Unusually Stable Chromium(V) Perfluoropinacolate Complexes

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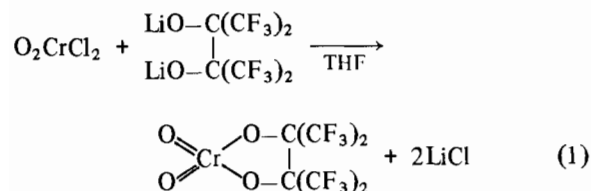
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Abstract

Ligand substitution of chromyl chloride with the chelating dilithium perfluoropinacolate Li_2(PFP) does not afford the desired chromyl perfluoropinacolate O_2Cr(PFP) as previously reported. Instead a facile reductive di-substitution of O_2CrCl_2 occurs to yield bis(perfluoropinacolato)oxochromate(V), $OCr(PFP)_2^-$, and its structure is established as the pyridinium-pyridine salt **II** by X-ray crystallography. The selective hydrolysis of **II** affords an unusual binuclear bis-μ-oxochromate(V) salt **V**, the X-ray crystal structure of which consists of unique chains of binuclear chromium(V) dianions $[OCr(PFP)-\mu-O]_2^{2-}$ that are linked by aquo-lithium ion bridges. The relationship of these unusually stable oxochromate(V) salts to the previously reported simple alkali salts of $OCr(PFP)_2^-$ and potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V) is discussed.

Introduction

Chromyl complexes (O_2CrX_2) with X = chloro, hydroxo, acetato, and nitrato ligands have been extensively used to effect the oxidation of both inorganic and organic donors [1, 2]. The oxidative reactivity of chromyl complexes generally increases with the electronegativity of the substituent X, the trifluoroacetato derivative being a significantly more potent oxidant than the acetato analogue [3]. We were thus attracted to the report of the perfluoropinacolato(PFP) complex **I**, formulated as O_2Cr-$(PFP)_2 \cdot THF$, that was prepared in tetrahydrofuran by the direct ligand exchange of chromyl chloride with dilithium perfluoropinacolate in an apparent 1:1 stoichiometry [4], i.e.

$$O_2CrCl_2 + \begin{array}{c} LiO-C(CF_3)_2 \\ | \\ LiO-C(CF_3)_2 \end{array} \xrightarrow{THF}$$

$$\begin{array}{c} O \\ \diagdown \\ O \diagup Cr \diagdown \begin{array}{c} O-C(CF_3)_2 \\ | \\ O-C(CF_3)_2 \end{array} \end{array} + 2LiCl \qquad (1)$$

Indeed our repetition of the synthetic procedure afforded blue–purple needles of **I** with its melting point, elemental and spectral (IR, UV–Vis, ^{1}H, ^{13}C and ^{19}F NMR) analyses in excellent accord with the published report. However, despite the strong electron-withdrawing properties of the perfluoropinacolato ligand, the purple **I** was surprisingly inert, even to secondary alcohols and other easily oxidized donors. In order to resolve this anomalous behavior, we now report the isolation and structural characterization of the series of crystalline (perfluoropinacolato)chromium(V) complexes obtained from the metathetical partners in eqn. (1).

Results and Discussion

The treatment of dilithium perfluoropinacolate (THF adduct) as a slurry in carbon tetrachloride with chromyl chloride yielded the blue–purple complex **I** described by Conroy and Dresdner [4]. Dissolution in dichloromethane afforded a deep blue solution showing a major absorption band at $\lambda_{max} = 311$ nm and a weak, broad band at 564 nm; and ^{1}H NMR analysis indicated the presence of ~2 eq. of tetrahydrofuran. Sublimation of **I** *in vacuo* led to purple crystals (**Ia**) and a residual light red powder (**Ib**) in a roughly 1:3 weight ratio. Dissolution of **Ia** and **Ib** in dichloromethane yielded the same blue solution with the characteristic pair of absorption bands (λ_{max} 310, 563 nm) found in **I** (*vide supra*). Indeed ^{1}H NMR analysis showed that **Ib** was related to **Ia** simply by the loss of tetrahydrofuran in the course of sublimation.

I
{[$O_2Cr(PFP)_2$].THF}

Ia : X=THF   {$Li^+[OCr(PFP)_2]^-$.THF}
Ib : X=None {$Li^+[OCr(PFP)_2]^-$}
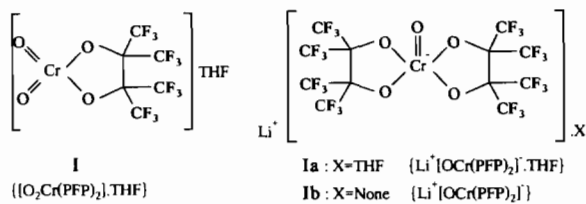
Various attempts at X-ray crystallography of the blue–purple **Ia** were unfortunately beset by crystal degradation, presumably arising from the radiation-
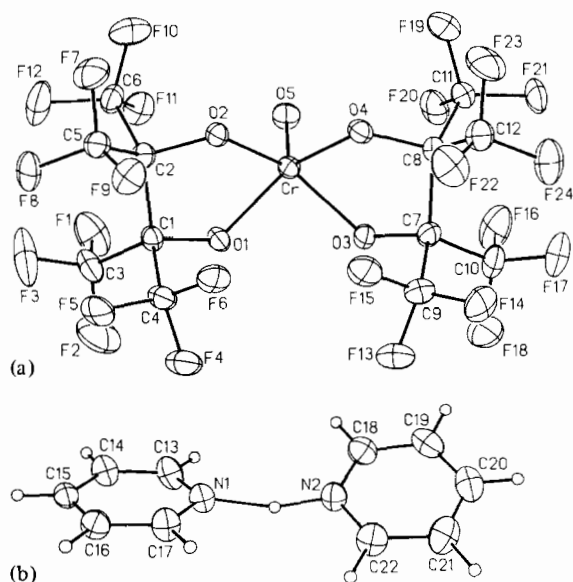
Fig. 1. (a) ORTEP view of the oxochromate(V) anion OCr-(PFP)$_2^-$ in II, showing the envelopes of the thermal ellipsoids with 20% equiprobability. (b) View of the hydrogen-bonded pyridinium-pyridine cation (py)$_2$H$^+$. The thermal ellipsoids are 20% equiprobability envelopes with the hydrogens as spheres of arbitrary diameter.

induced separation of THF. Accordingly Ib was converted with the stronger pyridine ligand to the blue complex II with unchanged spectral (UV–Vis)
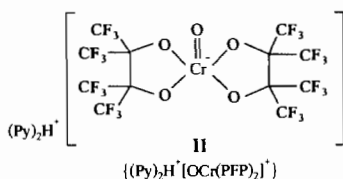

characteristics. A single crystal of II was successfully grown from a solution of dichloromethane and carbon tetrachloride in the triclinic space group P$\bar{1}$ with cell constant $a = 9.860$, $b = 12.095$, $c = 14.809$ Å, and $\alpha = 93.83$, $\beta = 106.32$, $\gamma = 113.69°$. The X-ray structure was solved by interpretation of the Patterson Map using the SHELXTL program which

revealed the position of the chromium atom in the asymmetric unit, and the remaining non-hydrogen atoms were located in the subsequent difference Fourier syntheses. The ORTEP diagram in Fig. 1(a) clearly identifies in II the square pyramidal configuration about the chromium center arising from the terminal oxo ligand and the four oxygens from a pair of chelating perfluoropinacolato ligands. Thus the blue–purple crystal II was not the expected pyridine complex of chromyl perfluoropinacolate, but instead the chromophoric unit consisted of the anionic oxochromate(V) with the basic skeletal structure
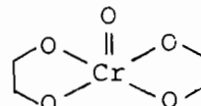
The cationic counterion was comprised of the hydrogen-bonded dipyridine (py)$_2$H$^+$ shown in Fig. 1(b). The measurement of the magnetic moment $\mu_{eff} = 2.38$ BM confirmed the d^1 configuration of the chromium(V) center in II. Moreover the ESR spectrum consisted of a broad unresolved signal at $\langle g \rangle = 1.9791$ similar to that found in other chromium(V) complexes [5].

Owing to the presence of the common chromophore (λ_{max} 307, 568 nm) in the pyridine derivative II, the structure of the parent blue–purple complex I was readily ascribed to the corresponding lithium salt of bis(perfluoropinacolato)oxochromate(V) with THF solvate. Indeed the potassium, cesium and tetraethylammonium salts III of OCr(PFP)$_2^-$ have been

IIIa : R=K   {K$^+$[OCr(PFP)$_2$]$^-$}
IIIb : R=Et$_4$N {Et$_4$N$^+$[OCr(PFP)$_2$]$^-$}
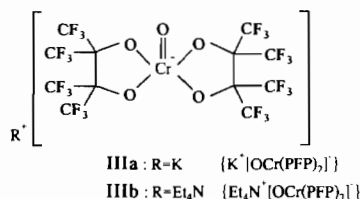
independently synthesized from perfluoropinacol and CrO$_4^{2-}$ in boiling aqueous ethanol acidified with sulfuric acid [6]. These simple oxochromate salts are characterized by magnetic moments and $\langle g \rangle$ values diagnostic of chromium(V) complexes (see Table 1),

TABLE 1. Magnetic parameters of (perfluoropinacolato)oxochromate(V) and related salts

Oxochromate(V) salt	μ_{eff} [a]	$\langle g \rangle$ [b]
Li$^+$OCr(PFP)$_2^-$·THF (Ia)	2.03	1.9798
(py)$_2$H$^+$OCr(PFP)$_2^-$ (II)	2.38	1.9791
K$^+$OCr(PFP)$_2^-$ (IIIa)	1.84 (1.79)[c]	1.9790 (1.9794)[d]
Et$_4$N$^+$OCr(PFP)$_2^-$ (IIIb)	2.22 (2.33)[c]	1.9771
[Li$_{aq}$(py)]$_2^{2+}$[OCr(PFP)-μ-O]$_2^{2-}$ (V)	2.20	silent
K$^+$OCr(HMB)$^-$ (IV)	2.05[c]	(1.9780)[e]

[a]In acetonitrile solutions at 25 °C (see 'Experimental'). [b]In the solid state at 22 °C. [c]From ref. 6a. [d]From ref. 6b. [e]From ref. 9.

and their electronic spectra share the same major and minor absorption bands in common with the blue complexes I and II (Table 2). It has been thus established that the perfluoropinacol-substituted oxochromate(V) $OCr(PFP)_2^-$ is common to all the salts generated from chromium(VI) precursors whether they be chromyl chloride or chromate and employed in non-polar aprotic as well as aqueous media. The accompanying one-electron reduction of the metal center in the course of synthesis is undoubtedly due to the relative ease with which the perfluorinated ligand undergoes oxidative (retro-pinacol) cleavage [7].

The five-coordinate structure of the perfluoropinacolato derivative of oxochromate(V) in Fig. 1 is strikingly akin to that of the 2-hydroxy-2-methylbutyrato(HMB) derivative IV prepared earlier by

IV

{K⁺[OCr(HMB)]⁻}
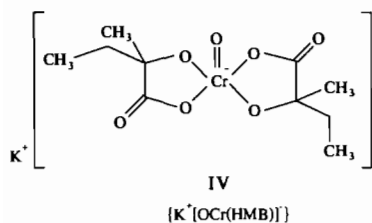
Krumpolc and Roček [8]. The bond distances in Table 3 and the bond angles in Table 4 indicate that the square pyramidal coordination sphere around the chromium(V) center in II is essentially the same as that found in IV [9]. It is thus interesting to note the difference in their oxidative reactivity. The carboxylato derivative IV, though not a powerful oxidant [10], is capable of converting a variety of inorganic and organic donors under conditions in which the perfluoropinacolato complex I is reluctant to react. In this regard, both oxochromium(V) anions

TABLE 2. UV–Vis spectra of oxochromate(V) salts

Oxochromate(V) salt	Solvent	λ_{max} (nm) (ϵ_{max} (M⁻¹ cm⁻¹))
Ia	CH₂Cl₂	311(2290), 564(117)
	THF	313(4550), 586(232)
Ib	CH₂Cl₂	309(2270), 562(115)
II	CH₂Cl₂	307(2080), 568(120)
	THF	312(1980), 584(138)
IIIa	MeOH	312(2340), 572(172)
	CH₂Cl₂	309(2250), 560(28)
IIIb	MeOH	311(2720), 570(159)
	CH₂Cl₂	313(1820), 578(127)
V	CH₂Cl₂	315(3370), 426(749), 610(81)
	THF	323(1930), 425(500), 620(38)

TABLE 3. Bond distances (Å) in $(py)_2H^+OCr(PFP)_2^-$ (II)

Cr–O(1)	1.861(5)	O(2)–C(2)	1.401(8)
Cr–O(3)	1.883(3)	O(4)–C(8)	1.376(7)
Cr–O(5)	1.533(4)	C(1)–C(3)	1.562(14)
F(2)–C(3)	1.295(10)	C(2)–C(5)	1.564(11)
F(4)–C(4)	1.322(8)	C(7)–C(8)	1.632(9)
F(6)–C(4)	1.319(11)	C(7)–C(10)	1.566(12)
F(8)–C(5)	1.304(10)	C(8)–C(12)	1.520(14)
F(10)–C(6)	1.308(10)	N(1)–C(17)	1.322(11)
F(12)–C(6)	1.323(9)	C(13)–C(14)	1.354(11)
F(14)–C(9)	1.298(10)	C(15)–C(16)	1.364(14)
F(16)–C(10)	1.288(13)	N(2)–C(18)	1.321(13)
F(18)–C(10)	1.317(10)	N(2)–H(N)	1.223(78)
F(20)–C(11)	1.316(12)	C(19)–C(20)	1.341(18)
F(22)–C(12)	1.319(12)	C(21)–C(22)	1.389(14)
F(24)–C(12)	1.316(9)		

are substantially less reactive in comparison to their cationic counterpart $OCr(salen)^+$ with essentially the same square pyramidal configuration about the chromium(V) center [11]. (Note the relevant oxo–chromium(V) bond distances of 1.53, 1.55 and 1.55 Å in $OCr(PFP)_2^-$, $OCr(HMB)^-$ and $OCr(salen)^+$, respectively.)

The perfluoropinacolate ligands in $OCr(PFP)_2^-$ were sufficiently stable to substitution to withstand the strenuous hydrolysis in boiling aqueous (acidified) ethanol requisite for its synthesis [6]. However a perfluoropinacolate ligand could be selectively removed by mild hydrolysis under basic conditions. For example, a dark blue solution of I in a 1:3 mixture of dichloromethane/carbon tetrachloride turned green within several hours at 25 °C when a small amount of water and pyridine was added. Upon standing for several days at room temperature, the solution yielded green crystals of V in approximately 90% yield. Measurement of the magnetic moment of V indicated the retention of the chromium(V) center, but no ESR signal was observed at room temperature. Aside from the bathochromic shift of the low energy band to λ_{max} 610 nm and the appearance of a shoulder at ~450 nm, the UV–Vis absorption spectrum as well as the IR spectrum of V was much like that of the oxochromate(V)


V

{[Li.aq.(Py)]₂²⁺ [OCr(PFP)-μ-O]₂²⁻}
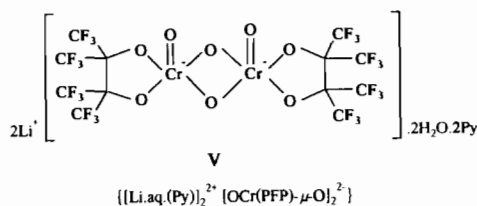
precursor. Single crystals of V were obtained from a mixture of dichloromethane, pyridine and carbon tetrachloride in the triclinic space group $P\bar{1}$ with cell constants a = 1.786, b = 12.625, c = 14.013 Å and

TABLE 4. Selected bond angles (°) in $(py)_2H^+OCr(PFP)_2^-$ (II)

O(1)–Cr–O(2)	82.6(2)	C(8)–C(7)–C(9)	111.2(7)
O(2)–Cr–O(3)	146.3(2)	C(8)–C(7)–C(10)	116.9(6)
O(2)–Cr–O(4)	87.0(2)	O(4)–C(8)–C(7)	103.5(5)
O(1)–Cr–O(5)	104.8(2)	C(7)–C(8)–C(11)	111.6(6)
O(3)–Cr–O(5)	105.8(2)	C(7)–C(8)–C(12)	117.6(5)
Cr–O(1)–C(1)	118.6(4)	F(13)–C(9)–F(14)	108.3(5)
Cr–O(3)–C(7)	118.1(4)	F(14)–C(9)–F(15)	108.7(8)
O(1)–C(1)–C(2)	105.9(5)	F(14)–C(9)–C(7)	114.7(7)
C(2)–C(1)–C(3)	117.1(5)	F(16)–C(10)–F(17)	109.3(8)
C(2)–C(1)–C(4)	111.8(6)	F(17)–C(10)–F(18)	106.6(6)
O(2)–C(2)–C(1)	103.6(4)	F(17)–C(10)–C(7)	110.7(9)
C(1)–C(2)–C(5)	118.0(5)	F(19)–C(11)–F(20)	106.0(6)
C(1)–C(2)–C(6)	113.6(6)	F(20)–C(11)–F(21)	108.5(7)
F(1)–C(3)–F(2)	104.9(9)	F(20)–C(11)–C(8)	113.5(7)
F(2)–C(3)–F(3)	107.3(8)	F(22)–C(12)–F(23)	105.4(8)
F(2)–C(3)–C(1)	110.8(6)	F(23)–C(12)–F(24)	106.0(8)
F(4)–C(4)–F(5)	106.7(6)	F(23)–C(12)–C(8)	111.6(6)
F(5)–C(4)–F(6)	108.2(7)	C(13)–N(1)–C(17)	118.8(7)
F(5)–C(4)–C(1)	112.3(5)	C(17)–N(1)–H(N)	121.3(33)
F(7)–C(5)–F(8)	107.7(5)	C(13)–C(14)–C(15)	117.5(9)
F(8)–C(5)–F(9)	108.4(6)	C(15)–C(16)–C(17)	119.5(8)
F(8)–C(5)–C(2)	111.5(7)	C(18)–N(2)–C(22)	119.2(8)
F(10)–C(6)–F(11)	107.8(6)	C(22)–N(2)–H(N)	119.2(40)
F(11)–C(6)–F(12)	108.5(8)	C(18)–C(19)–C(20)	119.6(10)
F(11)–C(6)–C(2)	113.4(5)	C(20)–C(21)–C(22)	116.8(11)
O(3)–C(7)–C(8)	105.0(4)	N(1)–H(N)–N(2)	156.5(55)

$\alpha = 69.47$, $\beta = 71.69$ and $\gamma = 83.64°$. The X-ray crystallography of the lime green crystal of **V** established the binuclear bis-μ-oxo chromium(V) chromophoric unit
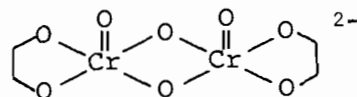
as illustrated in the diagram in Fig. 2. The square pyramidal coordination about each chromium(V) consisted of a terminal oxo, a pair of μ-oxo and a chelating perfluoropinacolato ligand similar to that in $OCr(PFP)_2^-$ (see Tables 5 and 6). The cationic
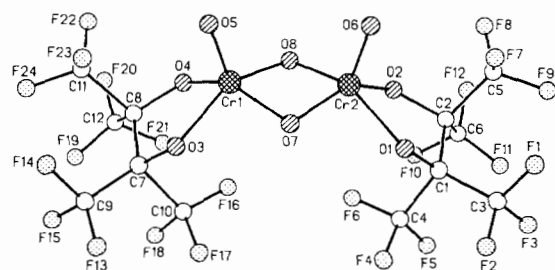

Fig. 2. View of the binuclear chromium(V) dianion $[OCr(PFP)-\mu-O]_2^{2-}$ in **V** showing the labelling scheme.

counterions in **V** were a pair of retained lithium ions, and they served together with pyridine and water as complex bridges, i.e.
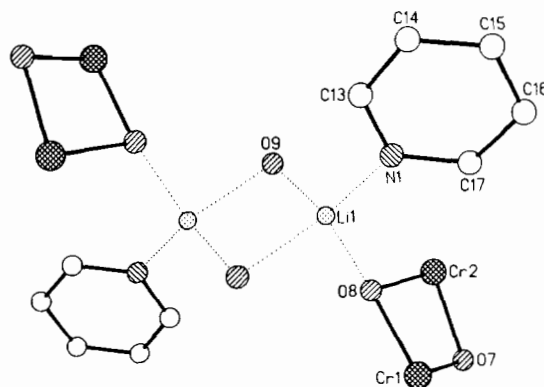
between the binuclear chromium(V) chromophoric units via the μ-oxo centers to form the pseudo polymeric chain, the stereoscopic view of which is shown in Fig. 3.

The binuclear chromium(V) salt **V** was readily reconverted to the oxochromate(V) **II** in dichloromethane solution by treatment with perfluoropinacol in the presence of catalytic amounts of trifluoroacetic acid.

TABLE 5. Selected bond distances (Å) in $(Li_{aq}py)_2^{2+}$-$[OCr(PFP)-\mu-O]_2^{2-}$ (V)

Cr(1)–O(3)	1.905(7)	O(7)–Li(2)	1.954(15)
Cr(1)–O(5)	1.570(7)	C(1)–C(2)	1.569(13)
Cr(1)–O(8)	1.818(5)	C(1)–C(4)	1.586(21)
Cr(2)–O(2)	1.904(5)	C(2)–C(6)	1.532(16)
Cr(2)–O(7)	1.806(5)	C(7)–C(9)	1.503(18)
F(1)–C(3)	1.282(18)	C(8)–C(11)	1.658(21)
F(3)–C(3)	1.305(17)	N(1)–C(13)	1.312(16)
F(5)–C(4)	1.345(17)	N(1)–Li(1)	1.977(24)
F(7)–C(5)	1.309(17)	C(14)–C(15)	1.332(28)
F(9)–C(5)	1.357(15)	C(16)–C(17)	1.388(25)
F(11)–C(6)	1.299(15)	N(2)–C(22)	1.311(25)
F(13)–C(9)	1.249(17)	C(18)–C(19)	1.372(41)
F(15)–C(9)	1.336(16)	C(20)–C(21)	1.298(38)
F(17)–C(10)	1.331(13)	Li(1)–O(9)	1.973(18)
F(19)–C(12)	1.296(17)	Li(2)–O(10)	1.971(20)
F(21)–C(12)	1.422(17)		
F(23)–C(11)	1.254(17)	Li(1)...Li(1')	2.681(34)
O(1)–C(1)	1.376(13)	Li(2)...Li(2')	2.647(43)
O(3)–C(7)	1.368(12)	Cr(1)...Cr(2)	2.628(2)

Experimental

Materials

Chromyl chloride (boiling point (b.p.) 115–116 °C) was prepared from chromium trioxide

(Aldrich) as previously described [12]. Hexafluoroacetone [13] (Aldrich, anhydrous) was used either as received or recovered from the sesquihydrate (DuPont) by treatment with conc. sulfuric acid. K_2CrO_4 (J. T. Baker) was used as received. Dilithium perfluoropinacolate was prepared as the THF adduct from hexafluoroacetone and lithium sand [14] as described by Conroy and Dresdner [4]. Perfluoropinacol (b.p. 128–129 °C) was prepared from hexafluoroacetone and triethyl phosphite according to the procedure of Cripps and Willis [15].

Instrumentation

UV–Vis absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer (2 nm resolution) and all measurements were carried out in either dichloromethane or THF with 1.0 cm quartz cells equipped with greaseless teflon stopcocks. IR spectra were measured in KBr disks on a Nicolet 10DXFT IR spectrometer (4 cm^{-1} resolution). ^1H, ^{13}C and ^{19}F NMR spectra were measured in CD_3CN at room temperature on a JEOL FX90Q NMR spectrometer and chemical shifts are given in ppm relative to either TMS or $CFCl_3$ as an internal standard. ESR spectra were recorded on a Varian Century Line E-112 spectrometer equipped with a Metrolab Precision NMR Teslameter PT 2025 at room temperature. Cyclic voltammetry was carried
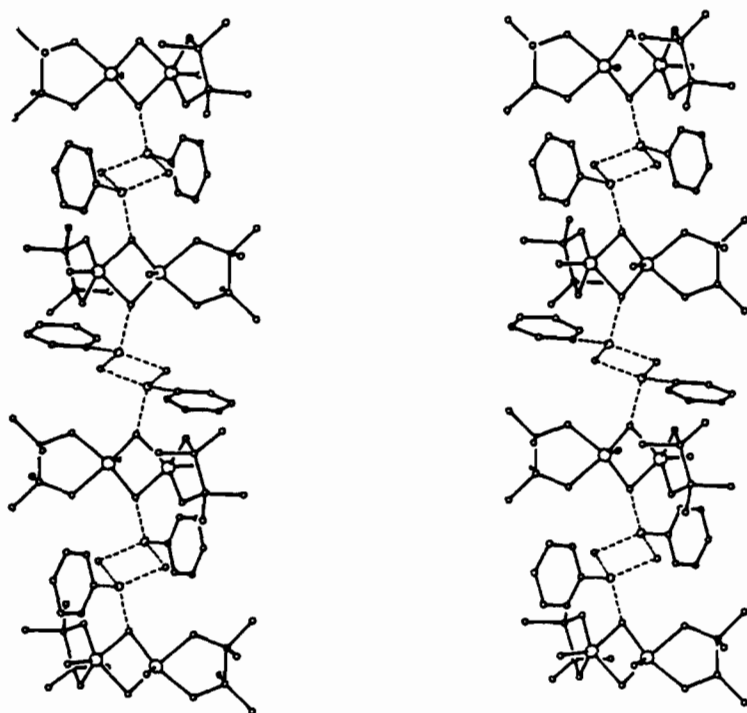

Fig. 3. Stereoscopic view of the pseudo polymeric chain along the *bc* axis in V, showing the aquo-lithium ion (pyridine) bridges. Hydrogens and fluorines are omitted for clarity.

TABLE 6. Selected bond angles (°) in $(Li_{aq}py)_2^{2+}[OCr(PFP)-\mu-O]_2^{2-}$ (V)

O(3)–Cr(1)–O(4)	81.1(2)	F(7)–C(5)–F(8)	109.9(13)
O(4)–Cr(1)–O(5)	106.9(3)	F(8)–C(5)–F(9)	104.9(10)
O(4)–Cr(1)–O(7)	145.7(3)	F(8)–C(5)–C(2)	109.2(8)
O(3)–Cr(1)–O(8)	144.8(3)	F(10)–C(6)–F(11)	108.3(13)
O(5)–Cr(1)–O(8)	108.5(3)	F(11)–C(6)–F(12)	107.3(11)
O(1)–Cr(2)–O(2)	81.4(2)	F(11)–C(6)–C(2)	114.9(8)
O(2)–Cr(2)–O(6)	108.8(3)	O(3)–C(7)–C(8)	106.6(9)
O(2)–Cr(2)–O(7)	143.3(3)	C(8)–C(7)–C(9)	125.2(9)
O(1)–Cr(2)–O(8)	148.0(3)	C(8)–C(7)–C(10)	105.3(8)
O(6)–Cr(2)–O(8)	106.1(3)	O(4)–C(8)–C(7)	108.3(7)
Cr(2)–O(1)–C(1)	117.1(5)	C(7)–C(8)–C(11)	105.1(8)
Cr(1)–O(3)–C(7)	118.3(5)	C(7)–C(8)–C(12)	121.4(11)
Cr(1)–O(7)–Cr(2)	92.4(2)	F(13)–C(9)–F(14)	104.2(13)
Cr(2)–O(7)–Li(2)	124.5(6)	F(14)–C(9)–F(15)	107.9(11)
Cr(1)–O(8)–Li(1)	128.8(6)	F(20)–C(12)–C(8)	115.2(14)
O(1)–C(1)–C(2)	106.8(8)	C(13)–N(1)–C(17)	115.5(13)
C(2)–C(1)–C(3)	118.2(9)	C(17)–N(1)–Li(1)	124.6(9)
C(2)–C(1)–C(4)	110.1(8)	C(13)–C(14)–C(15)	121.0(16)
O(2)–C(2)–C(1)	105.6(7)	N(1)–Li(1)–O(9')	121.7(8)
C(1)–C(2)–C(5)	111.4(7)	O(7)–Li(2)–N(2)	103.6(9)
C(1)–C(2)–C(6)	118.9(11)	N(2)–Li(2)–O(10)	134.9(10)
F(1)–C(3)–F(2)	103.9(10)	N(2)–Li(2)–O(10')	120.6(9)
F(2)–C(3)–F(3)	104.1(11)	Li(1)–O(9)–H(9A)	109.3(4)
F(2)–C(3)–C(1)	112.4(10)	Li(1)–O(9)–Li(1')	85.5(7)
F(4)–C(4)–F(5)	106.6(12)	H(9B)–O(9)–Li(1')	113.1(5)
F(5)–C(4)–F(6)	107.6(10)	Li(2)–O(10)–H(10B)	110.0(5)
F(5)–C(4)–C(1)	114.3(10)	H(10A)–O(10)–Li(2')	130.9(6)

out on a Princeton Applied Research model 173 potentiostat/galvanostat equipped with a model 176 current-to-voltage converter, which provided a feedback compensation for ohmic drop between the working and reference electrodes. The voltammograms were recorded on a Houston Omnigraphic Series 2000 X-Y recorder. All melting points were determined with a MEL-TEMP Laboratory Devices and were uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Preparation of Li⁺OCr(PFP)₂⁻·THF (I)

Dilithium perfluoropinacolate (10 g, 0.03 mol) was suspended in 70 ml of carbon tetrachloride and a solution of chromyl chloride (2.4 ml, 0.03 mol) in 10 ml of carbon tetrachloride added dropwise to the stirred mixture over a 20-min period under an argon atmosphere at 25 °C (cf. ref. 4). After stirring for an additional 2 h, the solvent was removed *in vacuo*, and the dark brown solid was transferred to a soxhlet extractor and treated with CCl₄ for 20 h. The extract was concentrated *in vacuo* and the residue redissolved in CCl₄ (110 ml). Upon cooling the solution to −20 °C, a dark purple solid separated. When dried *in vacuo*, it yielded 3 g of LiOCr(PFP)·THF whose ¹H NMR spectrum (internal standard method with benzene) indicated the presence of ∼2 eq. of THF. Melting point (m.p.) 165–166 °C. UV–Vis (CH₂Cl₂) λmax, 311, 564 nm; (THF) 313, 586 nm. IR (KBr):

3001(w), 2903(w), 1266(s), 1225(s), 1212(s), 1083(s), 1031(m), 993(m), 944(s), 878(s), 766(m), 755(m), 736(m), 706(m), 588(m) cm⁻¹. ¹H NMR (CD₃CN) δ 1.80(m), 3.64(m). ¹³C NMR (CD₃CN): δ 26.14, 68.28. ¹⁹F NMR (CD₃CN): ϕ = 68.97. *Anal.* Calc. for $C_{12}O_5F_{24}CrLi \cdot 1.5$ THF: C, 25.52; H, 1.43. Found: C, 25.38, H, 1.55%. The magnetic susceptibility of I was measured at 295 K by the Evans method in acetonitrile-d_3 (χ_0 = 0.682 × 10⁻⁶) using 1,4-dimethoxybenzene as the standard and a ligand diamagnetism of 0.27 × 10⁻³ [16, 17]. The same procedure was used for the measurements given in Table 1.

Removal of THF from I

Tetrahydrofuran plays a unique role in the synthesis of dilithium perfluoropinacolate [4] and it persisted in the blue–purple crystal of I, despite a large dilution by solvent during the synthesis of the oxochromate(V) salt. Furthermore thermolysis at 110 °C *in vacuo* was required to remove the THF to form the light red powder Ib (*vide supra*); even then a significant amount (22%) survived as the purple sublimate Ia, as described below.

LiOCr(PFP)₂·THF (I) (110 mg) was heated *in vacuo* at 110 °C for 7 h in a microsublimator to yield purple crystals of LiOCr(PFP)·THF (Ia) (24 mg, 22%); m.p. 152–153 °C (lit. [4] m.p. 152.0–152.5 °C). The residue consisted of a light red powder

LiOCr(PFP)$_2$ (Ib) (70 mg, 73%) which showed no (THF) resonance in the ^{1}H NMR spectrum; m.p. 220 °C (decomp.). UV–Vis (CH$_2$Cl$_2$) λ_{max} 309, 562 nm. IR (KBr): 1262(s), 1221(s), 1209(s), 1083(s), 1025(m), 993(m), 943(s), 878(s), 765(m), 756(m), 737(m), 706(m), 587(m) cm^{-1}. ^{19}F NMR (CD$_3$CN): ϕ = 69.64.

Conversion of Ib to the Pyridine Salt II

LiOCr(PFP)$_2$ (Ib) (205 mg) was suspended in 3 ml of dichloromethane and 80 μl of pyridine added whereupon the reddish slurry was converted into a blue solution. After standing at −20 °C for 2 days, a dark blue powder of (py)$_2$H$^+$OCr(PFP)$_2^-$ (II) (224 mg) separated; m.p. 144 °C. *Anal.* Calc. for C$_{17}$H$_6$O$_5$-NF$_{24}$Cr·0.7py: C, 28.38; H, 1.10; N, 2.74. Found: C, 28.63; H, 1.37; N, 2.57%. UV–Vis (CH$_2$Cl$_2$) λ_{max} 307, 568 nm; (THF) 312, 584 nm. IR(KBr): 3122(w), 3094(w), 3064(w), 1496(w), 1430(w), 1258(s), 1230(s), 1210(s), 1169(m), 1085(s), 1019(m), 991(m), 938(s), 877(s), 765(m), 752(s), 735(m), 727(w), 580(m) cm^{-1}. ^{19}F NMR (CD$_3$CN): ϕ = 70.43.

Upon further standing small amounts (12 mg) of green crystals of V separated; m.p. 142–143 °C. *Anal.* Calc. for C$_{12}$H$_4$O$_{10}$F$_{24}$Cr$_2$Li$_2$·2.6py: C, 27.61; H, 1.58; N, 3.35. Found: C, 27.62; H, 1.39; N, 2.70%. UV–Vis (CH$_2$Cl$_2$), λ_{max} 315, 450, 610 nm; (THF) 323, 450, 620 nm. IR(KBr): 3360(br), 1603(w), 1493(w), 1446(w), 1265(s), 1235(s), 1199(s), 1159(w), 1141(w), 1105(m), 1070(w), 1039(w), 1017(m), 991(w), 948(m), 874(m), 765(w), 750(m), 735(w), 719(m), 704(m), 646(m), 590(w) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 8.61, 7.88, 7.59(m, 2:1:2). ^{19}F NMR (CD$_3$CN): ϕ = 68.57 and 69.85.

Preparation of Li$_2$[OCr(PFP)-μ-O]$_2$·2H$_2$O·2py (V)

LiOCr(PFP)·THF (I) (461 mg) and 10 ml dichloromethane were treated with 0.4 ml of pyridine. To the dark blue solution was added water (0.1 ml) and CCl$_4$ (30 ml), and the mixture allowed to stand at room temperature for two days. A small amount of the green solid of V (16 mg) was separated and the mixture concentrated *in vacuo*. The dark green oil was washed with hexane and recrystallized from a mixture of dichloromethane, pyridine and carbon tetrachloride to afford an additional 77 mg of V. Repetition of the procedure yielded an additional 150 mg or a total of 243 mg (86%) of V.

Aqueous Preparation of OCr(PFP)$_2^-$ Salts (III)

The potassium salt KOCr(PFP)$_2$ (IIIa) was prepared from K$_2$CrO$_4$ and perfluoropinacol according to the procedure of Willis [6]. Yield of IIIa 50%, m.p. 237 °C (decomp.). UV–Vis (MeOH): λ_{max} 311, 572 nm; (CH$_2$Cl$_2$) 309, 560 nm. The potassium salt IIIa was dissolved in 20% vol./vol. aqueous methanol and treated with tetraethylammonium chloride to

afford light blue crystals of Et$_4$NOCr(PFP)$_2$ (IIIb) in 90% yield; m.p. 188–189 °C (decomp.). *Anal.* Calc. for C$_{20}$H$_{20}$O$_5$NF$_{24}$Cr: C, 27.86; H, 2.34; N, 1.62. Found: C, 27.70; H, 2.30; N, 1.62%. UV–Vis (MeOH), λ_{max} 311, 570 nm; (CH$_2$Cl$_2$) 313, 578 nm. IR(KBr): 3003(w), 2964(w), 1486(m), 1458(w), 1446(w), 1400(m), 1250(s), 1232(s), 1207(s), 1174(m), 1161(m), 1141(w), 1103(m), 1085(s), 1009(m), 989(m), 938(s), 874(s), 785(w), 763(m), 755(s), 735(m), 727(w), 704(s), 587(m), 577(m), 544(w), 514(w) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 3.14(br. q), 1.20(br. t). ^{19}F NMR (CD$_3$CN) ϕ = 70.25.

Reaction of LiOCr(PFP)$_2$·THF (I) with Tetraethylammonium Chloride

When a solution of I (151 mg) in 10 ml of water was treated with 43 mg of tetraethylammonium chloride, light blue crystals (138 mg, 89%) which were identical with IIIb (*vide supra*) separated.

Reconversion of the Binuclear Chromium(V) Complex V to the Oxochromate Salt II

A mixture of V (34 mg) and perfluoropinacol (169 mg) was dissolved in 4 ml of dichloromethane. The green solution turned dark immediately upon the addition of trifluoroacetic acid (30 μl) and then dark blue within 10 min. The solution was stirred for an additional hour, and then concentrated *in vacuo*. The blue purple solid was washed with hexane and treated with a solution of pyridine (40 μl) in dichloromethane (3 ml). Workup afforded 26 mg (89%) yield of the blue crystals, II.

X-ray Crystallography of the Perfluoropinacolate Derivatives of Oxochromate(V)

(py)$_2$H$^+$OCr(PFP)$_2^-$ (II)

A large, dark royal blue fragment of II having approximate dimensions 0.60 × 0.50 × 0.45 mm was cut from a very large irregular lump and mounted in a thin-walled glass capillary tube in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromated by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement were cell constants: a = 9.860(5), b = 12.095(6), c = 14.809(7) Å; α = 93.83(4), β = 106.32(4), γ = 113.69(4)°; V = 1519 Å^3; molecular formula: (C$_5$H$_5$N)$_2$H$^+$·C$_{12}$O$_5$F$_{24}$Cr$^-$; formula weight: 891.35; formula units per cell: Z = 2; density: ρ = 1.95 g cm^{-3}; absorption coefficient: μ = 5.47 cm^{-1}; radiation (Mo Kα): λ = 0.71073 Å; collection range: 4° $\leqslant$ 2θ $\leqslant$ 55°; scan width: $\Delta\theta$ = 1.30 + (Kα_2 − Kα_1)°; scan speed range: 2.5 to 15.0° min^{-1}; total data collected: 6931; independent data, $I > 3\sigma(I)$: 3968; total variables: 490; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$: 0.067; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$: 0.046; weights: $w = \sigma(F)^{-2}$. The Laue symmetry was determined to be $\bar{1}$, and the space

group was shown to be either $P1$ or $P\bar{1}$. Intensities were measured using the θ–2θ scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every two hours or every 100 data collected, and these showed only a 10% decay over the five days of the experiment. In reducing the data, Lorentz and polarization corrections were applied, however no correction for absorption was made due to the small absorption coefficient. The structure was solved by the SHELXTL Patterson interpretation program, which revealed the position of the Cr atom in the asymmetric unit. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single non-variable isotropic temperature factor. The difference electron density map was essentially featureless at this point, so the choice for a counterion was H^+. The two pyridine molecules in the asymmetric unit exhibited unusual behavior, with both nitrogens in very close proximity for a hydrogen-bonded pyridinium-pyridine cation. Since there is precedent for such a moiety [18], a hydrogen atom was artificially introduced between the two nitrogen positions and allowed to refine freely. This atom refined to a chemically reasonable location, and thus the structure was taken to be that of a pyridinium-pyridine salt of an oxochromate(V). The alternating cation–anion pairs in the unit cell is shown in Fig. 4. After all shift/e.s.d. ratios were less than 0.1, convergence was reached at the agreement factors listed above and in Table 7. No unusually
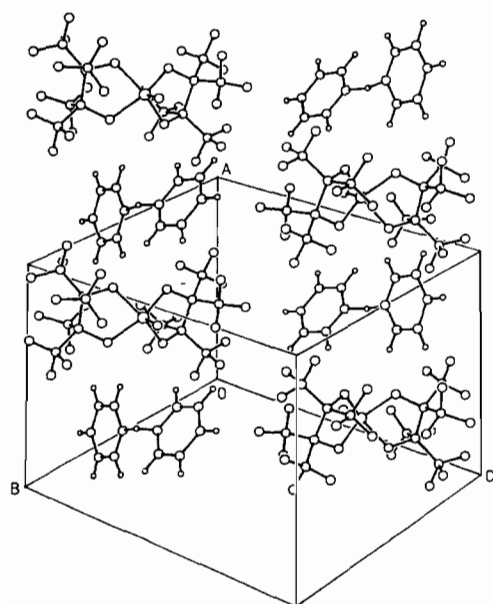

Fig. 4. View of the anion/cation packing in the unit cell of II.

TABLE 7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) in $(py)_2H^+OCr\text{-}(PFP)_2^-$ (II)

	x	y	z	U_{eq} [a]
Cr	2141(1)	1964(1)	6970(1)	41(1)
F(1)	2990(7)	−1083(5)	7459(4)	113(4)
F(2)	4440(7)	−219(5)	8831(4)	140(4)
F(3)	2183(7)	−1548(5)	8575(5)	153(5)
F(4)	4527(5)	1677(4)	9640(3)	86(2)
F(5)	2472(5)	409(4)	9879(3)	89(3)
F(6)	2511(5)	2009(4)	9307(3)	74(2)
F(7)	−2035(5)	−852(4)	7714(3)	97(3)
F(8)	−477(5)	−1362(4)	8691(3)	93(3)
F(9)	−301(5)	446(4)	8948(3)	81(3)
F(10)	−1458(6)	−1090(4)	6195(3)	107(3)
F(11)	758(5)	−942(3)	6254(3)	78(2)
F(12)	−528(6)	−2187(4)	6982(3)	118(3)
F(13)	5708(5)	4827(4)	8997(3)	101(3)
F(14)	4687(6)	6083(4)	8755(3)	109(3)
F(15)	3306(5)	4216(4)	8804(3)	85(3)
F(16)	5391(6)	5034(4)	6265(4)	115(3)
F(17)	5375(6)	6502(4)	7113(4)	123(3)
F(18)	6783(5)	5638(5)	7715(4)	134(3)
F(19)	470(6)	3572(4)	5194(3)	106(3)
F(20)	2641(6)	3521(4)	5360(3)	86(3)
F(21)	2525(5)	5250(3)	5440(3)	100(3)
F(22)	1493(6)	5132(4)	7933(4)	105(3)
F(23)	274(6)	4935(5)	6474(4)	121(4)
F(24)	2590(6)	6330(4)	7125(4)	121(4)
O(1)	3197(4)	1209(3)	7744(3)	45(2)
O(2)	512(4)	1010(3)	7387(3)	44(2)
O(3)	4066(4)	3385(3)	7283(3)	47(2)
O(4)	1354(5)	3127(4)	6930(3)	50(2)
O(5)	1785(5)	1348(4)	5938(3)	60(2)
C(1)	2408(7)	375(5)	8234(4)	47(3)
C(2)	561(7)	−52(6)	7686(4)	48(3)
C(3)	2993(10)	−650(8)	8268(6)	75(5)
C(4)	2973(8)	1127(7)	9279(5)	61(4)
C(5)	−575(8)	−462(7)	8282(5)	61(4)
C(6)	−166(9)	−1093(6)	6747(5)	65(4)
C(7)	4054(7)	4519(6)	7408(4)	51(3)
C(8)	2266(7)	4268(6)	6793(5)	54(3)
C(9)	4438(9)	4951(7)	8502(5)	70(4)
C(10)	5411(10)	5437(7)	7098(7)	83(5)
C(11)	2004(9)	4164(7)	5678(5)	71(4)
C(12)	1671(10)	5169(7)	7084(7)	80(5)
N(1)	8100(7)	2697(6)	8301(4)	71(4)
C(13)	7315(9)	2920(8)	8826(6)	87(5)
C(14)	7944(9)	3327(7)	9792(6)	79(5)
C(15)	9442(9)	3488(6)	10230(5)	67(4)
C(16)	10245(9)	3243(7)	9693(6)	77(5)
C(17)	9552(9)	2854(7)	8738(6)	79(5)
N(2)	6886(7)	2011(6)	6407(5)	74(4)
C(18)	5822(10)	2360(7)	5940(7)	83(5)
C(19)	5284(10)	2156(8)	4977(8)	94(6)
C(20)	5819(12)	1570(9)	4469(7)	101(6)
C(21)	6891(11)	1182(8)	4920(7)	97(6)
C(22)	7423(9)	1447(8)	5918(7)	87(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.4 e Å^{-3}. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

$Li_2[OCr(PFP)-\mu-O]_2\cdot 2H_2O\cdot 2Py$ (V)

A very small, lime green square column of **V** having approximate dimensions $0.09 \times 0.10 \times 0.44$ mm was mounted in a random orientation. The sample was coated with a thin layer of epoxy since the dry solid was known to decompose slowly, presumably due to loss of solvent. The crystallographic data were: space group: $P\bar{1}$, triclinic, cell constants: $a = 11.786(3)$, $b = 12.625(4)$, $c = 14.013(5)$ Å; $\alpha = 69.47(2)°$, $\beta = 71.69(2)$, $\gamma = 83.64(2)°$; $V = 1853$ Å^3; molecular formula: $2Li^+\cdot C_{12}O_8F_{24}Cr_2^{2-}\cdot 2H_2O\cdot 2C_5H_5N$; formula weight 1040.26; formula units per cell: $Z = 2$; density: $\rho = 1.86$ g cm^{-3}; absorption coefficient: $\mu = 7.38$ cm^{-1}; radiation (Mo $K\alpha$): $\lambda = 0.71073$ Å; collection range: $4° \leqslant 2\theta \leqslant 45°$; scan width: $\Delta\theta = 1.20 + (K\alpha_2 - K\alpha_1)°$; scan speed range: 2.0 to 15.0° min^{-1}; total data collection 4840; independent data, $I > 3\sigma(I)$: 2507; total variables: 565; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$: 0.054; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$: 0.038; weights: $w = \sigma(F)^{-2}$. The structure was solved as described above to reveal the positions of the two Cr atoms in the asymmetric unit. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all pyridine hydrogens were entered in ideal calculated positions and constrained to riding motion with a single non-variable isotropic temperature factor. The water molecules were freely refined as ideal rigid bodies. The dinuclear chromium(V) units formed pseudo-polymeric chains in the solid state via Li...H$_2$O bridges, and each lithium was refined as Li$^+$, using the ionic scattering factor rather than that of the neutral atom. Reasonable anisotropic thermal parameters were obtained from the refinement. After all shift/e.s.d. ratios were less than 0.2, convergence was reached at the agreement factors listed above and in Table 8. No unusually high

TABLE 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) in $(Li_{aq}py)_2^{2+}$-$[OCr(PFP)-\mu-O]_2^{2-}$ (V)

	x	y	z	U_{eq}
Cr(1)	5918(1)	1873(1)	6824(1)	45(1)
Cr(2)	3783(1)	2462(1)	7808(1)	46(1)
F(1)	893(7)	2504(8)	10667(5)	151(5)
F(2)	2224(6)	2208(6)	11373(4)	123(4)

(continued)

TABLE 8. *(continued)*

	x	y	z	U_{eq}
F(3)	1500(6)	3810(6)	10978(5)	122(4)
F(4)	4334(6)	2838(6)	10364(5)	123(4)
F(5)	3726(6)	4573(6)	10008(5)	124(5)
F(6)	4791(5)	3967(5)	8756(5)	93(4)
F(7)	958(5)	2763(6)	8794(5)	88(4)
F(8)	1056(5)	4367(6)	7558(5)	123(4)
F(9)	273(6)	4286(6)	9159(6)	125(5)
F(10)	3563(7)	5777(5)	8090(6)	116(4)
F(11)	1827(6)	5678(5)	9226(5)	113(4)
F(12)	2009(6)	6021(5)	7594(5)	112(4)
F(13)	9011(6)	521(7)	8323(6)	144(5)
F(14)	9331(9)	163(7)	6932(8)	178(7)
F(15)	10253(6)	1547(6)	6972(6)	134(4)
F(16)	7145(6)	3432(5)	7491(5)	90(4)
F(17)	7696(7)	2108(7)	8703(6)	153(5)
F(18)	8988(7)	3312(7)	7445(7)	149(6)
F(19)	10220(6)	3348(5)	5357(5)	108(4)
F(20)	9279(6)	3935(6)	4229(5)	128(4)
F(21)	8612(7)	4406(6)	5615(7)	140(5)
F(22)	8493(7)	2190(7)	4235(6)	143(5)
F(23)	8224(6)	708(6)	5605(6)	106(4)
F(24)	9915(6)	1506(6)	4891(6)	135(5)
O(1)	3128(5)	2296(5)	9283(4)	50(3)
O(2)	3232(5)	3971(4)	7656(4)	47(3)
O(3)	7175(5)	1251(4)	7441(4)	52(3)
O(4)	7173(5)	2853(4)	5799(4)	45(3)
O(5)	5699(5)	1026(4)	6305(4)	59(3)
O(6)	2903(5)	1835(5)	7555(4)	61(3)
O(7)	4912(4)	1460(4)	8195(4)	44(3)
O(8)	4935(5)	3085(4)	6544(4)	45(3)
C(1)	2773(9)	3267(9)	9531(7)	57(5)
C(2)	2424(9)	4143(7)	8552(7)	52(5)
C(3)	1833(13)	2961(11)	10626(9)	82(7)
C(4)	3922(13)	3689(10)	9651(10)	86(8)
C(5)	1155(11)	3846(13)	8514(9)	90(8)
C(6)	2432(14)	5406(10)	8395(10)	91(8)
C(7)	8243(9)	1811(9)	7009(8)	65(6)
C(8)	8306(9)	2544(8)	5840(7)	54(5)
C(9)	9203(11)	1017(15)	7343(12)	117(9)
C(10)	7999(14)	2730(13)	7673(10)	103(9)
C(11)	8719(13)	1658(14)	5155(10)	105(9)
C(12)	9170(12)	3527(11)	5216(12)	96(8)
N(1)	3907(7)	3187(8)	4515(7)	71(5)
C(13)	3696(12)	3758(11)	3605(10)	107(8)
C(14)	3134(15)	3299(17)	3133(13)	150(13)
C(15)	2758(12)	2231(17)	3583(14)	135(13)
C(16)	2992(12)	1602(11)	4485(12)	114(9)
C(17)	3558(11)	2121(12)	4936(8)	98(8)
N(2)	3621(13)	−800(8)	8652(10)	80(6)
C(18)	4045(15)	−1125(11)	7863(18)	118(11)
C(19)	3454(24)	−1376(16)	7267(19)	156(15)
C(20)	2237(28)	−1289(19)	7611(21)	176(20)
C(21)	1739(17)	−971(13)	8435(18)	141(14)
C(22)	2451(18)	−739(10)	8928(10)	106(8)
Li(1)	4620(15)	3961(13)	5196(12)	64(8)
Li(2)	4578(15)	−56(13)	9249(13)	72(9)
O(9)	3803(5)	5296(6)	5528(4)	51(3)
O(10)	6175(5)	−290(5)	9458(5)	62(3)

correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.5 e/$\mathring{A}^3$.

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