

Fig. 1. Perspective view of the structure of diethoxybis(4,4-trifluoro-1-phenyl-1,3-butanedionato)titanium(IV).

indicate almost complete π -electron delocalization over the β -diketonolato group.

The remainder of the structure is normal, but with rather large thermal parameters for the terminal atoms, F(1), F(2), F(3) and C(12).

Acta Cryst. (1990). **C46**, 1635–1637

Bis(1H⁺-pyrazinium N⁴-oxide) Dichromate

BY MARK R. PRESSPRICH AND ROGER D. WILLETT

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630, USA

AND R. M. SHEETS, W. W. PAUDLER AND G. L. GARD

Department of Chemistry, Portland State University, Portland, Oregon 97207-0751, USA

(Received 26 May 1989; accepted 8 December 1989)

Abstract. $2C_4H_5N_2O^+ \cdot Cr_2O_7^{2-}$, $M_r = 410.2$, monoclinic, $P2_1$, $a = 8.003(2)$, $b = 6.132(2)$, $c = 14.493(4)$ Å, $\beta = 94.50(2)^\circ$, $V = 708.8(3)$ Å³, $Z = 2$, $D_x = 1.92$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 15.5$ cm⁻¹, $F(000) = 412$, $T = 293$ K, $R = 0.0602$ for 1980 unique observed reflections with $F \geq 3\sigma(F)$. The structure consists of discrete dinegative dichromate anions hydrogen bonded to monopositive pyrazinium *N*-oxide cations ($N-H \cdots O = 2.724, 2.644$ Å). A strong hydrogen bond to the bridging O atom in the $Cr_2O_7^{2-}$ anion leads to significant lengthening of the bridging Cr—O bonds. A short C—H \cdots O interaction (3.180 Å) is also observed.

Introduction. Previously we reported the crystal structures of pyrazinium chlorochromate (Pressprich, Willett, Paudler & Gard, 1990) and bis(pyrazinium) trichromate (Pressprich, Willett, Poshusta, Saunders, Davis & Gard, 1988). In addition, a bond-length

All calculations were performed on a PDP 11/34 computer with the Enraf–Nonius (1979) *SDP* crystallographic programs.

References

- BHARARA, P. C., DGUPTA, V. & MEHROTRA, R. C. (1975). *Synth. React. Inorg. Met. Org. Chem.* **5**, 49–67.
- CROMER, D. T. & IBERS, J. A. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, p. 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, I. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–89. Birmingham: Kynoch Press.
- DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* **B29**, 589–595.
- Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
- KELLER, H. J., KEPPLER, B., KRÜGER, U. & LINDER, R. (1981). European Patent Application No. 49 486.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–353.
- WRIGHT, D. A. & WILLIAMS, D. A. (1968). *Acta Cryst.* **B24**, 1107–1114.

correlation for chromate anions of the form $(Cr_nO_{3n+1})^{2-}$ was presented (Pressprich *et al.*, 1988). In a continuation of our studies with effective and selective organic oxidants that involve high-valence chromium(VI) complexes, the interesting bis(pyrazinium *N*-oxide) dichromate was prepared: $2C_4H_4N_2O + 2CrO_3 \xrightarrow{H_2O} (C_4H_4N_2HO)_2Cr_2O_7$. The new orange dichromate salt is stable when stored dry and in the absence of light; its melting point, with decomposition, is 359–360 K. We have found it to be an effective and efficient oxidant in converting cyclic saturated and unsaturated alcohols to their corresponding ketones (Wu, Sheets & Gard, unpublished results). While infrared data supports an ionic complex, it was necessary to carry out a crystal structure study for an exact determination.

Experimental. *Preparation and analysis.* A solution containing 1.0845 g (10.84 mmol) of CrO_3 in 1.0 ml

of water was added dropwise with stirring to a solution cooled with an ice bath and containing 1.0273 g (10.70 mmol) of pyrazine *N*-oxide in 14.0 ml of H₂O. The dark-red solution which formed was warmed to room temperature and was maintained at room temperature with stirring (5 min). The solution was cooled to 273 K and the orange solid which formed was collected on a sintered glass funnel and washed twice with ice water. The product was dried under vacuum (≈ 0.1 Pa) for 12–15 h. Yield, 1.2705 g (58%); m.p. 359–360 K with decomposition.

The infrared spectrum had bands (cm⁻¹): 3079(*w,b*), 1637(*w*), 1616(*vw*), 1595(*w*), 1560(*w*), 1540(*vw*), 1501(*vw*), 1461(*m*), 1426(*wm*), 1373(*sh*), 1342(*wm*), 1293(*vw*), 1215(*w*), 1173(*wm*), 931(*s,b* with *sh* at 944), 901(*m*), 885(*m*), 857(*m*), 829(*m*), 793(*w*), 744(*m,b*), 710(*wm*), 702(*wm*), 664(*w*), 540(*wm*), 532(*wm*), 519(*wm*), 484(*wm*), 418(*w*). Calculated for C₈H₁₀N₄O₂Cr₂O₇: C, 23.42; H, 2.24; N, 13.66; Cr, 25.37%. Found: C, 23.44; H, 2.29; N, 13.74; Cr, 25.39%.

Crystallography. A crystal with dimensions 0.30 × 0.35 × 0.10 mm was selected and mounted on a Nicolet R3m/E diffractometer system. Cell constants from 25 reflections in the range 25 < 2θ < 30° (Campana, Shepherd & Litchman, 1981). 2738 reflections were measured by ω scans {3 ≤ 2θ ≤ 65°, [(sinθ)/λ]_{max} = 0.756 Å⁻¹, -13 ≤ h ≤ 13, 0 ≤ k ≤ 10, 0 ≤ l ≤ 22}, with 2738 unique, 1980 observed [F ≥ 3σ(F)] reflections, R_{int} = 0.032. Scan speeds ranged from 2.00 to 29.30° min⁻¹, with a 1.0° scan range. Two check reflections were measured every 98 reflections, data scaled for a 10% decrease in intensity. Empirical (ψ-scan) absorption correction assuming an ellipsoidal crystal [T(min.) = 0.859, T(max.) = 0.957], Lorentz and polarization corrections.

Structure solution programs were from the SHELXTL package (Sheldrick, 1984, 1986). Atomic scattering factors of SHELXTL used. Systematic absences (0k0, k odd) indicate P2₁ and P2₁/m as possible space groups. From ||E|² - 1| statistics, the noncentrosymmetric space group was chosen. Direct methods and subsequent electron density difference maps yielded all but H atoms. The origin was defined by constraining the y coordinate of the Cr(1) atom to 0.0. The function minimized was Σw(|F_o| - |F_c|)², w = [σ²(F) + (g)F²]⁻¹, g refined to 0.001283. Refinement of the structure continued with the following conditions: anisotropic thermal parameters for all non-H atoms; H-atom isotropic thermal parameters approximately 20% larger than the corresponding heavy atom; C—H and N—H distances restricted to 0.96 Å; H atoms constrained to idealized geometries. The N atoms at the *para* positions of the cations were protonated rather than the O atoms (see Discussion). Final refinement of 207 least-squares

Table 1. Non-hydrogen atomic coordinates (× 10⁴) and equivalent isotropic thermal parameters (Å² × 10³) for (C₄H₄N₂HO)₂Cr₂O₇

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cr(1)	5655 (2)	0	3255 (1)	29 (1)
Cr(2)	2310 (2)	-1039 (4)	1934 (1)	29 (1)
O(1)	2711 (10)	102 (20)	995 (5)	52 (3)
O(2)	377 (8)	-750 (15)	2085 (5)	39 (2)
O(3)	2771 (10)	-3626 (16)	1918 (6)	49 (3)
O(4)	3464 (8)	277 (14)	2910 (5)	36 (2)
O(5)	6624 (9)	-900 (17)	2394 (5)	48 (3)
O(6)	6261 (11)	2369 (15)	3601 (7)	55 (3)
O(7)	5875 (9)	-1726 (17)	4091 (5)	51 (3)
O(10)	10128 (9)	4180 (15)	5693 (5)	47 (3)
N(11)	9528 (10)	2359 (14)	5879 (5)	27 (2)
C(12)	10571 (12)	798 (18)	6266 (7)	31 (3)
C(13)	9933 (12)	-1167 (21)	6505 (7)	34 (3)
N(14)	8241 (10)	-1532 (15)	6374 (6)	33 (3)
C(15)	7220 (12)	-10 (23)	5972 (7)	35 (3)
C(16)	7859 (12)	1891 (19)	5715 (7)	35 (3)
O(20)	7605 (14)	-255 (16)	264 (6)	64 (3)
N(21)	7623 (11)	1591 (16)	610 (6)	36 (3)
C(22)	6151 (13)	2448 (24)	820 (7)	41 (4)
C(23)	6162 (16)	4533 (21)	1214 (8)	51 (5)
N(24)	7539 (17)	5588 (18)	1399 (7)	60 (4)
C(25)	8999 (13)	4712 (20)	1171 (7)	40 (3)
C(26)	9023 (12)	2694 (24)	779 (7)	39 (3)

parameters gave *R* = 0.060, *wR* = 0.079 (*R* = 0.111, *wR* = 0.095 for all reflections), (Δ/σ)_{max} = 0.012 and (Δ/σ)_{mean} = 0.004. The left-handed alternative was rejected on the basis of a higher *wR* = 0.095 for the 3σ data set. Excursions in the final electron density difference map ranged from -0.48 to 0.99 e Å⁻³ [near Cr(2)]. A lack of any possible mirror plane perpendicular to the *b* axis shows P2₁ to be the correct space group. Non-H atomic coordinates are presented in Table 1 and selected bond lengths and angles in Table 2.*

Discussion. This X-ray analysis confirms the ionic complex structure supported by infrared spectroscopy. The structure consists of discrete dinegative dichromate anions hydrogen bonded to monoprotonated pyrazinium *N*-oxide cations. The analysis, however, reveals further interesting details, including the presence of a significant C—H...O hydrogen-bonding interaction.

Protonation of pyrazine 1-oxide to form a monoprotonated cation may conceivably occur at either of two sites: the O atom or the N atom with the lone pair of electrons (see Fig. 1). H atoms were not located in Fourier difference maps but for structural

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52857 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Non-hydrogen bond lengths (Å) and bond angles (°) for (C₄H₄N₂HO)₂Cr₂O₇*

Cr(1)—O(4)	1.793 (6)	C(12)—C(13)	1.363 (16)
Cr(1)—O(5)	1.617 (8)	C(13)—N(14)	1.370 (12)
Cr(1)—O(6)	1.600 (9)	N(14)—C(15)	1.343 (14)
Cr(1)—O(7)	1.609 (9)	C(15)—C(16)	1.338 (17)
Cr(2)—O(1)	1.586 (9)	O(20)—N(21)	1.238 (14)
Cr(2)—O(2)	1.589 (7)	N(21)—C(22)	1.346 (15)
Cr(2)—O(3)	1.629 (10)	N(21)—C(26)	1.316 (14)
Cr(2)—O(4)	1.816 (7)	C(22)—C(23)	1.400 (19)
O(10)—N(11)	1.253 (12)	C(23)—N(24)	1.287 (18)
N(11)—C(12)	1.362 (13)	N(24)—C(25)	1.351 (17)
N(11)—C(16)	1.368 (13)	C(25)—C(26)	1.362 (18)
O(4)—Cr(1)—O(5)	109.6 (4)	C(12)—N(11)—C(16)	118.9 (9)
O(4)—Cr(1)—O(6)	105.5 (4)	N(11)—C(12)—C(13)	119.7 (9)
O(5)—Cr(1)—O(6)	113.6 (5)	C(12)—C(13)—N(14)	119.7 (10)
O(4)—Cr(1)—O(7)	108.6 (4)	C(13)—N(14)—C(15)	120.5 (10)
O(5)—Cr(1)—O(7)	109.0 (5)	N(14)—C(15)—C(16)	119.6 (9)
O(6)—Cr(1)—O(7)	110.4 (5)	N(11)—C(16)—C(15)	121.6 (10)
O(1)—Cr(2)—O(2)	109.5 (4)	O(20)—N(21)—C(22)	117.8 (10)
O(1)—Cr(2)—O(3)	110.8 (5)	O(20)—N(21)—C(26)	121.9 (11)
O(2)—Cr(2)—O(3)	109.6 (5)	C(22)—N(21)—C(26)	120.3 (11)
O(1)—Cr(2)—O(4)	110.3 (4)	N(21)—C(22)—C(23)	118.1 (11)
O(2)—Cr(2)—O(4)	106.5 (4)	C(22)—C(23)—N(24)	121.4 (12)
O(3)—Cr(2)—O(4)	110.0 (4)	C(23)—N(24)—C(25)	119.5 (11)
Cr(1)—O(4)—Cr(2)	127.0 (4)	N(24)—C(25)—C(26)	120.3 (10)
O(10)—N(11)—C(12)	118.8 (8)	N(21)—C(26)—C(25)	120.3 (10)
O(10)—N(11)—C(16)	122.3 (9)		

and chemical reasons the N atom rather than the O atom is believed to be protonated. The shortest interionic oxygen-to-oxygen distance is O(10)⋯O(7) = 3.238 Å while the shortest interionic nitrogen-to-oxygen distances are N(14)⋯O(4) = 2.644 and N(24)⋯O(5) = 2.724 Å. Protonation of the *para* nitrogen of the *N*-oxide pyrazinium cations leading to strong hydrogen bonding explains the shorter N⋯O distances. Fig. 2 includes the resultant N—H⋯O hydrogen bonds: N(14)—H(14)⋯O(4) (N—H⋯O = 161°) and N(24)—H(24)⋯O(5) (N—H⋯O = 154°). Paudler & Humphrey (1970) have also found, *via* a *pK_a* correlation for base-catalyzed H—D exchange of some pyrazine 1-oxides, that the N atom with the lone pair of electrons in pyrazine 1-oxide is more basic than the O atom.

The N(14)—H(14)⋯O(4) hydrogen bond strongly distorts the dichromate anion. The bridging Cr(1)—O(4) and Cr(2)—O(4) bonds are lengthened, the latter significantly: 1.793 (6) and 1.816 (7) Å, respectively, *versus* the expected bond length of 1.780 Å (Pressprich *et al.*, 1988). In fact, the 1.816 Å value is larger than that found for any other bridging Cr—O distance in a dichromate anion. Associated with the lengthening of the bridging bonds is a shortening of the terminal Cr—O bonds so that the average Cr—O bond length (1.655 Å) is practically identical with the average value of 1.656 Å previously found.

The longest terminal Cr—O bond is Cr(2)—O(3) (1.629 Å) and its length may be attributed to a weak C—H⋯O hydrogen bond. The short C(23)—H(23)⋯O(3) distance of 3.180 Å and the near

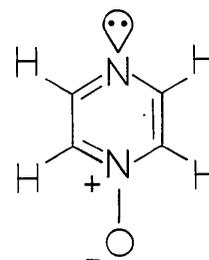
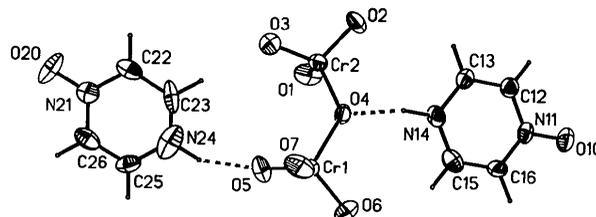
Fig. 1. Pyrazine *N*-oxide.

Fig. 2. Thermal-ellipsoid plot of the formula unit (at the 50% probability level). H atoms are represented by small circles. Hydrogen-bonding interactions are represented by dashed lines.

linearity of the C(23)—H(23)⋯O(3) interaction geometry, C—H⋯O = 169°, support the idea of significant C—H⋯O hydrogen bonding. Pressprich *et al.* (1990) have discussed this issue with consideration of other chromium-containing compounds. The role of C—H⋯O interactions in a series of organic compounds has also been examined (Taylor & Kennard, 1982).

This work was supported by the National Science Foundation (grant No. DMR 88-03382). MRP and RDW thank the Boeing Company and the National Science Foundation (grant No. CHE-8408407) for establishment of the crystal structure laboratory at Washington State University. GLG acknowledges gratefully the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References

- CAMPANA, C. F., SHEPHERD, D. F. & LITCHMAN, W. N. (1981). *Inorg. Chem.* **20**, 4039–4044.
- PAUDLER, W. W. & HUMPHREY, S. A. (1970). *J. Org. Chem.* **35**, 3467–3470.
- PRESSPRICH, M. R., WILLETT, R. D., PAUDLER, W. W. & GARD, G. L. (1990). *Inorg. Chem.* In the press.
- PRESSPRICH, M. R., WILLETT, R. D., POSHUSTA, R. D., SAUNDERS, S. C., DAVIS, H. B. & GARD, G. L. (1988). *Inorg. Chem.* **27**, 260–264.
- SHELDRIK, G. M. (1984). *SHELXTL Users Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- SHELDRIK, G. M. (1986). *SHELXTL Users Manual*. Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.
- TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.