Fig. 1. Perspective view of the molecule with atom numbering.

Lee, Luangdilok, Haller, Anzai & Hatano, 1983). These distances are slightly shorter than in similar ferrous derivatives [2·001 (3) Å]. As a consequence of the increased charge, there is a small decrease in radii for iron(III) compared with iron(II). This leads to decreased bond lengths in the coordination group. The P—C distances in $P(CH_3)_2C_6H_5$ [average 1·807 (4) Å] are in good agreement with other metal phosphine complexes (Oumous, Lecomte, Protas, Poncet, Barbe & Guilard, 1984). The axial Fe—$P(CH_3)_2C_6H_5$ [2·350 (1) Å] is longer than in the iron(III) complex containing the same ligand

[2·284 (1) Å]: this is consistent with an increase in the oxidation state and a decrease in π back bonding from iron to the axial ligand.

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Diethoxybis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)titanium(IV)

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Abstract. $[Ti(C_{10}H_6F_3O_2)_2(C_2H_5O)_2]$, $M_r = 568·32$, monoclinic, $C2/c$, $a = 8·951$ (2), $b = 17·182$ (2), $c = 17·072$ (2) Å, $\beta = 99·95$ (8)°, $V = 2586$ Å^3, $Z = 4$, $D_x = 1·460$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0·7107$ Å, $\mu = 4·02$ cm^{-1}, $F(000) = 1160$, room temperature, $R = 0·088$ for 978 observed reflections with $I > 3\sigma$. The molecule has a crystallographic twofold axis which passes through Ti. The Ti atom is octahedrally coordinated by four O atoms from two β-diketone ligands, and by two ethoxy O atoms in a *cis* arrangement. Ti—O distances range from 1·760 to 2·090 Å.

Introduction. The first synthesis of the title compound was described by Bharara, Dgupta & Meh-

rotra (1975), and it was later reported that compounds of this type have antineoplastic action (Keller, Keppler, Krüger & Linder, 1981). We have undertaken a structural study of this compound, which was synthesized by a new method.

Experimental. Crystals suitable for X-ray analysis were obtained by slow evaporation from ethanol at room temperature. The crystal used for data collection measured 0·2 × 0·3 × 0·4 mm and was mounted with its longest dimension nearly coincident with the φ axis of an Enraf–Nonius CAD-4 diffractometer. With graphite-monochromated Mo $K\alpha$ radiation the cell parameters were obtained from a least-squares refinement of diffractometer settings for 25 reflec-

tions ($6\cdot5 < \theta < 13\cdot3°$). The intensities of reflections with $\theta \le 25°$ were measured in the $\omega/2\theta$ scan mode, with a variable scan rate and ω-scan angle of $(0\cdot80 + 0\cdot35\tan\theta)°$; three reflections were monitored during the data collection and no significant changes were observed. 2686 unique reflections were measured, $R_{int} = 0\cdot03$, 978 with $I > 3\sigma(I)$ were considered observed. Maximum counting time for each reflection 60 s. All reflections were corrected for Lorentz, polarization and absorption effects (North, Phillips & Mathews, 1968); min., max. transmission coefficients 0·85, 0·99.

The structure was solved by Patterson–Fourier methods, and refined by full-matrix least squares with anisotropic temperature factors. H atoms were located from a difference Fourier map calculated at $R = 0\cdot092$ and included in the refinement with isotropic thermal parameters. Convergence was obtained at $R = 0\cdot088$ and $wR = 0\cdot082$. Such high values of R might be ascribed to the very low percentage of observed data caused by high thermal motion, especially of the terminal atoms. In the last cycles of refinement, modified unit weights (Dunitz & Seiler, 1973) were used. The atomic scattering factors were those of Cromer & Waber (1974) and the anomalous-dispersion correction coefficients given by Cromer & Ibers (1974) were employed. In the final difference map $\Delta\rho$ was within $\pm0\cdot60$ e Å^{-3}; max. $\Delta/\sigma = 0\cdot033$.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1,* bond lengths and inter-bond angles are in Table 2; a perspective view of the molecular structure is shown in Fig. 1.

Fig. 1 shows that crystals of the title compound consist of discrete isolated molecules. The molecule has a crystallographic twofold axis passing through Ti, which is coordinated to six O atoms. Each β-diketone ligand cordinates octahedrally with Ti to form two six-membered rings, which are related to each other by the twofold axis; the two ethoxy O atoms, related by the same axis, are in a cis orientation. Within the coordination polyhedron, the Ti—O(2) distance is 2·009 (1) and Ti—O(3) is 2·090 (2) Å, a difference which might be expected from the low symmetry of the ligand chelating to Ti. The distance Ti(1)—O(1)(ethoxy group) is 1·760 (2) Å, which is comparable with the corresponding mean value found in the structure of titanium tetramethoxide (Wright & Williams, 1968).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52872 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2)$$
$$+ ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq} (Å^2)
Ti(1)	0·000	0·0707 (1)	0·250	6·22 (3)
O(1)	−0·1318 (6)	0·0054 (4)	0·1970 (4)	7·5 (1)
O(2)	0·1401 (5)	0·0897 (3)	0·1719 (3)	6·77 (9)
O(3)	−0·1141 (5)	0·1645 (3)	0·1887 (3)	6·4 (1)
F(1)	0·3326 (7)	0·2044 (7)	0·0859 (5)	16·2 (2)
F(2)	0·4191 (8)	0·1427 (9)	0·1569 (7)	15·1 (3)
F(3)	0·3166 (8)	0·0831 (8)	0·0597 (5)	19·0 (2)
C(1)	−0·0780 (8)	0·2149 (4)	0·1430 (5)	5·9 (1)
C(2)	0·0642 (8)	0·2097 (6)	0·1145 (5)	6·9 (2)
C(3)	0·1569 (7)	0·1480 (6)	0·1315 (4)	6·9 (1)
C(4)	−0·182 (1)	0·2794 (5)	0·1191 (6)	6·1 (2)
C(5)	−0·170 (1)	0·3294 (8)	0·0570 (7)	8·1 (2)
C(6)	−0·277 (2)	0·3896 (7)	0·0389 (9)	9·2 (3)
C(7)	−0·388 (2)	0·4008 (8)	0·082 (1)	9·8 (3)
C(8)	−0·401 (1)	0·3530 (9)	0·1415 (9)	10·3 (3)
C(9)	−0·302 (1)	0·2909 (6)	0·1631 (7)	7·7 (2)
C(10)	0·3031 (8)	0·1459 (8)	0·0974 (6)	8·6 (2)
C(11)	−0·291 (2)	0·000 (1)	0·167 (2)	12·9 (6)
C(12)	−0·391 (3)	−0·059 (1)	0·173 (4)	25 (2)

Table 2. *Bond distances (Å) and angles (°) for non-hydrogen atoms*

Ti(1)—O(1)	1·760 (2)	C(4)—C(9)	1·430 (4)
Ti(1)—O(2)	2·009 (1)	C(5)—C(6)	1·404 (6)
Ti(1)—O(3)	2·090 (2)	C(6)—C(7)	1·347 (7)
C(1)—C(2)	1·443 (3)	C(7)—C(8)	1·328 (7)
C(1)—C(4)	1·460 (4)	C(8)—C(9)	1·393 (6)
C(1)—O(3)	1·245 (3)	C(10)—F(1)	1·255 (5)
C(2)—C(3)	1·348 (5)	C(10)—F(2)	1·312 (6)
C(3)—O(2)	1·240 (4)	C(10)—F(3)	1·276 (6)
C(3)—C(10)	1·521 (3)	C(11)—C(12)	1·365 (11)
C(4)—C(5)	1·381 (5)	C(11)—O(1)	1·434 (6)

O(1)—Ti(1)—O(1^i)	100·8 (2)	O(2)—C(3)—C(10)	112·9 (3)
O(2)—Ti(1)—O(2^i)	161·3 (1)	C(2)—C(3)—C(10)	118·4 (3)
O(3)—Ti(1)—O(3^i)	79·0 (1)	C(1)—C(4)—C(5)	123·9 (3)
O(1)—Ti(1)—O(2)	101·7 (1)	C(1)—C(4)—C(9)	117·3 (3)
O(1)—Ti(1)—O(2^i)	90·28 (9)	C(5)—C(4)—C(9)	118·8 (3)
O(1)—Ti(1)—O(3)	90·5 (1)	C(4)—C(5)—(6)	119·3 (4)
O(1)—Ti(1)—O(3^i)	167·1 (1)	C(5)—C(6)—C(7)	121·4 (4)
O(2)—Ti(1)—O(3)	81·3 (7)	C(6)—C(7)—C(8)	120·1 (4)
O(2)—Ti(2)—O(3^i)	84·2 (1)	C(7)—C(8)—C(9)	122·8 (4)
Ti(1)—O(1)—C(11)	139·4 (4)	C(4)—C(9)—C(8)	117·7 (4)
Ti(1)—O(2)—C(3)	130·6 (2)	F(1)—C(10)—F(2)	102·8 (4)
Ti(1)—O(3)—C(1)	133·9 (2)	F(1)—C(10)—F(3)	111·3 (4)
O(3)—C(1)—C(2)	120·6 (3)	F(2)—C(10)—F(3)	102·9 (4)
O(3)—C(1)—C(4)	118·8 (2)	F(1)—C(10)—C(3)	117·0 (3)
C(2)—C(1)—C(4)	120·6 (3)	F(2)—C(10)—C(3)	102·9 (4)
C(1)—C(2)—C(3)	121·5 (3)	F(3)—C(10)—C(3)	112·3 (4)
O(2)—C(3)—C(2)	128·8 (2)	O(1)—C(11)—C(12)	130·0 (8)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The significant deviation of the coordination octahedron from ideal may be ascribed to the different environments of the six donor O atoms.

The chelate ring Ti(1), O(2), O(3), C(1), C(2) and C(3) is nearly planar with a maximum deviation of 0·124 Å at O(2). The phenyl rings are twisted with respect to the (β-diketoenolato)titanium ring by 9·9°. In the chelate ring the two endocyclic C—O [C(1)—O(3) and C(3)—O(2)] and C—C [C(1)—C(2) and C(2)—C(3)] bond distances have values which
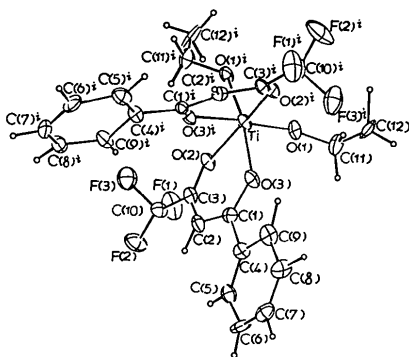
Fig. 1. Perspective view of the structure of diethoxybis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)titanium(IV).

indicate almost complete π-electron delocalization over the β-diketoenolato 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).

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

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Bis(1H^+-pyrazinium N^4-oxide) Dichromate

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Abstract. $2C_4H_5N_2O^+.Cr_2O_7^{2-}$, $M_r = 410 \cdot 2$, monoclinic, $P2_1$, $a = 8 \cdot 003$ (2), $b = 6 \cdot 132$ (2), $c = 14 \cdot 493$ (4) Å, $\beta = 94 \cdot 50$ (2)°, $V = 708 \cdot 8$ (3) Å^3, $Z = 2$, $D_x = 1 \cdot 92$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 15 \cdot 5$ cm^{-1}, $F(000) = 412$, $T = 293$ K, $R = 0 \cdot 0602$ 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···O = $2 \cdot 724$, $2 \cdot 644$ 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···O interaction ($3 \cdot 180$ 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 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 $1 \cdot 0845$ g ($10 \cdot 84$ mmol) of CrO_3 in $1 \cdot 0$ ml