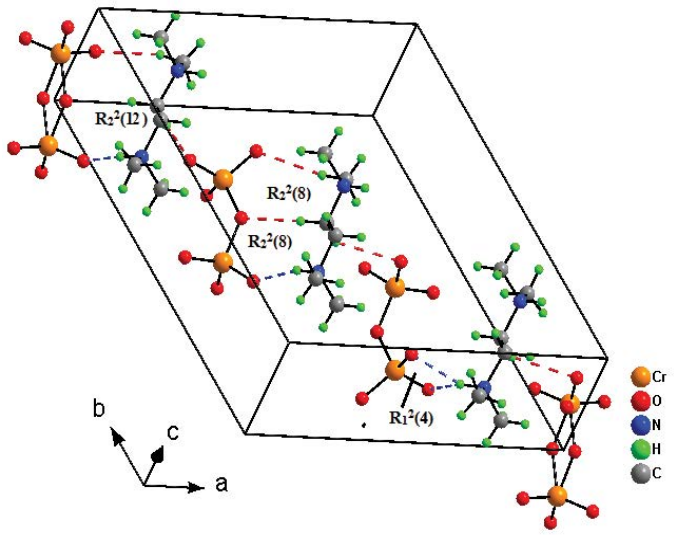

Figure 4 A perspective view of one chain of (I), showing $R_2^2(12)$, $R_2^2(8)$ and $R_1^2(4)$ ring motifs along [1-10] direction. Hydrogen bonds are represented by dashed lines (C-H…O (red); N-H…O (blue)).

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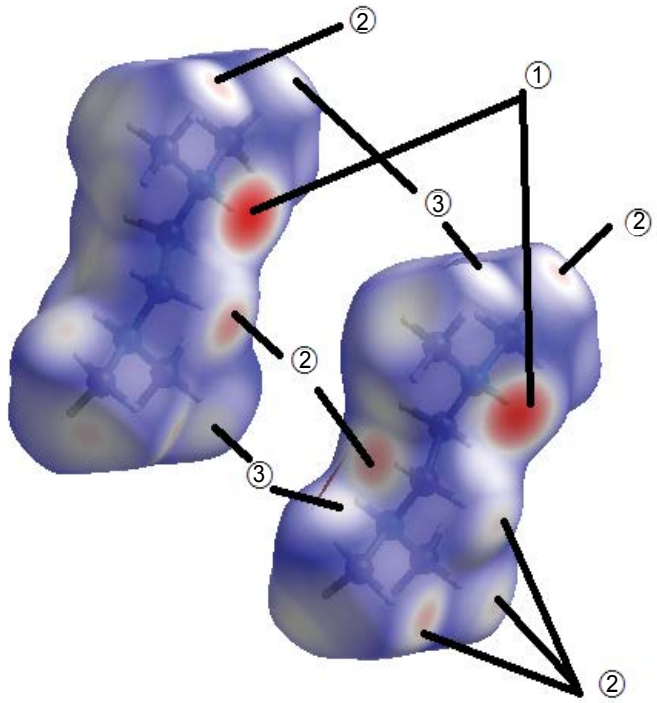

Figure 5 View of the three dimensional Hirshfeld surfaces (3D-HS) for the two dications of (I). (3D-HS mapped with d_{norm}).

title salt, H…O contacts, which are attributed to N-H…O and C-H…O hydrogen-bonding interactions, appear as one sharp spike in the 2D-FP with a prominent long spike at $d_e + d_i = 1.8$ Å. They have the most significant contribution to the total Hirshfeld surfaces (63%). The H…H contacts appear in the middle of the scattered points in the two-dimensional fingerprint maps with a single broad peak at $d_e = d_i = 1.25$ Å and a percentage contribution of 37%.

Conclusion

In summary, we reported one new organic dichromate, $(C_6H_{18}N_2)[Cr_2O_7]$ using a slow evaporation method and it crystallizes in the triclinc space group P-1. In the structure the organic cations and inorganic anions are each arranged in rows parallel to *c* axis and alternate with each other along [1-10] direction, forming a layered arrangement parallel to (110) plane. The stability and the cohesion of the structute is ensured by N-H…O hydrogen bonds and weak C-H…O interactions. 3D-HS and 2D-FP reveal that the structure is dominated by H…O and H…H contacts. Our future research efforts will be devoted to the synthesis of differents organic dichromates with new organic base such as amine or diamine to exploit this related systems and study the relationship between the crystal structures and properties of this related materials.

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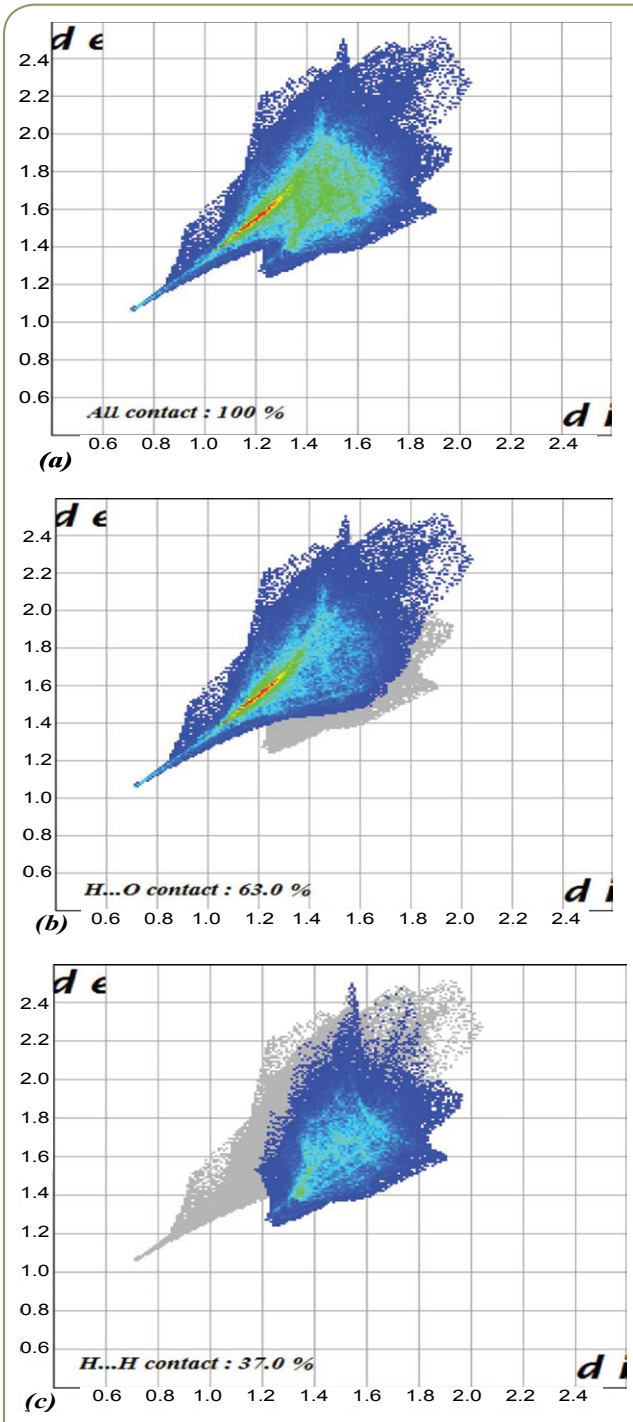

Figure 6 Two-dimensional full fingerprint plots (2D-FP) for the two dications of (I) (a), and 2D-FP resolved into H…O (b) and H…H (c) close contacts.

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References

1 Cainilli G, Cardillo G (1984) Chromium oxidations in organic chemistry. Springer-Verlag Berlin.

2 Guerrero AF, Kim HJ, & Schlecht, M F (1988). Oxychlorination of alkenes by chlorochromate reagents: A facile preparation of α-chloroketones, and competition by substituent-directed oxidation. Tetrahedron 51 : 6707-6709.

3 Khadhrani H, Ben Smail R, Driss A (2006) Crystal structure of a new organic dichromate $[C_6H_{18}N_2]_3[C_2O_4][Cr_2O_7]_2{\cdot}4H_2O$. CR Chimie 9:1322-1327.

4 Khadhrani, H, Ben Smail, R, Driss, Jouini, T (2006), $[(CH_3)_2NH(CH_2)_2NH(CH_3)_2]Cr_2O_7H_2O]$, un nouveau dichromate organique. Acta Cryst. E62, m146.

5 Ben Smail R, Chebbi H, Driss A (2007), bis(ethylenediammonium) dichromate oxalate . Acta Cryst. E63, 1859-1860.

6 Ben Smail R, Chebbi H, Srinivasan B, Zid MF (2015) synthesis, spectroscopic characterization and room-temperature structure of bis(4-aminopyridinium) dichromate. J Structural Chem (accepted).

7 Chebbi H, Ben Smail R, Zid MF (2016) Crystal structure of 1-cyclohexylpiperazine-1,4-diium dichromate (VI). J Structural Chem 57: 632-635.

8 Brown ID (2002) The Chemical Bond in Inorganic Chemistry. The Bond Valence Model. IUCr Monographs on Crystallography. 12: Oxford University Press.

9 Adams S (2003) softBV University of Gottingen, Germany.

10 Spackman MA, Kinnon JJ (2002) Fingerprinting intermolecular interactions in molecular crystals. Cryst Eng Comm 4: 378-392.

11 Spackman MA, Jayatilaka D (2009) Hirshfeild surface analysis Crys. Eng Comm 11: 19-32.

12 Rohl AL, Moret M, Kaminsky W, Claborn K, Mckinnon JJ, et al. (2008) Hirshfeld Surfaces Identify Inadequacies in Computations of Intermolecular Interactions in Crystals Pentamorphic 1,8-Dihydroxyanthraquinone. Cryst Growth Des 8: 4517-4525.

13 Parkin A, Barr G, Dong W, Gilmore CJ, Jayatilaka CC, et al. (2007) Comparing entire crystal structures: structural genetic fingerprinting. Cryst Eng Comm 9: 648-652.

14 Sheldrick GM (2008) A short history of SHELX. Acta Cryst A64: 112-122.

15 Brandenburg K (2006) DIAMOND. Crystal Impact GbR Bonn Germany.

16 Ying Z, Shouwen J, Zhaohui T, Yi L, Lanqing W, et al. (2016) Crystal and Molecular Structures of Four Organic Acid–Base Adducts from Hexamethylenetetramine, N,N,N,N-Tetramethylethylenediamine, and Organic Acids. J Chem Crystallogr 46: 188-202.

17 Baoueb L, Jouini A (1998) J Solid State Chem 141: 343-351.

18 Thabet H, Jouini A, Hassane ES (1997) Bis(N,N,N',N'-tetramethylethylenediammonium) Cyclotetraphosphate Tetrahydrate. Acta Cryst C 53: 318-320.

19 Gharbi A, Charfi M, Jouini A (1996) N,N,N',N'-Tetramethylethylenediammonium Dihydrogendiphosphate Dihydrate. Acta Cryst C 52: 2246-2248.

20 Clark GM, Morley R (1976) Inorganic pyro-compounds Ma [(X2O7) b]. Chem Soc Rev 5: 269.

21 Kolitsch U (2003) Crystal structure of dirubidium dichromate(VI) $Rb_2Cr_2O_7$ a fourth polymorph. Z Kristallogr 218: 401-402.

22 Srinivasan BR, Naik AR, Nather C, Bensch W (2004) Piperazinium dichromate. Acta Cryst. E60: 1384-1386.

23 Martin ZP, Gili P, Romero R, RuizPerez C, Solans X, et al. (1995) Preparation and characterization of the dichromates of the organic bases: 2, 4′-bipyridine, 2, 2′-dipyridylamine and 4, 4′-bipyridine. Polyhedron 14: 2907-2917

24 Jin ZM, Ma XJ, Zhang Y, Tu B, Hu ML, et al. (2006) Bis (2,6-dimethyl-pyridinium) dichromate. Acta Cryst E62: 106-108

25 Sieron L (2007) bis(2-amino-2-thiazolinium) dichromate(VI). Acta Cryst E63: m2068.

26 Vetrivel S, Vinoth E, Mullai RU, Aruljothia R, Nizam MM, et al. (2016) Crystal structure of 1,4-bis(3-ammoniopropyl)-piperazine-1,4-diium bis[dichromate(VI)]. Acta Cryst E72: 616-619.

27 Blessing RH(1986) Hydrogen bonding and thermal vibrations in crystalline phosphate salts of histidine and imidazole. Acta Cryst B42: 613-621.

28 Brown ID (1976) On the geometry of O-H...O hydrogen bonds. Acta Cryst A32: 24-31.

29 Etter MC, Donal Md, Bernstein J (1990) Graph-set analysis of hydrogen-bond patterns in organic crystals Acta Cryst B46: 256-262.

30 Bernstein J, David RE, Shimoni NL, Chang NL (1995) hydrogen-bond pattern functionality and graph sets. Angew Chem Int Ed Engl 34: 1555-1573.

31 Wolff SK, Grimwood DJ, Kinnon MC, Turner MJ, Jayatilaka D, et al. (2012) Crystal Explorer. University of Western Australia.

32 Fabbiani FPA, Arlin JB, Buth G, Dittrich B, Florence AJ (2011) Acta Cryst C67: 120-124.