A new hybrid framework based on a 'superoctahedral' $[V_7O_6F_{30}]^{14-}$ polyanion†

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Solvothermal synthesis has led to the isolation of an unusual hybrid framework solid $[CH_3NH_3]_8[Cu(Py)_4]_3[V_7O_6F_{30}]$ in which the novel $[V_7O_6F_{30}]^{14-}$ polyanion is linked *via* $[Cu(py)_4]^{2+}$ moieties into a doubly interpenetrated cubic lattice.

There is an increasing tendency in solid state chemistry towards the use of 'molecular' building blocks in the construction of extended framework materials, which may consequently exhibit 'extended' physical properties such as porosity, magnetic, electronic, optical activity or other features. Several examples of this modular approach to building new solids occur in polyoxometalate chemistry, where polyoxomolybdate or polyoxovanadate units are linked together, for example, by Ag(I) cations,[1] Cu–bipy moieties,[2] $[Zn(H_2O)_4]^{2+}$ groups[3] or lanthanide complexes.[4] We have recently been exploring solvothermal vanadium oxyfluoride (VOF) chemistry, and have shown the existence of a rich variety of oligomeric, anionic VOF species.[5] We have also shown that, with judicious choice of counter-cation and synthetic conditions, particular VOF units may be crystallised in polar, optically-active arrays[6] or condensed into extended chain or ladder-like networks of magnetic interest.[7] So far, however, our studies have not resulted in VOF materials with three-dimensional covalent connectivity. One strategy for achieving this goal is to use complex cations, as in the polyoxometalate examples above. Poeppelmeier and co-workers have shown that copper–amine complexes, notably $[Cu(py)_4]^{2+}$, can be used to link monomeric metal oxyfluoride units, such as $[MoO_2F_4]^{2-}$, $[VOF_5]^{2-}$ and $[VOF_4]^{2-}$ into chains, often with controllable structural features such as polarity or chirality.[8–10] Inspired by this work, we have explored the possibilities of incorporating such linking cations into our own VOF chemistry. The present paper reports the first example of a three-dimensional framework Cu-VOF, $[CH_3NH_3]_8[Cu(Py)_4]_3[V_7O_6F_{30}]$ (**1**), which exhibits several novel structural features.

The title compound **1** was prepared by a solvothermal reaction.‡ Single crystal diffraction,§ powder X-ray diffraction (see ESI†) and chemical analysis are consistent with a phase-pure material with composition $[CH_3NH_3]_8[Cu(Py)_4]_3$-$[V_7O_6F_{30}]$. Thermogravimetric analysis reveals a continuous weight loss of 44.8% between 200–240 °C which corresponds to the loss of pyridine (38.4%) and methyl ammonium (6.5%).

The structure of **1** exhibits a remarkably high symmetry, which may be understood by breaking it down into its constituent building units. At the core of the structure is a 'superoctahedral' unit consisting of seven vanadium-centered octahedra (Fig. 1). The central octahedron, V(2), is best assigned as a $V^{IV}F_6$ unit¶ which, although somewhat at variance with bond valence sum analysis[11] (bond valence sums (vu) for the metal centres: V(1) = 3.94, V(2) = 3.11, Cu(1) = 1.75) corresponds with the overall coherence of the model and, in particular, provides an excellent fit to the magnetic data (see below). The outer six crystallographically equivalent octahedra, V(1), exhibit the characteristic 'off-centre' distortion due to the short vanadyl bond, and unambiguously contain V^{IV}. These six octahedra each share a fluorine ligand with V(2), but are not directly bonded to each other. We therefore assign the resultant stoichiometry of the heptameric superoctahedron as $[V_7O_6F_{30}]^{14-}$. These units are linked together into a three-dimensional covalent network *via* the $[Cu(py)_4]^{2+}$ cations (Fig. 1).

The resultant solid crystallises as a continuous inorganic net, and should be regarded as an 'extended inorganic hybrid'[12] rather than a metal–organic framework, with the inorganic network being 'decorated' by the pyridyl groups. For clarity, the framework is presented in Fig. 2, which shows the metal atoms only. It can be seen to consist of two

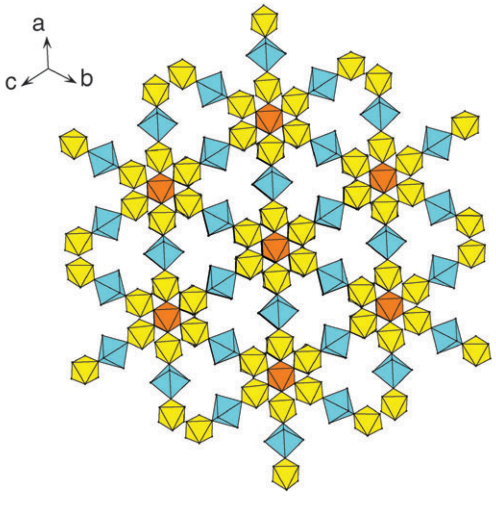

Fig. 1 Polyhedral representation of the inorganic framework, viewed down the [111] direction. Organic moieties not shown, for clarity.

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† Electronic supplementary information (ESI) available: Powder XRD patterns, analytical data and magnetic measurements. CCDC 669272. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718417d

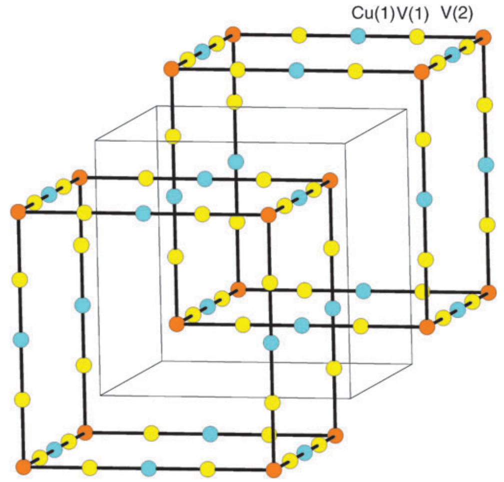

Fig. 2 Schematic crystal structure of **1**, represented as two interpenetrated *pcu* lattices, showing only the metal atom positions. The unit cell is also outlined.

interpenetrated primitive cubic units (each of which may be regarded as an 'augmented' and 'expanded' *pcu* in the notation of O'Keeffe[13]), which result in a pseudo body-centered cubic overall structure; the body-centering being broken by the 'propeller-like' rotations of the pyridyl groups. The role of the second amine moiety can be seen in Fig. 3, which shows one 'face' of the superoctahedral unit, and its mode of linkage to both the $[Cu(py)_4]^{2+}$ unit and the $[CH_3NH_3]^+$ moiety. The latter are H-bonded to the fluorine atoms of three neighbouring VOF_5 units in such a way that the C–N bond lies directly along the three-fold axis of each octahedral face.

Magnetic susceptibility data for **1** were collected on a Quantum Design MPMS SQUID. Data were recorded in a 5000 Oe field while warming the sample from 2 to 300 K in 4 K steps, following consecutive zero-field cooling (ZFC) and field cooling (FC) cycles. The $1/\chi$ *versus* T plot (see ESI†) fits well to a Curie–Weiss law above 30 K, with no evidence of long-range magnetic ordering, although both the negative Weiss constant ($\theta = -11.9$ K) and the fall-off of χT *versus* T (Fig. 4) suggest short-range antiferromagnetic correlations. The value of $\mu_{eff} = 5.46$ BM, derived from the Curie–Weiss plot is in excellent agreement with that expected for a system of ten non-interacting spin-$\frac{1}{2}$ centres per formula unit ($7\ V^{4+} + 3\ Cu^{2+}$; $\mu_{ideal} = 5.48$ BM), which confirms the model proposed, and the assignment of V(2) as V^{4+}. In particular, for a non-interacting system of nine $S = \frac{1}{2}$ + one $S = 1$ centres the μ_{ideal} would reach 5.91 BM. It can be seen (Fig. 4) that χT tends towards saturation at 300 K, the ideal value for the model proposed being 3.75 $cm^3\ mol^{-1}$ K (*cf.* 4.37 $cm^3\ mol^{-1}$ K for the alternative V^{3+}-containing model).

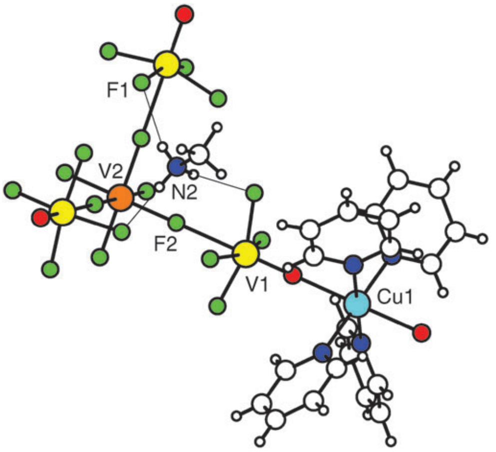

Fig. 3 Portion of the structure of **1**, showing one 'face' of the superoctahedron and its interaction with the $[Cu(py)_4]^{2+}$ and $[CH_3NH_3]^+$ moieties. Bond lengths (Å): Cu(1)–O(1) 2.242(3), V(1)–O(1) 1.644(3), V(1)–F(1) 1.8963(13), V(1)–F(2) 2.419(3), V(2)–F(2) 1.943(3). The V(2)–Cu(1) vector corresponds to half of the unit cell axis (see Fig. 2).

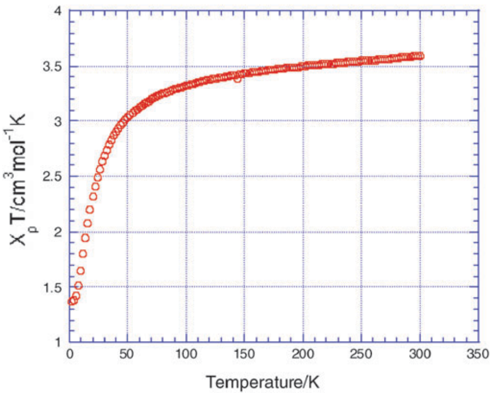

Fig. 4 χT *versus* T plot for **1**.

In summary, we have prepared and characterised a novel hybrid material which exhibits a unique framework topology. This is the first example of a three-dimensionally connected hybrid metal (oxy)fluoride of this type, and also the first time that the heptanuclear superoctahedron has been observed (although a related bimetallic unit, $[Ni(TaF_6)_6]^{4-}$ has been reported[14]). It is particularly interesting that the two distinct amines included in the reaction mixture undertake discrete roles in the crystal structure. It is tempting to speculate that the presence of the $[CH_3NH_3]^+$ moiety may be key in construction of the heptanuclear unit, *via* the hydrogen bonding interactions shown in Fig. 3, and therefore in the structure-direction of the overall framework. Further work is ongoing to explore different amine combinations in similar systems, in order to further expand on the rich structural chemistry of vanadium oxyfluorides which we have so far discovered.

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Notes and references

‡ Single crystals of $[CH_3NH_3]_8[Cu(Py)_4]_3[V_7O_6F_{30}]$ were synthesised by a solvothermal method. Initially 0.200 g (1.09×10^{-3} mol) of V_2O_5 was weighed into a 27 mL Teflon-lined stainless steel autoclave and dissolved with 0.5 mL (2.89×10^{-2} mol) of 48% HF at room temperature for 5 min. To the resultant solution, 5 mL (6.18×10^{-2} mol) of pyridine, 0.15 mL (2.26×10^{-3} mol) of methylamine, 0.5 mL (2.77×10^{-2} mol) of water and finally 0.100 g (1.25×10^{-3} mol) of

CuO were added and stirred well until fully dissolved. The reaction vessel was sealed and heated to 160 °C for 24 h, and then cooled to room temperature over an additional 24 h. Blue cubic crystals were recovered by vacuum filtration. Phase purity was confirmed by elemental analysis, together with comparison of observed and simulated powder X-ray diffraction patterns. Elemental and crystallographic analysis are in good agreement with the structural formula $[CH_3NH_3]_8[Cu(Py)_4]_3[V_7O_6F_{30}]$: calcd: C, 33.76%; H, 4.49%; N 11.58%, measured: C, 33.22%; H, 4.38%; N 11.68%.

§ Crystal data for $[CH_3NH_3]_8[Cu(Py)_4]_3[V_7O_6F_{30}]$: M_r = 2418.97, dimensions 0.13 × 0.1 × 0.08 mm^3, cubic, space group $P n\bar{3}n$, Z = 2, ρ_{calcd} = 1.790 g cm^{-3}, $F(000)$ = 2444, $2\theta_{max}$ = 25.3°, a = 16.4943(14) Å, V = 4487.5(7) $Å^3$, T = 93(2) K. A total of 25 150 reflections were collected of which 694 were independent (R_{int} = 0.0304). The structure was solved using SHELX97. The structure was refined to final R_1 = 0.0340 for 644 data $[I > 2\sigma(I)]$ with 64 parameters, wR_2 = 0.1008 for all data, GOF = 1.183 and residual electron density max/min = 0.420/−0.605 e $Å^{-3}$. Hydrogen atoms of the pyridine groups were placed geometrically, and treated as riding, whereas those of the $[CH_3NH_3]^+$ moiety were located and refined isotropically. Powder XRD was carried out on a Stoe STADI/P diffractometer using Cu $K_{\alpha 1}$ X-rays. Single crystal X-ray diffraction data were collected with a Rigaku Mercury CCD with silicon monochromated Mo K_α. The datasets were corrected for absorption *via* multiscan methods. The structure was solved by direct methods and refined by full-matrix least-squares techniques, using the SHELXS, SHELXL and WinGX packages.

¶ V^{IV} invariably occurs in VOF_5 octahedra, incorporating the VO^{2+} cation, in related systems[5–7] whereas, for V^{III}, VF_6 octahedra are common.[15] Nevertheless, there is a precedent for $V^{IV}F_6$ octahedra—in VF_4 itself.[16] The discrepancy in the bond valence sum in **1** may be explained by a possible local displacement of V(2) from its ideal site—this possibility is manifest in the somewhat high atomic displacement parameter at this site (see ESI). The alternative assignment of V(2) as V^{III} would require supplementary charge balance, *e.g.* by a single protonation site, or a single F/O substitution.

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