

A three-dimensional heterometallic Cu^I/V^{IV} 1,2-bis(1,2,4-triazol-4-yl)ethane framework: a new insight into the structure of vanadium oxyfluoride coordination hybrids

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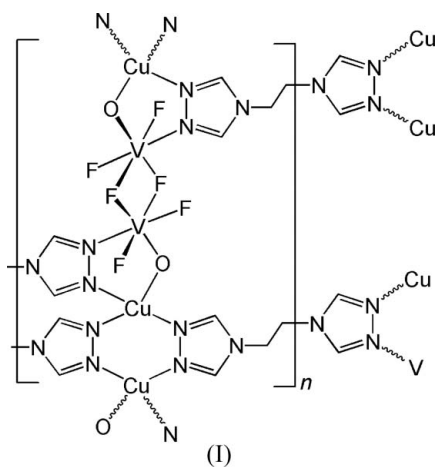
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The bitopic ligand 1,2-bis(1,2,4-triazol-4-yl)ethane (tr₂eth) provides an unprecedented short-distance *N*¹:*N*²-triazole bridging of Cu^I and V^{IV} ions in poly[bis[μ₄-1,2-bis(1,2,4-triazol-4-yl)ethane]di-μ₂-fluorido-tetrafluorido-di-μ₂-oxido-dicopper(I)divanadium(IV)], [Cu₂V₂F₆O₂(C₆H₈N₆)₂]_n. The Cu^I ions and tr₂eth linkers afford a two-dimensional square-grid topology involving centrosymmetric (tr)Cu(μ-tr)₂Cu(tr) [tr is triazole; Cu–N = 1.9525 (16)–2.0768 (18) Å] binuclear net nodes, which are expanded in a third dimension by centrosymmetric [V₂O₂F₆]²⁻ pillars. The concerted μ-tr and μ-O bridging between the Cu^I and V^{IV} ions allows a multi-centre accommodation of the vanadium oxyfluoride moiety on a cationic Cu/tr₂eth matrix [Cu–O = 2.1979 (15) Å and V–N = 2.1929 (17) Å]. The distorted octahedral coordination of [VONF₄] is completed by two terminal and two bridging F⁻ ions [V–F = 1.8874 (14)–1.8928 (13) and 2.0017 (13)–2.1192 (12) Å, respectively]. The resulting three-dimensional framework has a primitive cubic net topology and adopts a threefold interpenetration.

Comment

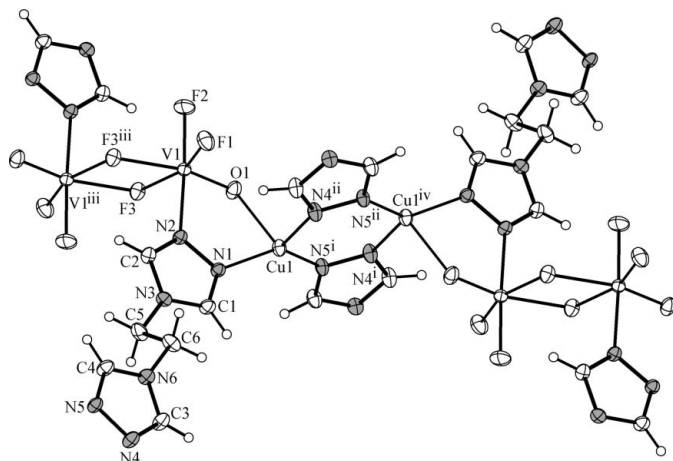
In recent years, the structure-directing properties of vanadium oxyfluoride (VOF) species have found a range of applications in crystal design with a view to preparing magnetic materials (Aldous, Goff *et al.*, 2007) and in the construction of polar optically active arrays (Stephens *et al.*, 2005). In particular, both discrete and oligomeric VOF units have been exploited as bifunctional anionic linkers between complex cations, such as [CuPy₄]²⁺, to generate polymeric chains (Welk *et al.*, 2000; Mahenthirarajah *et al.*, 2008) and complicated three-dimensional frameworks (Mahenthirarajah & Lightfoot, 2008). Even

more versatile possibilities may be found with the utilization of VOF anions as polynucleating linkers between polynuclear complex cations, or as pillaring groups between extended metal–organic layers (Noro *et al.*, 2002). Such systems possess a special and as yet completely unexplored potential for sustaining the inorganic/organic integrity of framework solids. Our present strategy considers further modification of the VOF unit by substitution of the fluoride ligands and setting up additional V–N bonds with the metal–amine portion of the structure, which could complement the short inorganic *M*–O–*M* links (Lysenko *et al.*, 2006). We have therefore examined a prototypical polydentate ligand, namely 1,2-bis(1,2,4-triazol-4-yl)ethane (tr₂eth), typically used to support short *N*¹:*N*²-triazole bridges between pairs of metal ions (Habib, Hoffmann, Hoppe & Janiak, 2009). We report here the structure of a [Cu₂(tr₂eth)₂{V₂O₂F₆}] complex, (I), that features an exceptional concerted organic/inorganic linkage between two types of metal ions, leading to a multi-centre structure and an extremely tight accommodation of the anionic VOF unit in the cationic metal–organic matrix.



The asymmetric unit of (I) includes one Cu^I cation, one organic ligand and one-half of a [V₂O₂F₆]²⁻ anion, which resides across an inversion centre (Fig. 1). Selected geometric parameters are given in Table 1. It is important from synthetic considerations that both metals appear in a reduced form (Cu^I and V^{IV}). Such behaviour of V₂O₅/HF systems is well known for hydrothermal reactions (Aldous, Stephens & Lightfoot, 2007), while Cu^{II} ions under similar conditions are also readily reduced in the presence of triazole ligands (Habib, Hoffmann, Hoppe, Steinfeld & Janiak, 2009).

Atom Cu1 adopts a distorted [CuN₃O] coordination tetrahedron in which the Cu–N bond lengths [1.9525 (16)–2.0768 (18) Å] are characteristic of tetracoordinate Cu(μ-tr)₂-Cu complexes [tr is triazole; Cu–N = 1.991 (3)–2.082 (3) Å; Drabent *et al.*, 2003]. The Cu1–O1 bond is slightly elongated [2.1979 (15) Å] and therefore the metal ion approaches the plane of the three N-donor atoms as close as 0.2388 (11) Å. The present complex VOF unit is sustained with two [VNOF₄] octahedra sharing the F–F edge. It may be directly related to a previously reported binuclear anion, [V₂O₂(μ-F)₂F₄(H₂O)₂]²⁻

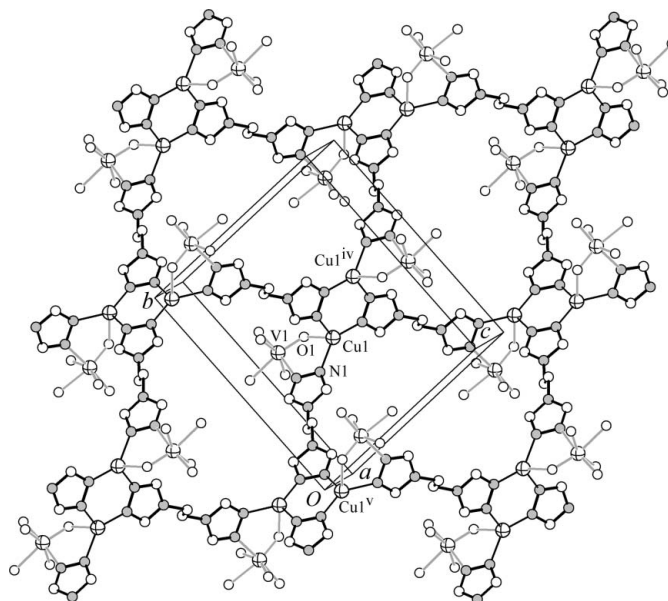

Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Note the unprecedented triazole bridge between the Cu^{I} and V^{IV} ions. [Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $2 - x, 1 - y, -z$; (iv) $2 - x, 1 - y, 1 - z$.]

(Bukove *et al.*, 1981), as a result of substitution of the weakly bound aqua ligands (which are *cis* positioned with respect to the $\text{V}=\text{O}$ bond) by triazole groups, with the formation of triazole/oxide double bridges. Notably, the coordination of the oxide ligand to the Cu^{I} ion results in elongation of the short $\text{V}=\text{O}$ bond to 1.6275 (15) Å, which may be compared with the same distance in the tetramethylammonium and 4,4'-bipyridinium ionic salts of the above diaqua anion [1.607 (5) and 1.606 (2) Å, respectively; Aldous, Stephens & Lightfoot, 2007]. This also produces a shortening of the $\text{V1}-\text{F3}$ bond compared with the corresponding *trans*-fluoride ligand [the latter is 2.1192 (12) Å in (I) versus 2.173 (3) Å reported by Bukove *et al.* (1981)]. The distorted coordination octahedron around the V^{IV} ion is completed by two terminal and two bridging fluorides and a relatively distant triazole N-donor atom [$\text{V1}-\text{N2} = 2.1929$ (17) Å].

The bis(triazole) ligands adopt a μ_4 -coordination, with the triazole halves providing a double connection for two Cu^{I} ions [$\text{Cu1}\cdots\text{Cu1}^{\text{iv}} = 3.6104$ (5) Å; symmetry code: (iv) $2 - x, 1 - y, 1 - z$], as well as unprecedented bridging of the heterometallic $\text{Cu}^{\text{I}}/\text{V}^{\text{IV}}$ pair [$\text{Cu1}\cdots\text{V1} = 3.4174$ (5) Å] (Fig. 1). Thus, the triazole and oxide bridges are complementary and they act in synergy for the incorporation of the VOF fragment into the $-(\text{VVCuCu})_n-$ polymeric chains. The latter run along the *c* direction and include alternation of the above $\text{Cu}(\mu\text{-tr})_2\text{-Cu}$, $\text{Cu}(\mu\text{-tr})(\mu\text{-O})\text{V}$ and $\text{V}(\mu\text{-F})_2\text{V}$ fragments [$\text{V1}\cdots\text{V1}^{\text{iii}} = 3.3367$ (7) Å; symmetry code: (iii) $2 - x, 1 - y, -z$], whereas the double functionality of the bis(triazole) linkers allows propagation of this geometry in two other directions. Recently, we have demonstrated the utility of combining triazole and oxide bridging for the design of metal oxide-organic frameworks (Lysenko *et al.*, 2010).

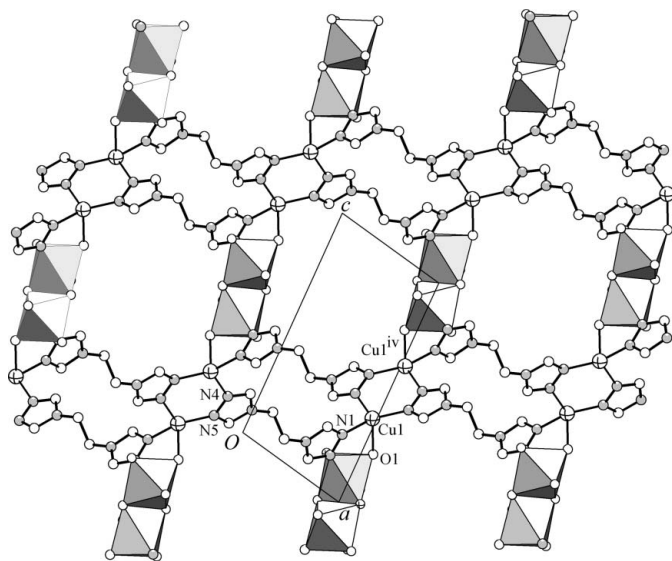
The entire three-dimensional connectivity in (I) may be best described in terms of a primitive cubic framework (NaCl) composed of organic and oxyfluoride links. Thus, the Cu^{I} ions


Figure 2

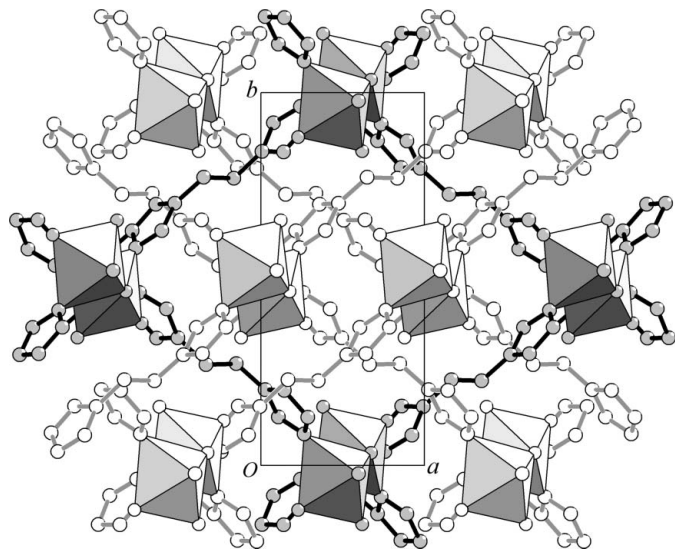
The copper(I)-bis(triazole) subtopology in the structure of (I), in the form of the planar square-grid net supported by the dinuclear nodes. N atoms are shaded grey and the paler bonds indicate the location of the $[\text{V}_2\text{O}_2\text{F}_6]^{2-}$ moieties, which reside above and below the layer plane. [Symmetry codes: (iv) $2 - x, 1 - y, 1 - z$; (v) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.]

and bis(triazole) ligands afford a distinct subtopology of the structure, which exists in the form of a two-dimensional square-grid net parallel to $(\bar{1}03)$ (Fig. 2). The net nodes are sustained by characteristic $(\text{tr})\text{Cu}(\mu\text{-tr})_2\text{Cu}(\text{tr})$ dimers, which themselves typically dominate self-assembly in such systems involving either monofunctional (Drabent *et al.*, 2003) or bitopic triazole ligands (Habib, Hoffmann, Hoppe, Steinfeld & Janiak, 2009). These layers are stacked on top of one another, separated by 11.2220 (16) Å, and are interconnected by inorganic $[\text{V}_2\text{O}_2\text{F}_6]^{2-}$ units acting as pillars which expand the structure in the third dimension (Fig. 3). For the accommodation of such pillaring with building blocks on the two axial sides of the layer, the available functionality at the $\text{Cu}_2(\text{tr})_4$ nodes includes unsaturated coordination positions at the Cu^{I} ions in combination with uncoordinated triazole N atoms. This case perfectly complements the bonding preferences of the coordinatively unsaturated $[\text{V}_2\text{O}_2\text{F}_6]^{2-}$ blocks and enables a double interaction ($\text{Cu}-\text{O}$ and $\text{V}-\text{N}$) between the counterparts.

The resulting three-dimensional array is open since it contains channels of *ca* 6.0×6.5 Å (calculated using PLATON; Spek, 2009) running along the *c* direction, while the porosity of the structure is eliminated by the interpenetration of three identical frameworks (Fig. 4). This is a relatively rare threefold class Ia interpenetration, where equivalent nets are related by a single translation vector (Blatov *et al.*, 2004). Close interaction between the interpenetrating frameworks occurs by means of weak $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonding, involving the terminal fluoride ligands and the CH groups of the triazole groups, with the shortest $\text{C}\cdots\text{F}$ separation being only 2.803 (2) Å (Table 2).


Figure 3

A projection on the *ac* plane showing the mode of interconnection of the copper(I)-bis(triazole) layers (which are orthogonal to the drawing plane) by $[V_2O_2F_6]^{2-}$ pillars (shown as polyhedra). H atoms have been omitted for clarity. [Symmetry code: (iv) $2 - x, 1 - y, 1 - z$.]


Figure 4

The interpenetration of three topologically identical three-dimensional frameworks in the structure of (I), shown in projection on the *ab* plane. A single framework is shaded grey and marked with black bonds.

In conclusion, our findings suggest a flexible approach for the development of hybrid heterometallic frameworks incorporating metal oxyfluoride units. The utility of triazole ligands for the concerted organic/oxide bridging of Cu^I and V^{IV} ions provides a new design tool for the integration of organic and inorganic counterparts, which could find wider application in the synthesis of functionalized MOF materials.

Experimental

1,2-Bis(1,2,4-triazol-4-yl)ethane (*tr*₂eth) was prepared in 65% yield by reacting ethylenediamine (1.50 g, 1.67 ml, 25.0 mmol) and di-

methylformamide azine (8.87 g, 62.5 mmol) in boiling xylene (12 ml) in the presence of $TsOH \cdot H_2O$ (0.38 g, 2.0 mmol) as catalyst. Complex (I) was prepared under hydrothermal conditions starting with V_2O_5 and 48% HF solution. In a typical reaction, $Cu(OAc)_2 \cdot H_2O$ (19.9 mg, 0.10 mmol), *tr*₂eth (16.4 mg, 0.10 mmol), V_2O_5 (18.1 mg, 0.10 mmol), aqueous HF (100 μ l) and water (5 ml) were added to a Teflon vessel, which was placed in a steel bomb and heated to 448 K for 24 h. The mixture was then cooled slowly to room temperature over a period of 60 h and afforded pale-brown crystals of (I) (yield 13.4 mg, 38%).

Crystal data

$[Cu_2V_2F_6O_2(C_6H_8N_6)_2]$
 $M_r = 703.33$
 Monoclinic, $P2_1/n$
 $a = 6.1630$ (6) Å
 $b = 13.7698$ (10) Å
 $c = 12.4856$ (11) Å
 $\beta = 101.370$ (8)°

$V = 1038.77$ (16) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 2.99$ mm⁻¹
 $T = 213$ K
 $0.15 \times 0.12 \times 0.12$ mm

Data collection

Stoe IPDS diffractometer
 Absorption correction: numerical
 [*X-RED* (Stoe & Cie, 2001) and
X-SHAPE (Stoe & Cie, 1999)]
 $T_{min} = 0.663$, $T_{max} = 0.716$

8977 measured reflections
 2499 independent reflections
 2157 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.068$
 $S = 1.02$
 2499 reflections

163 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.66$ e Å⁻³
 $\Delta\rho_{min} = -0.47$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—N5 ⁱ	1.9525 (16)	V1—F1	1.8874 (14)
Cu1—N1	2.0007 (16)	V1—F2	1.8928 (13)
Cu1—N4 ⁱⁱ	2.0768 (18)	V1—F3	2.0017 (13)
Cu1—O1	2.1979 (15)	V1—F3 ⁱⁱⁱ	2.1192 (12)
V1—O1	1.6275 (15)	V1—N2	2.1929 (17)
N5 ⁱ —Cu1—N1	139.07 (7)	O1—V1—F3 ⁱⁱⁱ	167.19 (7)
N5 ⁱ —Cu1—N4 ⁱⁱ	113.20 (7)	F1—V1—F3 ⁱⁱⁱ	86.41 (5)
N1—Cu1—N4 ⁱⁱ	103.15 (7)	F2—V1—F3 ⁱⁱⁱ	90.19 (6)
N5 ⁱ —Cu1—O1	105.62 (7)	F3—V1—F3 ⁱⁱⁱ	71.90 (5)
N1—Cu1—O1	84.41 (6)	O1—V1—N2	87.30 (7)
N4 ⁱⁱ —Cu1—O1	101.04 (7)	F1—V1—N2	86.76 (6)
O1—V1—F1	103.23 (7)	F2—V1—N2	172.91 (7)
O1—V1—F2	98.48 (7)	F3—V1—N2	93.68 (6)
F1—V1—F2	87.91 (7)	F3 ⁱⁱⁱ —V1—N2	84.82 (6)
O1—V1—F3	98.61 (7)	V1—F3—V1 ⁱⁱⁱ	108.10 (5)
F1—V1—F3	158.15 (6)	V1—O1—Cu1	125.94 (8)
F2—V1—F3	89.53 (6)		

Symmetry codes: (i) $x + \frac{3}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 2, -y + 1, -z$.

All H atoms were located in difference Fourier maps and then refined as riding, with aromatic C—H = 0.94 Å and methylene C—H = 0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1...F1 ^{iv}	0.94	2.23	2.999 (2)	138
C2—H2...F1 ^v	0.94	2.18	2.994 (2)	144
C4—H4...F2 ^v	0.94	1.97	2.803 (2)	147

Symmetry codes: (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3051). Services for accessing these data are described at the back of the journal.

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