Studies of Metal Formates. The Synthesis and *X*-Ray Structure† of Potassium Tetraformato-oxovanadate(IV), $K_2[VO(HCO_2)_4]$

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The title compound has been prepared and its structure determined by single-crystal *X*-ray diffraction. It is orthorhombic, space group *Pbca*, and has $a = 6.8668(4)$, $b = 14.908(3)$, $c = 20.414(4)$ Å, and $Z = 8$. The structure was refined to $R = 0.0230$ from 1 596 reflections. The compound is believed to represent the first example of an anionic complex of the vanadyl ion (VO^{2+}) with a simple monocarboxylic acid and contains infinite zig-zag chains with axial–equatorial formate bridges. The vanadium is in a pseudo-octahedral environment with approximately C_{4v} symmetry [V–O(axial) 1.598(2), 2.212(2) Å].

A number of structures are known for the anionic complexes of vanadyl (VO^{2+}) with di-, poly-, and multi-functional carboxylic acids. For example, the ammonium salts of monomeric oxalate[1] and dimeric tartrate[2] anions are known, whereas the compounds of the simple monocarboxylic acids are in general less well characterised. The only neutral V^{IV} carboxylate species of any kind to have been investigated by *X*-ray methods is a tetrahydrofuran adduct of the benzoate, where an interesting asymmetric variant of the oxo-centred trinuclear carboxylate-bridged $[M_3O(RCO_2)_6L_3]$ (*e.g.* M = Cr, Mn, Fe; R = alkyl or aryl; L = H_2O, pyridine) structure was found.[3] A magnetically normal hydrated formate $VO(HCO_2)_2 \cdot H_2O$ is known,[4] whilst the anhydrous higher alkanoates, which have not been crystallised, are believed from their antiferromagnetic properties to be linear oxo-bridged polymers.[5]

We are currently investigating the oxovanadium(IV) formates, which form a series of highly condensed pseudo-tetragonal sheet polymers of general formula $VO(HCO_2)_2 \cdot L$ (where L = H_2O, HCO_2H, NH_4F, or KF). In the course of our investigations we prepared the title compound which is the first anionic vanadyl complex of a simple monocarboxylic acid to be characterised, and we now report its crystal structure.

Experimental

The magnetic moment was measured at room temperature (18 °C) by the Gouy method (estimated error ±0.05 B.M.); the e.s.r. spectra were recorded on a Varian E-4 *X*-band spectrometer with pitch–KCl as reference.

Preparation of $K_2[VO(HCO_2)_4]$.—This preparation must be carried out in the presence of excess potassium ion to avoid reprecipitation of vanadyl formate and with sufficient free formic acid to avoid aerial oxidation. Potassium carbonate (1.0 g) and vanadyl formate hydrate (0.5 g) were dissolved in the minimum of methanol–formic acid (98%) (1:1 v/v) by gently warming. When effervescence ceased the mixture was simmered to dissolve any residual solid and to reduce the volume until a thick paste formed on cooling. This material was treated with an approximately equal volume of formic acid (98%), warmed to dissolve, cooled and diluted with 15% (v/v) formic acid (98%) in methanol. The resulting supersaturated solution could be filtered and allowed to stand (48 h) in a stoppered vessel to yield blue crystals or heated for a few minutes to obtain a microcrystalline product. Yield 1.0 g (Found: C, 14.8; H, 1.3; K, 24.0; V, 14.8. Calc. for $C_4H_4K_2O_9V$: C, 14.8; H, 1.2; K, 24.05; V, 15.7%).

X-Ray Crystallography.—Air-stable blue crystals were obtained after 48 h from a supersaturated solution of the compound in methanol–formic acid containing potassium formate (see above). Crystals were mounted in glass capillaries and examined by *X*-ray photographic methods to establish cell dimensions and space group.

Crystal data. $C_4H_4K_2O_9V$, $M = 325.2$, orthorhombic, $a = 6.8668(4)$, $b = 14.908(3)$, $c = 20.414(4)$ Å, $U = 2\,089.8$ Å^3, $D_m = 2.05(2)$, $Z = 8$, $D_c = 2.067$ g cm^{-3}, $F(000) = 1\,288$, $\mu(\text{Mo-}K_\alpha) = 17.14$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, space group *Pbca* (no. 61).

Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Cell dimensions were obtained from 25 accurately centred reflections. 2 147 Reflections were recorded [$1.5 < \theta < 25°$, h(0—8), k(0—17), l(0—24)] from a room-temperature crystal (0.4 × 0.25 × 0.35 mm). The systematic absences led to the space group *Pbca* (*hkl*, none; $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h \neq 2n$). The three check measurements showed no change during the experiment and after removing systematically absent reflections there remained 1 832 unique reflections. An empirical psi scan absorption correction was applied to the data [transmission: 95.3 (min.), 99.4%(max.)]. Reflections (236) with $F < 3\sigma(F)$ were omitted, leaving 1 596 reflections used for the refinement.

Solution and refinement of the structure. The K and V atoms were located from an *E*-map produced by SHELX (EEES, parachor 2.36). The remaining C and O atoms were found by a series of structure factor and electron-density syntheses. Least-squares refinement with isotropic atoms reduced *R* to *ca.* 0.07. Introducing anisotropic thermal parameters for K and V reduced *R* to *ca.* 0.04 and the electron-density map showed clearly the H atoms (0.6—0.3 e Å^{-3}), which were introduced in fixed positions into the model. Full-matrix least-squares refinement converged at $R = 0.0230$, $R' = 0.0240$ [146 parameters, anisotropic (K, V, O, C) and isotropic (H) atoms, $w = 1/\sigma^2(F)$, fixed H-atom positions with common refined thermal parameter, max. shift/error 0.27, reflections/parameters 10.9]. The final difference electron-density synthesis showed all features in the range 0.28 to −0.21 e Å^{-3}. The final atomic co-ordinates are given in Table 1. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX (O, C, H) and ref. 6 (V, K) and all calculations

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† *Supplementary data available* (No. SUP 56456, 5 pp.): thermal parameters, full bond lengths and angles, packing diagram. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: B.M. ≈ 9.27×10^{-4} A m^2, G = 10^{-4} T.

Table 1. Fractional atomic co-ordinates with estimated standard deviations in parentheses *

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
V	−0.057 84(6)	0.301 78(2)	0.111 97(2)	O(8)	0.0523(2)	0.2065(1)	0.0514(1)
K(1)	0.105 48(8)	0.103 26(4)	0.193 07(3)	O(9)	0.2499(3)	0.1647(1)	−0.0285(1)
K(2)	−0.259 73(9)	0.529 77(4)	0.056 95(3)	C(1)	0.2418(4)	0.4394(2)	0.0998(1)
O(1)	0.0795(3)	0.2850(1)	0.1740(1)	C(2)	−0.4179(4)	0.2052(2)	0.1544(1)
O(2)	0.1052(2)	0.3995(1)	0.0698(1)	C(3)	−0.2292(4)	0.4242(2)	0.2093(1)
O(3)	0.3498(3)	0.4959(1)	0.0774(1)	C(4)	0.2001(4)	0.2134(2)	0.0165(1)
O(4)	−0.2490(3)	0.2023(1)	0.1311(1)	H(1)	0.2860	0.4096	0.1439
O(5)	−0.5168(3)	0.1421(1)	0.1693(1)	H(2)	−0.4606	0.2734	0.1577
O(6)	−0.2261(3)	0.3972(1)	0.1504(1)	H(3)	−0.1283	0.3957	0.2391
O(7)	−0.3163(2)	0.4901(1)	0.2290(1)	H(4)	0.2963	0.2579	0.0309

* H-Atom positions were not refined.

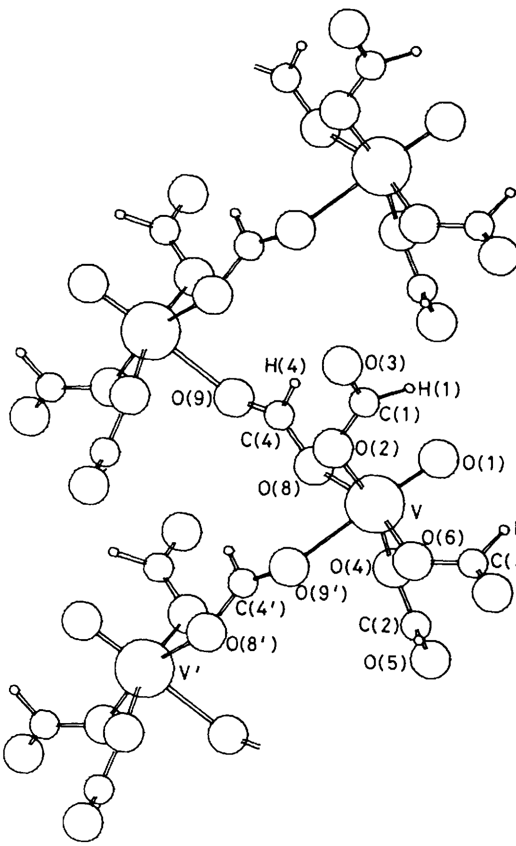

Figure. The anion of $K_2[VO(HCO_2)_4]$ showing the polymeric structure and the atom numbering scheme; atoms are drawn with arbitrary radius

were performed using the programs SHELX,[7] PLUTO,[8] and XANADU[9] on an ICL2976 computer.

Results and Discussion

The structure of the anion of $K_2[VO(HCO_2)_4]$ consists of infinite zig-zag chains parallel to *a*, in which the vanadium atoms are linked in an axial–equatorial manner by bridging formate. The structure and atom numbering scheme is shown in the Figure which illustrates the pseudo-octahedral co-ordination of the V atom and the presence of both terminal and bridging formate groups. Bond lengths and angles are presented in Table 2. The co-ordination about the vanadium is, as expected, approximately C_{4v} with a long (2.212 Å) 'axial' V–O bond *trans* to the short V=O bond (1.598 Å) and with the V atom lying 0.27 Å out of the equatorial plane (*cf.* refs. 1 and 2). Inspection of the VOCO torsion angles (ω) shows an '*anti*' conformation * for the non-bridging formate groups with C–O(V) considerably longer (0.05 Å) than the C–O remote from the vanadium. The '*syn*' conformation for the formate groups has been found in $K[Sn(HCO_2)_3]$.[10] The bridging formate adopts the '*anti–anti*' conformation with C–O distances less disparate in length and this may be compared with $[Cd(HCO_2)_2(H_2O)_2]$ in which both '*anti–anti*' and '*anti–syn*' have been recognised.[11] The non-bonded distance K···O appears normal when compared with $K[Sn(HCO_2)_3]$ (2.74 Å)[10] and the potassium alums (2.92 Å).[12]

The room-temperature magnetic moment (1.79 B.M.) is

Table 2. Selected bond lengths (Å) and angles (°) *

V–O(1)	1.598(2)	C(1)–O(2)	1.268(3)
V–O(2)	2.028(2)	C(1)–O(3)	1.212(3)
V–O(4)	2.019(2)	C(2)–O(4)	1.254(3)
V–O(6)	1.994(2)	C(2)–O(5)	1.200(3)
V–O(8)	2.030(2)	C(3)–O(6)	1.268(3)
V–O(9′)	2.212(2)	C(3)–O(7)	1.218(3)
		C(4)–O(8)	1.244(3)
		C(4)–O(9)	1.220(3)
V···K(1)	3.572(1)	K(1)···O(min.)	2.70
V···K(2)	3.839(1)	K(2)···O(min.)	2.76
V···V′	5.922(1)	C–H *	0.98—1.06
O(1)–V–O(2)	97.0(1)	O(2)–V–O(6)	88.5(1)
O(1)–V–O(4)	96.6(1)	O(2)–V–O(8)	92.2(1)
O(1)–V–O(6)	98.2(1)	O(4)–V–O(6)	94.1(1)
O(1)–V–O(8)	98.8(1)	O(4)–V–O(8)	81.1(1)
O(2)–C(1)–O(3)	126.7(2)	V–O(2)–C(1)	122.8(2)
O(4)–C(2)–O(5)	126.3(3)	V–O(4)–C(2)	130.5(2)
O(6)–C(3)–O(7)	125.3(2)	V–O(6)–C(3)	127.5(2)
O(8)–C(4)–O(9)	127.6(2)	V–O(8)–C(4)	126.5(2)
		V–O(9′)–C(4′)	127.7(2)
V–O(2)–C(1)–O(3)	177		
V–O(4)–C(2)–O(5)	−173		
V–O(6)–C(3)–O(7)	170		
V–O(8)–C(4)–O(9)	−166		
V–O(9′)–C(4′)–O(8′)	156		

* Primed atoms represent the symmetry operation $x - \frac{1}{2}$, $\frac{1}{2} - y$, $-z$; H-atom positions were not refined.

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* '*anti*', |ω(VOCO)| ⩾ 90°; '*syn*', |ω(VOCO)| ⩽ 90°.

typical for oxovanadium(IV) (1.68—1.78 B.M.[13]) and is indicative of little or no magnetic interaction between the V atoms. The e.s.r. spectrum of the room-temperature powdered solid gave a single broad resonance [g(isotropic) = 2.00, linewidth 225 G].

Derivatives and Related Compounds.—Attempts were made to prepare related compounds with NH_4, Li, Na, or Ca cations. Only a sodium compound was obtained, and that was invariably solvated with apparently varying ratios of water and formic acid. Solvent could easily be pumped away leaving a microcrystalline solid with a complex *X*-ray powder pattern clearly not isomorphous with the potassium compound. A hydrated potassium compound, believed to be of the same stoicheiometry (K:V = 2:1), may be prepared from aqueous solution, but the highly viscous mother-liquor may take weeks to crystallise if not seeded.

Treatment of crystalline $K_2[VO(HCO_2)_4]$ with cold anhydrous formic acid results in the formation of a transparent gel, rather than the expected $VO(HCO_2)_2 \cdot HCO_2H$. Further treatment of the gel results in a fine fibrous pale blue solid which is completely amorphous to *X*-rays and believed from i.r. evidence to contain intact segments of the polymeric chains, highly cross-linked to each other. This interesting material is extremely hygroscopic [forming $VO(HCO_2)_2 \cdot H_2O$ on exposure to air] but analyses approximately as $VO(HCO_2)_2 \cdot 0.33KHCO_2 \cdot 1.33HCO_2H$, or alternatively $HVO(HCO_2)_3 \cdot 0.33KH(HCO_2)_2$ (Found: C, 19.3; K, 4.9; V, 22.8. Calc. for $C_{11}H_{15}KO_{25}V_3$: C, 17.9; K, 5.3; V, 20.7%).

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