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$[V_{12}O_{30}F_4(H_2O)_2]^{4-}$: One-pot synthesis and characterization of a novel fluorinated dodecavanadate

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ABSTRACT

A new synthetic strategy for one-pot synthesis of a fluorinated isopolyvanadate, $(NMe_4)_4[V_{12}O_{30}F_4(H_2O)_2]\cdot 9H_2O$, utilizing peroxidovanadate intermediates, and the stepwise characterization of the reaction mixture is reported herein. The characterization of the title compound was done by single-crystal X-ray diffraction and IR spectroscopy and the reactivity was monitored by ^{51}V NMR spectroscopy to elucidate the hydrolysis pathway. The $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ anion consists of four VO_5 units in the central layer and two groups of three VO_5F units capped by one $VO_4F(H_2O)$ unit in the outer layers of the anion. In the crystal structure, the anions form strong O–H···F hydrogen bonds running in the *a* axis direction.

Polyoxidometalates attract huge research interest due to their varied structural diversity, giving rise to a wide range of applications in fields such as catalysis, magnetism, medicine, electrochemistry, luminescence, and material science [1–7]. The incorporation of fluorine into polyoxidometalates is becoming an interesting route for obtaining new structural motifs. The benefits of introducing the fluorido ligand, such as reducing the surface charge, small size and high electronegativity [8–12] may open the route to new properties and applications of polyoxidometalate species. The ongoing research in the field of transition metals oxide fluoride anions has brought the most fruitful results in the synthesis and structural characterization of polyoxidofluoridomolybdates with potential applications in biological chemistry, catalysis and redox processes [13,14], ferroelectrics [15], as well as investigation and taking advantage of second-order Jahn–Teller distortion in pseudo-octahedral d^0 systems [16,17].

The family of structurally characterized fluorinated polyoxidomolybdates includes $[Mo_3O_4F_9]^{5-}$ [18], $[Mo_4O_8F_{10}]^{6-}$ [19], $[Mo_4O_{12}F_2]^{2-}$ [20], $[Mo_4O_{12}F_3]^{3-}$ [21], $[Mo_6O_{18}F_6]^{6-}$ [22], $[Mo_7O_{22}F_3]^{5-}$ [22], $[Mo_8O_{26}F_2]^{6-}$ [23] and $[Mo_{16}O_{53}F_2]^{2-}$ [24] together with series of low-nuclearity systems (monomeric and dimeric ions) and polymeric chains [25].

Despite the exhaustive chemistry of fluorido complexes of vanadium (V) including $[VOF_4]^-$ [26], $[VOF_5]^{2-}$ [27], $[VO_2F_2]^-$ [28,29], $[VO_2F_3]^{2-}$ [28,30], $[V_2O_4F_5]^{3-}$ [31], $[V_2O_6F_2]^{4-}$ [32], $[V_2O_2F_8(H_2O)]^{2-}$ [33], $[V_3O_3F_{12}]^{3-}$ [33] and $[V_4(O,F)_{20}]^{8-}$ [34], there are only two known mixed-valence fluorinated isopolyvanadates, $[H_6V^V_2V^{IV}_{10}O_{30}F_2]^{6-}$ [35] and $[V^{IV}_2V^V_{12}O_{36}F_4]^{8-}$ [36], and one vanadium(V) anion, $[HV^V_{11}O_{29}F_2]^{4-}$, which was prepared from $[V^{IV}_2V^V_8O_{26}]^{4-}$ by reaction with *tert*-butyl hydroperoxide and fluoride anions at room temperature in dichloromethane [37]. The molecular structure of $[HV^V_{11}O_{29}F_2]^{4-}$ consists of five VO_5 and six VO_5F units with two μ_3-F bridges and can be derived from $[H_6V^V_2V^{IV}_{10}O_{30}F_2]^{6-}$ by removal of one VO unit.

Herein we present a simple one-pot three-step synthesis of a fluorinated dodecavanadate starting from vanadium pentoxide. We also provide identification of intermediate products using ^{51}V NMR spectroscopy. The final product, $(NMe_4)_4[V_{12}O_{30}F_4(H_2O)_2]\cdot 9H_2O$, was characterized using single-crystal X-ray diffraction, elemental analyses, IR and ^{51}V NMR spectroscopies.

While for the syntheses of fluorinated Mo clusters solvothermal conditions have been found to be effective [13,14], the only known fluorinated vanadate $[HV^V_{11}O_{29}F_2]^{4-}$ was prepared by oxidation of the V^{IV}/V^V precursor mentioned above. In our efforts we focused on the synthesis of fluorinated vanadate directly from a V^V compound through peroxido complexes. ^{51}V NMR studies of the reaction system are depicted in Fig. 1a–d. Upon complete dissolution of V_2O_5 in $N(CH_3)_4OH$ (a) a colorless solution obtained contains mainly $V_4O_{12}^{4-}$ (55%, − 580 ppm) and $V_5O_{15}^{3-}$ (20%, − 591 ppm) together with traces of HVO_4^{2-} (1%, −539 ppm), $V_2O_7^{4-}$ (2%, −565 ppm) and $HV_2O_7^{3-}$ (3%, −569 ppm). The remaining peaks (−595, −597 and −599 ppm) corresponding to about 19% of total V^V may be ambiguously attributed to hexavanadates and protonated oligomers [38]. Excess of H_2O_2 added in the next step (b) results

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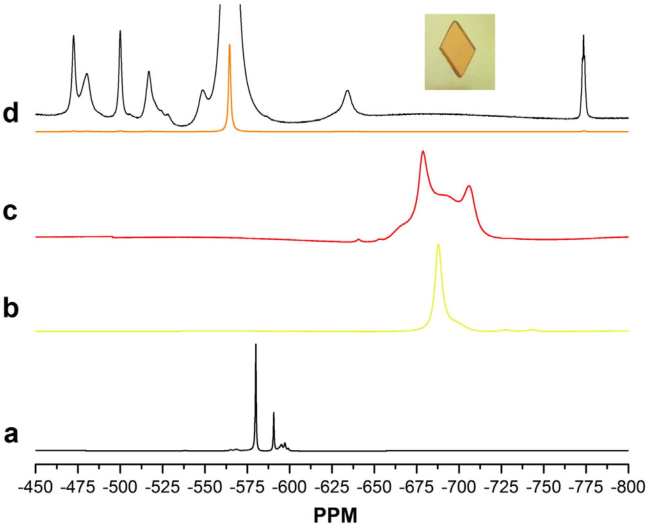

Fig. 1. ^{51}V NMR spectra of reaction mixtures collected in each step of the synthesis. Approximate concentrations of reactants are as follows: (a) $c(V^V) = 0.9$ mol dm^{-3}; (b) $c(V^V) = 0.7$ mol dm^{-3}, $c(O_2^{2-}) = 2$ mol dm^{-3}; (c) $c(V^V) = 0.7$ mol dm^{-3}, $c(O_2^{2-}) = 1.8$ mol dm^{-3}, $c(F^-) = 1.8$ mol dm^{-3}; (d) due to evaporation of the solvent and decomposition of H_2O_2 the concentrations of V^V and F^- increase while only a small amount of O_2^{2-} is expected in the solution.

in the formation of $[VO(O_2)_2H_2O]^-$ (93%, −689 ppm). A small amount of the triperoxido species $[VOH(O_2)_3]^{3-}$ (4%, −730 ppm) and an unknown species (3%, −744 ppm) are also present [39]. All chemical shifts of the peroxido species are systematically shifted by +3 ppm with respect to the commonly observed values in typical systems with total vanadate concentration less than 0.1 mol·dm^{-3} [38]. Addition of concentrated hydrofluoric acid (c) results in a rapid change in the color of the solution from yellow to dark red and rich evolving of dioxygen. ^{51}V NMR spectrum of the sparkling solution shows the presence of $[V_2O_2(O_2)_3F_3]^{3-}$ (37%, −679 ppm) [40] and $[VO(O_2)_2F]^{2-}$ (31%, −706 ppm) [41] besides $[VO(O_2)_2H_2O]^-$. Surprisingly, after one day standing at 4 °C the color of the solution changed from red to orange and the dominating species in the solution exhibited a resonance at −565 ppm (85% of total V^V) which corresponds to $[V_2O_4F_5]^{3-}$ [40]. A strong magnification of the spectrum showed resonances at −473, −480, −500, and −517 ppm which may refer to $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ containing four non-equivalent vanadium atoms in the ratio 2:2:1:1. Additional peaks at −550 and −634 ppm could be assigned to $[VO_2(H_2O)_4]^+$ [42] and to an unidentified fluorido-monoperoxido complex, respectively. A quintet at −774 ppm refers to $[VO_2F_4]^{3-}$ [43] or $[VOF_4]^-$ [44]. The composition of the solution remained unchanged, until crystallization taking place after 5–6 days and providing orange-red plate crystals of $(NMe_4)_4[V_{12}O_{30}F_4(H_2O)_2]\cdot 9H_2O$ [45,46]. A control experiment without addition of H_2O_2 resulted in direct formation of $[V_2O_4F_5]^{3-}$ and $[VO_2F_4]^{3-}/[VOF_4]^-$ upon addition of HF and no other species were present in the solution.

Single crystal X-ray analysis [47-50] revealed that the asymmetric unit of the title compound consists of one half of the $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ anion (Fig. 2) and two molecules of $N(CH_3)_4^+$; the symmetrically dependant parts generated through the crystallographic center of symmetry. The total number of molecules of water present in the crystal structure is uncertain, since the estimated value 9 is significantly influenced by the heavy disorder of one molecule, which is most likely superimposed by the residue of some remaining hydrogen peroxide. Nevertheless this disorder has a marginal impact on the precision of the structure; for three molecules of water it was even possible to locate the hydrogen atoms in the difference Fourier map.

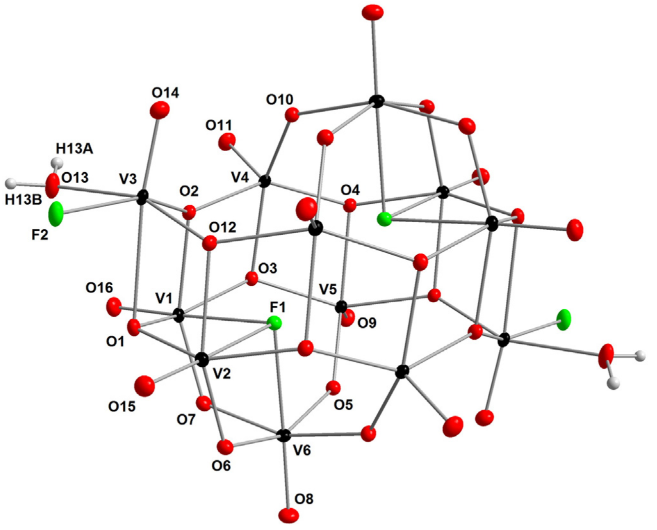

Fig. 2. Molecular structure of the fluorinated isopolyvanadate anion $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ together with the atomic labeling scheme. All non-hydrogen atoms are displayed as thermal ellipsoids at 50% probability level; H atoms are displayed as spheres of arbitrary radius. Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x-1, y, z$; (iii) $x+1, y, z$.

The $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ anion can be considered as a layered polyoxidometalate (Fig. 3). The cluster consists of four VO_5 units in the central layer and two groups of three VO_5F units capped by one $VO_4F(H_2O)$ unit in the outer layers. The structure is similar to the structures of reported $[H_6V^V_2V^{IV}_{10}O_{30}F_2]^{6-}$ [35], $[V^{IV}_2V^V_{12}O_{36}F_4]^{8-}$ [36] and $[HV^V_{11}O_{29}F_2]^{4-}$ [37]. The μ_3-F bridge is an interesting feature of all of these anions. The V-μ_3-F distances in $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ are V1–F1 2.213(1), V2–F1 2.2140(8) and V6–F1 2.1833(8) Å. The bond length V3–F2 of the terminal F^- ligand is 1.883(1) Å. A terminal F^- ligand can be found in $[V^{IV}_2V^V_{12}O_{36}F_4]^{8-}$ as well [36]. The water molecules coordinated in $VO_4F(H_2O)$ units significantly decrease the overall charge of the anion to −4. The bond length V3–O13 2.078(2) Å is a typical value for V–OH_2 bond. The hydrogen atoms H13A and H13B were easily found on the difference Fourier map. The bond lengths in twelve terminal V═O units fit in the range 1.579(1)–1.604(1) Å. Two types of oxido bridges are present in the structure, with eight V-μ-O bridges with bond lengths in the range 1.7746(9)–1.994(1) Å and ten V-μ_3-O bridges with bond lengths in the range 1.803(1)–2.036(1) Å. Due to the trans effect of the oxido ligand, the bond V3–O1 in the capping $VO_4F(H_2O)$ unit is unusually long (2.379(1) Å).

Some strong hydrogen bonds between the $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ anions in the crystal structure are present (Fig. 3), resulting in infinite chains running in the [1 0 0] direction (*a*-axis). The distance of F2···O13 is 2.683(2) Å, and F2···H13B is 1.93(3) Å and the angle of O13–H13···F2 has the value of 159(2)°. The supramolecular structure of the compound is composed by a large number of hydrogen bonds, which, unfortunately, cannot be evaluated completely, due to the disorder of some molecules of water of crystallization.

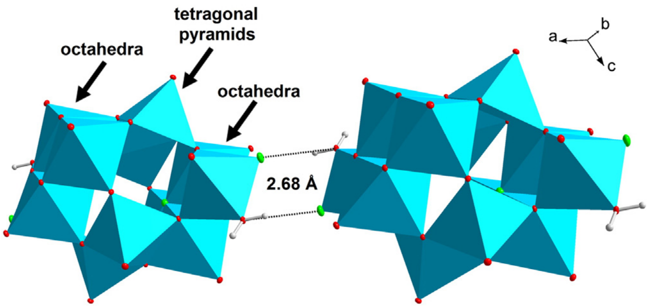

Fig. 3. Polyhedral view showing the layered structure of $[V_{12}O_{30}F_4(H_2O)_2]^{4-}$ and the O–H···F hydrogen bonds between the anions.