Dioxodifluoro- and Dioxodichloro-vanadate(v) Ions

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Summary The preparation and properties of the dioxodifluoro- and dioxodichloro-vanadate(v) ions are reported.

We have prepared the novel ions $VO_2F_2^-$ (I) and $VO_2Cl_2^-$(II) which are isoelectronic with CrO_2F_2 and CrO_2Cl_2. They are formed by mixing a solution of sodium metavanadate(v) with 40% HF and 25% HCl solutions. On the addition of aqueous solutions of the respective cations, the tetraphenylphosphonium and tetraphenylarsonium salts of (I) - (III) and (IV) (colourless), and of (II) - (V) and (VI) (yellow), are precipitated.

The compounds (III)—(VI) were characterised by elemental analysis, i.r. spectra, and powder patterns. The i.r. spectrum of (III) and (IV) up to 400 cm^{-1} shows bands due to the cations, and, in addition, the following strong absorptions: 970 [ν_s (VO)], 960 [ν_{as} (VO)], 660 [ν_s (VF)], and 631 cm^{-1} [ν_{as} (VF)], and for the corresponding chloro-compounds (V) and (VI): 971 [ν_s (VO)], 960 [ν_{as} (VO)], and 435 cm^{-1} [ν_s and ν_{as} (VCl)]. These absorptions are as expected for anions with C_{2v} symmetry. Using the approximation of Cotton and Wing[1] the stretching force constants $f_{VO} = 6{\cdot}73$, $f_{VF} = 3{\cdot}43$, $f_{VCl} = 2{\cdot}37$ mdynes/Å were calculated. According to Siebert[2] the bond orders $N_{VO} = 1{\cdot}9$, $N_{VF} = 1{\cdot}0$, and $N_{VCl} = 1{\cdot}1$ were estimated, indicating that there is essentially no π-contribution in the metal halogen bond, whereas it is, as expected, significantly increased in the VO bond compared with VO_4^{3-} ($f_{VO} = 4{\cdot}58$ mdynes/Å^3, $N_{VO} = 1{\cdot}4$).

The powder patterns of (III)—(VI) are nearly identical to those obtained from the corresponding monohalogenochromates (VI)[4] and permanganates[5] indicating that the structure of all the compounds should be very similar.

TABLE

Compound	a_0 (Å)	c_0 (Å)
$Ph_4PVO_2F_2$ (III)	12·23	7·22
$Ph_4AsVO_2F_2$ (IV)	12·41	7·09
$Ph_4PVO_2Cl_2$ (V)	12·56	7·54
$Ph_4AsVO_2Cl_2$ (VI)	12·80	7·40

Indexing of the reflexions yielded the cell dimensions given in the Table.

From the observed extinctions (hkl: $h + k + l = 2n$) a pseudotetragonal structure is suggested (approx. space group S_4^2—$I\bar{4}$). Because the central atoms should occupy the sites of S_4 symmetry, the space group S_4^2 is only exactly valid for the permanganates.[5] In the case of (III) and (IV) because of the similar size of the oxygen and fluorine atoms the orientation of the anions is probably statistical, as was observed in the case of $KCrO_3F$,[6] and the space group S_4^2 is effectively obtained. The calculated densities are in good agreement with the experimental values for two formulae per unit cell.

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