ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2016. Том 57, № 3 *Март – апрель* *С. 662 – 664*

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:546.76:546.21

CRYSTAL STRUCTURE OF 1-CYCLOHEXYLPIPERAZINE-1,4-DIIUM DICHROMATE(VI)

H. Chebbi[1,2], **R. Ben Smail**[1,3], **M.F. Zid**[1]

[1]*Université de Tunis El Manar, Faculté des Sciences de Tunis, Laboratoire de Matériaux et Cristallochimie, Tunis, Tunisia*
[2]*Université de Monastir, Institut Préparatoire aux Etudes d'Ingénieurs de Monastir, Monastir, Tunisia*
E-mail: chebhamouda@yahoo.fr
[3]*Université de Carthage, Institut Préparatoire aux Etudes d'Ingénieurs de Nabeul, Nabeul, Tunisia*

Received January, 14, 2015 *Revised — February, 11, 2015*

Single crystals of 1-cyclohexylpiperazine-1,4-diium dichromate(VI), $(C_{10}H_{22}N_2)[Cr_2O_7]$, were obtained by slow evaporation at room temperature from an aqueous solution of potassium dichromate, hydrochloric acid and 1-cyclohexylpiperazine. $(C_{10}H_{22}N_2)[Cr_2O_7]$ is triclinic ($P\overline{1}$) with $a = 10.351(2)$ Å, $b = 12.766(3)$ Å, $c = 6.111(1)$ Å, $\alpha = 91.50(2)°$, $\beta = 104.26(3)°$, $\gamma = 94.91(2)°$, $V = 778.8(3)$ Å^3, and $Z = 2$. The structure determination performed from single crystal X-ray diffraction data leads to R_1/wR_2 reliability factors of 0.032/0.078. The asymmetric unit of the title salt $C_{10}H_{22}N_2^{2+} \cdot Cr_2O_7^{2-}$, consists of one 1-cyclohexylpiperazine-1,4-diium dication and one dichromate dianion. These entities are linked together by N—H···O hydrogen bonds to form $\{(C_{10}H_{22}N_2)[Cr_2O_7]\}_n$ infinite chains lying parallel to the (100) plane and running along the c axis. The intermolecular N—H···O hydrogen bonds link these chains into a two-dimensional network structure consolidated through C—H···O weak interactions.

DOI: 10.15372/JSC20160326

Keywords: organic dichromate, synthesis, single crystal X-ray diffraction, crystal structure.

Since the discovery in 1979 of pyridinium dichromate as a mild reagent for the oxidation of alcohols [1], a large number of dichromates of protonated organic bases have been prepared and used as reagents in mild selective oxidation processes of organic substrates, such as quinolinium dichromate [2], tetramethylethylenediammonium dichromate [3], benzimidazolium dichromate [4], piperazinium dichromate [5], cetyltrimethylammonium dichromate [6], and others have been the subject of structural studies [7—10]. In continuation of our structural study of a new hybrid compound containing an organic cation and an $Cr_2O_7^{2-}$ inorganic oxidant anion [11—13], we present here the title compound $C_{10}H_{22}N_2^{2+} \cdot Cr_2O_7^{2-}$ (**I**).

Experimental. Synthesis of $(C_{10}H_{22}N_2)[Cr_2O_7]$(I). A mixture of potassium dichromate (0.29 g, 1 mmol, Merck, > 99 %), hydrochloric acid (0.06 ml, 2 mmol, 38 %), and 1-cyclohexylpiperazinium (0.17 g, 1 mmol, Acros Organics, 98 %) was dissolved in 100 ml of distilled water with stirring at room temperature for 1 h. Yellow crystals with prismatic shapes suitable for X-ray diffraction were obtained after two days of slow evaporation at room temperature.

X-ray crystallography. The X-ray diffraction analysis of compound **I** was performed on an automated four-circle Enraf-Nonius CAD-4 diffractometer with a graphite-monochromated MoK_α radiation source ($\lambda = 0.71073$ Å).

The crystallographic data for $(C_{10}H_{22}N_2)[Cr_2O_7]$: $C_{10}H_{22}N_2O_7Cr_2$, $FW = 386.30$, $T = 298$ K, crystal size $0.34{\times}0.24{\times}0.16$ mm, triclinic, $P\bar{1}$, $a = 10.351(2)$ Å, $b = 12.766(3)$ Å, $c = 6.111(1)$ Å, $\alpha = 91.50(2)°$, $\beta = 104.26(3)°$, $\gamma = 94.91(2)°$, $V = 778.8(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.647$ g/cm^3, $\mu(MoK_\alpha) = 1.427$ mm^{-1}, a total of 2259 reflections ($\theta_{min}/_{max} = 3.44/26.98°$), 1712 observed reflections ($I \geq 2\sigma(I)$), 194 parameters. GOOF = 1.025, $R_1 = 0.0323$, $wR_2 = 0.0783$ ($I \geq 2\sigma(I)$), $R_1 = 0.0554$, $wR_2 = 0.0872$ (all data), max / min diff. peak 0.23 / –0.28 e/Å^3.

The absorption correction was not done. The structure was solved by direct methods with SHELXS-97 and expanded using Fourier techniques [14]. Anisotropic displacements were used for C, N, O, and Cr while the H atoms were placed in calculated positions and refined using a riding model with C—H = 0.97 or 0.98 Å, N—H = 0.90 Å, and with isotropic temperature factors $U_{iso}(H) = 1.2\ U_{eq}(C, N)$. The H atom on N2 was freely refined. CIF file containing complete information about the structure of **I** was deposited with the Cambridge Crystallographic Data Center (No.1040579); the file is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. The molecular structure of **I** is shown in Fig. 1. The salt contains two components: the inorganic $Cr_2O_7^{2-}$ dianion and the organic $C_{10}H_{22}N_2^{2+}$ dication with all atoms located in general positions.

In the organic dication, both piperazinium and cyclohexyl rings possess spatial *chair* conformations (Fig. 1) with puckering parameters: $Q_T = 0.570(4)$ Å, $\theta = 177.9(3)°$, $\Phi = 138(93)°$ and $Q_T = 0.574(4)$ Å, $\theta = 0.0(4)°$, $\Phi = 38(32)°$, respectively [15]. These conformations have also been noted in the crystal structure of 1-cyclohexylpiperazine-1,4-diium tetrachloridozincate [16]. The differences in the molecular structure of 1-cyclohexylpiperazine-1,4-diium tetrachloridozincate relate to a variation in the orientation of piperazinium and cyclohexyl groups and in the nature of the intermolecular interactions between them. The different orientations are probably best described by the dihedral angles formed between the least-squares planes through the pairs of rings, i.e. 5.53(6)° and 67.72(5)° for dichromate **I** and the tetrachloridozincate compounds respectively. The N—C and C—C bonds lengths, and the C—C—N and C—N—C angles in the piperazinium ring are comparable with those observed for other compounds containing the piperazinium group, such as piperazinium chromate and piperazinium dichromate [17].

In the dichromate group each chromium atom is surrounded by a slightly distorted tetrahedron of four oxygen atoms; O—Cr—O are in the range of 107.8(1) and 110.8(2)°. The Cr—O (terminal) bond length ranges from 1.597(2) to 1.633(2) Å. As expected, the Cr—O (bridging) bond length is significantly longer and amounts to 1.783(2) Å. These values are in good agreement with those usually found in organic dichromates [2—13]. The bond valence sums calculated [18] from the bond lengths (valence units; Cr1: 5.7829, Cr2: 5.7870, O1: 2.3155, O2:1.7858, O3: 1.7767, O4: 1.7913, O5: 1.7884, O6: 1.7911, O7: 1.7727) are close to the expected valence states of the respective atoms. Four oxygen atoms of the dichromate dianion act as hydrogen acceptors, being involved in hydrogen bonds with the bifurcated N atoms of the piperazinium ring of the organic dication, with N···O distances falling in the range from 2.746(4) to 3.052(4) Å. A detailed packing analysis of the crystal structure of **I** revealed the formation of infinite $\{(C_{10}H_{22}N_2)\cdot[Cr_2O_7]\}_n$ infinite chains lying parallel to the (100) plane and running along the crystallographic *c* axis (Fig. 2).

In the chain, each $C_{10}H_{22}N_2^{2+}$ dication serves as a hydrogen bond donor to two neigh-

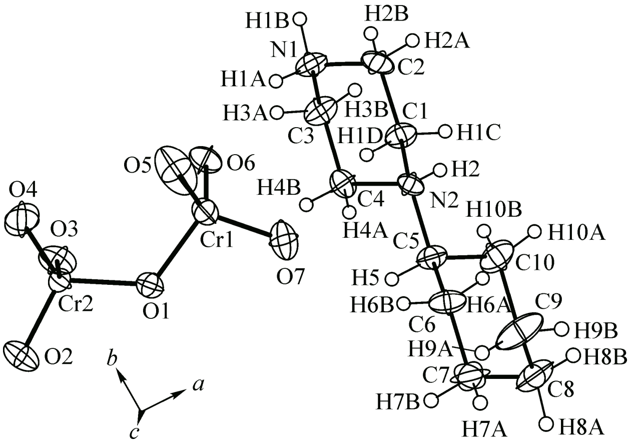

Fig. 1. Molecular structure of 1-cyclohexylpiperazine-1,4-diium dichromate salt showing the atom numbering scheme. Thermal ellipsoids are shown at the 50 % probability level

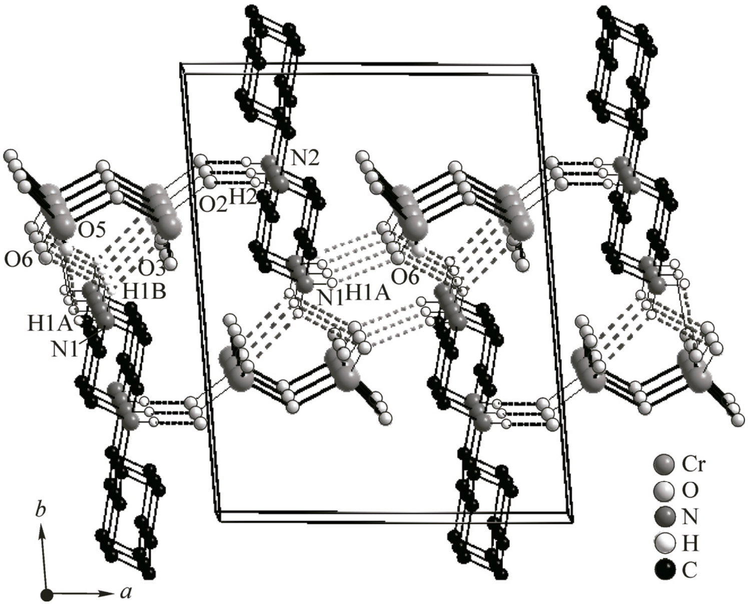

Fig. 2. View of the two-dimensional-network structure of **I** with hydrogen bonds represented as dashed lines. The H atoms not involved in H bonds are omitted

boring $Cr_2O_7^{2-}$ dianions *via* N1—H1B···O3; N1—H1B···O6 and N1—H1A···O5 hydrogen bonds, respectively. The relative propagation directions of the chain lie parallel to one another as shown in Fig. 2. Each chain is connected to their two neighbors *via* N2—H2···O2 and N1—H1A···O6 hydrogen bonds, respectively, to form a two-dimensional network parallel to the (010) plane (Fig. 2). In addition, C—H···O interactions play an important role in the crystal packing occurred *via* intermolecular weak interactions to consolidate the two-dimensional network. To our knowledge, only two organic dichromates with a two-dimensional network were found in the literature: benzimidazolium dichromate [19] and quinolinium dichromate [20]. In these compounds, the benzene rings of the heterocyclic aromatic benzimidazolium dications and quinolinium monocations, respectively, are oriented to the interlayer space. These rings do not make any hydrogen bond. This is the origin to form a two-dimensional network. In our structure, hexyl rings of 1-cyclohexylpiperazine-1,4-diium have played the same role of benzene.

REFERENCES

1. *Corey E.J., Schmidt G.* // Tetrahedron Lett. – 1979. – **20**, 5. – P. 399 – 402.
2. *Balasubramanian K., Prathiba V.* // Indian J. Chem. – 1986. – **B25**. – P. 326 – 327.
3. *Chandrasekhar S., Takhi M., Mohapatra S.* // Synth. Commun. – 1996. – **26** (**21**). – P. 3947 – 3951.
4. *Meng Q.-H., Feng J.-C., Bian N.-S., Liu B., Li C.-C.* // Synth. Commun. – 1998. – **28**. – P. 1097 – 1102.
5. *Movassagh B., Lakouraj M.M., Ghodrati K.* // Indian J. Chem. – 2002. – **B41**. – P. 1293 – 1295.
6. *Patel S., Mishra B.K.* // Tetrahedron Lett. – 2004. – **45**. – P. 1371 – 1372.
7. *Gholizadeh M., Pourayoubi M., Kia M., Rheingold A.L., Golen J.A.* // Acta Crystallogr. – 2012. – **E68**. – P. m305.
8. *Srinivasan B.R., Naik A.R., Näther C., Bensch W.* // Acta Crystallogr. – 2004. – **E60**. – P. m1384 – m1386.
9. *Fossé N., Brohan L.* // J. Solid State Chem. – 2001. – **145**. – P. 655 – 667.
10. *Pressprich M.R., Willett R.D., Sheets R.M., Paudler W.W., Gard G.L.* // Acta Crystallogr. – 1990. – **C46**. – P. 1635 – 1637.
11. *Khadhrani H., Ben Smail R., Driss A., Jouini T.* // Acta Crystallogr. – 2006. – **E62**. – P. m146 – m148.
12. *Khadhrani H., Ben Smail R., Driss A.* // C. R. Chim. – 2006. – **9**. – P. 1322 – 1327.
13. *Ben Smail R., Chebbi H., Driss A.* // Acta Crystallogr. – 2007. – **E63**. – P. m1859 – m1860.
14. *Sheldrick G.M.* // Acta Crystallogr. – 2008. – **A64**. – P. 112 – 122.
15. *Cremer D., Pople J.A.* // J. Am. Chem. Soc. – 1975. – **97**. – P. 1354 – 1358.
16. *Soudani S., Aubert E., Jelsch C., Ben Nacer C.* // Acta Crystallogr. – 2013. – **C69**. – P. 1304 – 1306.
17. *Srinivasan B.R., Sunder N.D., Näther C., Bensch W.* // Indian J. Chem. – 2003. – **A42**, N 11. – P. 2735 – 2741.
18. *Adams S.* SoftBV. Version 0.96. – Germany: University of Göttingen, 2004.
19. *Meng Q., Yan W., Xu S., Huang D.* // J. Chem. Crystallogr. – 2004. – **34**, N 5. – P. 333 – 336.
20. *Sundar T.V., Parthasarathi V., Thamotharan S., Sekar K.G.* // Acta Crystallogr. – 2003. – **E59**. – P. m327 – m329.