Polar ordering of polar octahedra in \([\text{C}_2\text{N}_2\text{H}_{10}]\text{[VOF}_4\text{(H}_2\text{O})]\)

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\([\text{C}_2\text{N}_2\text{H}_{10}]\text{[VOF}_4\text{(H}_2\text{O})]\) spontaneously crystallises in the polar space group \(P2_1\); strongly distorted V-centred octahedral units form polar chains via head-to-tail H-bonding which, in turn, cooperate via the organic template to form a crystal exhibiting a strong SHG signal. It is suggested that the polar ordering arises from a preference for misalignment of the polar octahedra with the polar chain direction, leading to favourable, asymmetric template-chain H-bonding interactions.

The rational design of polar crystalline solids has become an intriguing challenge for solid state chemists. Recently several differing examples of the polar ordering of guest species within host structures which could otherwise be centrosymmetric have been reported. These include the polar ordering of organic molecules within lamellar host frameworks, mediated by host–guest rather than guest–guest interactions,\(^1\) the polar ordering of ‘template’ organic species within a zeolite, mediated by polar ordering of fluoride ions in cages during synthesis,\(^2\) and the polar ordering of chloride ions within a metal phosphonate framework.\(^3\) In addition, the inherent polarity of particular chemical species has also been exploited in the design of chiral and/or polar structures; these specifically include ions with stereochemically active lone pairs, e.g. \(\text{IO}_3^-\) in \(\text{RbMoO}_3\text{(IO}_3\text{)}\)\(^4\) and distorted octahedral ions based around \(d^0\) or \(d^3\) metals. Poepelmeier and co-workers, in particular, have been successful in controlling the formation of polar and chiral crystal structures from species such as \([\text{VOF}_3\text{]}^{2-}\), \([\text{MoO}_3\text{F}_2\text{]}^{5-}\) and \([\text{MoO}_3\text{F}_3\text{]}^{6-}\) via ligand-mediated interactions.\(^5-7\) In this paper we present the unusual polar ordering of the polar \([\text{VOF}_4\text{(H}_2\text{O})]\)\(^{4+}\) ion, mediated by hydrogen bonding.

The title compound was prepared by hydrothermal reaction: \(\text{V}_2\text{O}_5\) (0.182 g, 1 mmol) was heated with 0.5 ml 48\% HF solution (14 mmol) and 5 ml water (278 mmol) at 100 °C for 1 hour. Ethylene glycol (5 ml; 99\%, 90 mmol) was then added to produce an orange solution. Subsequent addition of 0.5 ml ethylenediamine (99\%, 8 mmol) produced a solution of pH = 5, which was heated in a PTFE bottle at 100 °C for 2 days. Blue plate-like crystals were recovered from a blue solution upon completion of the reaction.

Single crystal diffraction\(^8\) and chemical analysis\(^9\) revealed a phase-pure material with composition \([\text{C}_2\text{N}_2\text{H}_{10}]\text{[VOF}_4\text{(H}_2\text{O})]\). The structural analysis unambiguously reveals a non-centrosymmetric crystal structure in the polar space group \(P2_1\). Charge-balance and bond-valence sums, together with the colour of the crystals, are consistent with the assignment of the oxidation state of vanadium as \(V^{4+}\). Thermogravimetric analysis reveals a weight loss of 7.9\% in the range 123–139 °C corresponding to loss of the water molecule (calculated 8.1\%), followed by a stability plateau until 245 °C, and a further gradual weight of about 38\% up to 550 °C. The final product of this heat treatment was identified by powder XRD as \(\text{VF}_3\) (PDF No. 6-209). Although the intermediate, dehydrated phase loses single crystal quality, powder X-ray diffraction shows that crystalinity is still maintained, though the resultant pattern suggests that this structure is apparently not closely related to that of the as-made material. The dehydration is not reversible.

The crystal structure exhibits discrete, highly anisotropic, \(\text{trans-[VOF}_4\text{(H}_2\text{O})]\) octahedra involving all possible H-bond donors in both the water ligand and the ethylenediammonium cation, \([\text{enH}_3\text{]}^{3+}\) (Fig. 1); the resultant interactions are such that all the dipoles are directed in the same sense along the \(b\)-axis of the crystal, thus resulting in the polar space group (Fig. 2) and significant SHG activity (below).

Although the factors governing crystallisation of polar crystals from achiral building units are extremely subtle and far from well understood (see for example the works of Hulliger and co-workers\(^8,9\) and also the recent commentary by Pidcock\(^10\)), we may speculate on the possible origins of this behaviour in the present example. Firstly, neighbouring octahedra may be regarded as linked ‘head-to-tail’ via \(\text{F}^-\text{H}_2\text{O}\) H-bonds to form infinite chains parallel to the \(b\)-axis (Fig. 3). This type of interaction is not surprising, and dipolar molecules or other units are often seen to favour the formation of polar chains in this manner. Secondly, the additional H atom of the water molecule acts as a donor to a fluorine atom, F(1), of a \([\text{VOF}_4\text{(H}_2\text{O})]\) group in an adjacent chain (Fig. 3). It is possible that the inherent requirement for optimisation of both the \(\text{intra-}\) and \(\text{inter-}\) chain H-bonds involving

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\(\text{Fig. 1}\) Asymmetric unit showing thermal ellipsoids at 50\% probability. Bond lengths (\(\text{Å}\)): V1–O1 1.637(2), V1–O2 2.264(2), V1–F1 1.895(1), V1–F2 1.943(2), V1–F3 1.936(1), V1–F4 1.911(1), N1–C1 1.475(3), C1–C2 1.523(4), C2–N2 1.492(3)
the water molecules leads naturally to a ‘misalignment’ of the \( O_2 \cdot \cdot \cdot \cdot \cdot OH_2 \) vector with the polar chain direction, and thence to a natural asymmetry in the local chemical environments of the four fluorine atoms within the octahedron, leading on to differing H-bonding possibilities for these F atoms, with subsequent potential for them becoming crystallographically, as well as chemically, different in the resultant lattice.

The resultant H-bonded ‘dimeric’ chains are linked further into three dimensions via intervening \([enH_2]^{2+}\) moieties (Figs. 2 and 4). The local environment around one \([enH_2]^{2+}\) moiety is strongly asymmetric, perhaps as a natural consequence of the symmetry-lowering caused by the misalignment of the octahedra with the polar axis. In particular, Fig. 4 shows the H-bonding scheme around each of the crystallographically unique N atoms: N(2) donates four H-bonds, whereas N(1) donates five; this includes the N(1)–H(1)…F(4) bond which, at 2.657(3) Å, is significantly stronger than all the other template-chain interactions. The asymmetry and strength of these interactions mean that overall there is sufficient ‘communication’ between neighbouring chains to produce a cooperative alignment in a polar fashion throughout the crystal.

This crystal structure is closely related to that of \([C_2N_2H_{10}]AlF_5(H_2O)\)\(^{13}\) which adopts the same space group and crystal packing, but does not contain the short vanadyl (V=O) bonds and therefore does not exhibit octahedral units with the same degree of polarisation (Al–F bond lengths in the narrow range 1.781–1.803 Å). It is clear therefore that the polar ordering within the crystal is not directly related to the polarity of the \([VOF_4(H_2O)]^{2-}\) octahedron itself. On the contrary, we suggest the mechanism above, whereby the polar ordering is initiated by the preferred intra- and inter-chain H-bonding patterns of the water molecule. An essential aspect of this model is, however, that there is the additional potential of asymmetric inter-chain interactions via the template moiety. This mechanism is supported by the observation that the \([VOF_4(H_2O)]^{2-}\) ion has been observed previously in two polymorphs of \(Cs_2[VOF_4(H_2O)]\). In both these cases, despite a similar anisotropy within the octahedral unit, and also a chain-like structure, there is no direct H-bonding within chains, and neighbouring chains are linked such that the overall packing gives rise to centrosymmetric crystal structures.\(^{12,13}\) Moreover, a V\(^{5+}\) analogue of the title compound, \([C_2N_2H_{10}][VOF_4(H_2O)]\)\(^2-\) has also been reported to crystallise in a centrosymmetric space group.\(^{14}\) It appears that inter-chain communication via H-bonding is essential to impose the net polar ordering, together with an appropriate number of cation–anion interactions. Hulliger\(^9\) has suggested that any secondary, lateral interactions between such chains need only have an interaction energy of the order 3 kJ mol\(^{-1}\) or even less, in order to induce polar alignment of neighbouring chains.

In order to confirm the non-centrosymmetry of the crystal structure second-harmonic generation (SHG) measurements were carried out using the 1064 nm radiation of a picosecond Nd:vanadate laser. A polycrystalline thin-film sample was prepared and studied relative to a LiNbO\(_3\) standard prepared in a similar way. Although the method is only semi-quantitative, reasonable limits on both SHG intensity and damage threshold can be defined. This method suggests an SHG activity
about 15–30 times less than that of LiNbO₃ (corresponding to \(\chi(2)\) about 4 to 6 times less), and a damage threshold of about 500 MW cm\(^{-2}\) for the type of laser used here, which is about an order of magnitude below that of LiNbO₃.

In summary, we have prepared and characterised a novel material which exhibits a significant SHG response. The crystal structure is built of highly polar building units, which pack together in polar alignment via a complex and subtle hydrogen-bonded network. The polarity of this network can be traced back to the co-operative H-bonding requirements of both the water molecule and the template. It is clear that further work in related systems, using a range of organic cations, is merited in order to shed further light on this interesting feature.

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Notes and references

\* Crystallographic data: \(\text{C}_2\text{H}_{12}\text{N}_2\text{F}_4\text{O}_2\text{V}_1\), \(M_r = 223.07\), monoclinic \(P21\), \(a = 6.584(3)\) Å, \(b = 5.827(2)\) Å, \(c = 9.948(4)\) Å, \(\beta = 97.232(2)\)°, \(V = 378.6(3)\) Å\(^3\), \(Z = 2\), \(\mu = 1.34\) mm\(^{-1}\), \(D_x = 1.96\) g cm\(^{-3}\), \(T = 93\) K, 2254 reflections measured of which 1263 unique and 1237 observed \((I > 2\sigma(I))\).

Final agreement factors \(R1 = 0.0223\), \(wR2 = 0.0525\) (observed data). Flack parameter (0.07(2)). CCDC reference number 274936. See http://dx.doi.org/10.1039/b508959j for crystallographic data in CIF or other electronic format.

\* Elemental analysis: obs. (calc.): C 10.68 (10.77), H 5.64 (5.42), N 12.78 (12.56)%.