Synthesis and characterization of a novel oxo-disulfidotetravanadate(V) anion with a bridging tetrasulfido ligand $[\{V(O)(S_2)_2\}_2(\mu^2\text{-}S_4)\{V(O)(S_2)_2\}_2]^{6-}$

Corine Simonnet-Jégat,[a] Stéphane Delalande,[a] Sabine Halut,[b] B. Marg[c] and Francis Sécheresse*[a]

[a] *Laboratoire d'Electrochimie et Chimie des Solides Inorganiques, lecsi, EP CNRS 0067, Université de Versailles, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France*

[b] *Laboratoire de Chimie des Métaux de Transition, URA CNRS 419, Université Pierre et Marie Curie, 75252 Paris Cedex 05, Paris, France*

[c] *Fakultät für Chemie, Universität Bielefeld, Postfach 100131, 33501 Bielefeld, Germany*

$NH_4[VO_3]$ reacts with aqueous polysulfide solutions in the presence of 4,4′-bipyridine to yield the tetranuclear anion $[V_4S_{20}O_4]^{6-}$ which contains four bipyramids connected *via* a zigzag S_4^{2-} bridge.

Vanadium–sulfur compounds have been studied for their relevance to coordination chemistry,[1–7] including comparisons with Mo–S and W–S species, bioinorganic chemistry,[8,9] and industrial catalytic processes.[10,11] The vanadyl ions $[VO]^{2+}$ present in crude oils transform under hydrodesulfuration conditions into polymeric vanadium sulfides which are responsible for the decrease of the activity of the catalyst.[10,11] In vanadium-containing nitrogenase, the metal centre is postulated to be located in a sulfur environment which has led to the development of chemistry of synthetic models. Our recent efforts have been focused on the characterization of tungsten and vanadium compounds present as soluble species in sulfur-rich media, and likely to be extracted by addition of a chelating agent[2] or by a template effect as described here.

This communication reports the preparation† and crystal structure‡ of a new sulfur-rich tetranuclear compound $[NH_4]_6[V_4S_{20}O_4]\cdot 5bpy\cdot 7H_2O$ **1** (bpy = 4,4′-bipyridine) obtained in moderate yield (40%) as red-brown crystals by reaction of solid $NH_4[VO_3]$ with an aqueous solution of ammonium polysulfides in the presence of 4,4′-bipyridine acting as a solid-state template reagent. Compound **1** is air-stable and slightly soluble in aqueous dilute alkaline media. The V=O and S–S stretching vibrations are found in the IR spectra as strong bands at 918 and 528 cm^{-1}, respectively.

The molecular structure of the tetranuclear anion $[V_4S_{20}O_4]^{6-}$ is shown in Fig. 1. The overall arrangement of **1** consists of a chain of two $\{V_2S_8O_2\}^{2-}$ subunits connected to each other by a zigzag S_4^{2-} tetrasulfide bridge. Each subunit contains two vanadium(V) ions in an approximate pentagonal-bipyramidal environment. The equatorial plane of each bipyramid of the subunit is defined by two η^2-S_2^{2-} ligands and a sulfur bridging atom shared as a common equatorial site. One of the axial positions is occupied by a terminal oxo ligand and the other by an intramolecular weakly bonded sulfur. The intramolecular V–S distances are long [*e.g.* V(1)–S(8) 2.905(4) Å] as observed in structurally related molybdenum[12] and tungsten compounds.[13–15] These separations correspond to a bonding distance comparable to the sum of the van der Waals radii of vanadium (2.43 Å)[19] and sulfur (2.12 Å).[19] The vanadium atoms are displaced by 0.47 Å from their equatorial mean planes towards the oxo ligand. All the S–S distances, including those in the tetrasulfido bridging ligand, lie in the region 2.03–2.06 Å as observed for the majority of disulfido-containing compounds. So far, this structure represents the first example of two pyramidal metallic subunits connected through a tetrasulfido ligand, with the vanadium atoms separated by 7.78 Å. The most closely structurally related compounds are $[Mo_4O_4S_{18}]^{2-}$,[12,16] isolated from non-aqueous media, and $[Nb_4Se_{22}]^{6-}$ prepared *via* solid-state methods;[17] both contain an η^1,η^1-S_2^{2-} bridging ligand rather than the unusual linear S_4^{2-} bridge present in **1**. Another feature of **1** is that it can be isolated as single crystals only in the presence of additional neutral 4,4′-bipyridine (5 bpy per anion), as solvent of crystallisation (closest V···N distance 4.97 Å), stacked with the tetranuclear anion, and acting as a lattice template molecule. A view of the packing is given in Fig. 2 showing the extensive hydrogen bonding in the crystals. Three types of hydrogen-bonding interactions are observed; (*i*) between water molecules, (*ii*) between bipyridine and water and (*iii*) between the V(3)–O(3) group and a water molecule. This

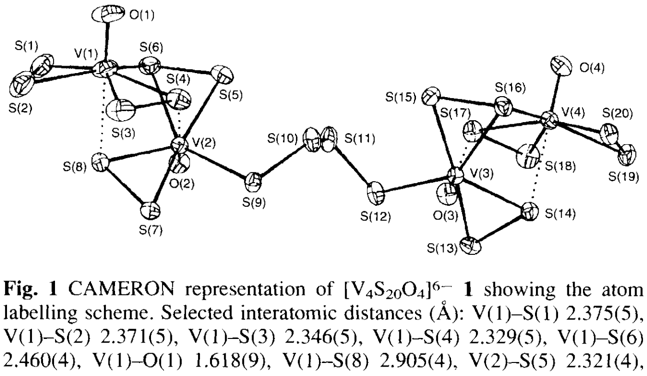

Fig. 1 CAMERON representation of $[V_4S_{20}O_4]^{6-}$ **1** showing the atom labelling scheme. Selected interatomic distances (Å): V(1)–S(1) 2.375(5), V(1)–S(2) 2.371(5), V(1)–S(3) 2.346(5), V(1)–S(4) 2.329(5), V(1)–S(6) 2.460(4), V(1)–O(1) 1.618(9), V(1)–S(8) 2.905(4), V(2)–S(5) 2.321(4), V(2)–S(6) 2.402(4),V(2)–S(7) 2.364(4), V(2)–S(8) 2.335(4), V(2)–S(9) 2.415(4), V(2)–O(2) 1.617(8), V(2)–S(4) 2.914(4), S(1)–S(2) 2.045(6), S(3)–S(4) 2.051(5), S(5)–S(6) 2.044(5), S(7)–S(8) 2.043(4), S(9)–S(10) 2.047(5), S(10)–S(11) 2.038(5), S(11)–S(12) 2.050(5).

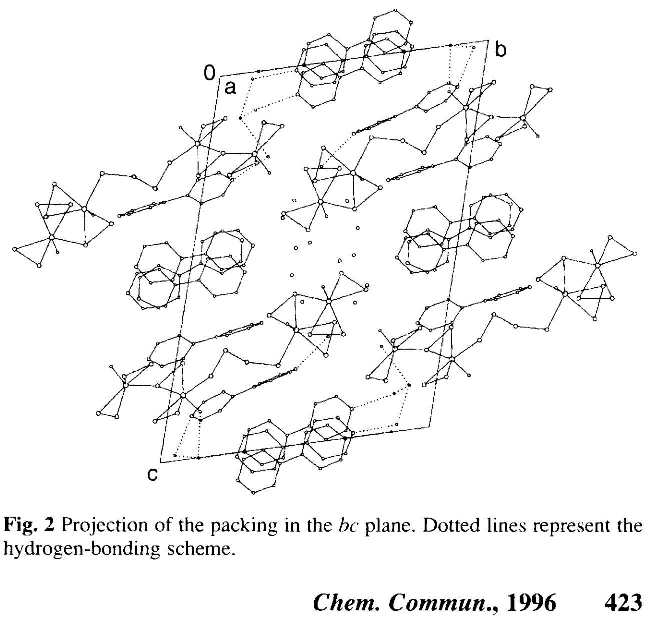

Fig. 2 Projection of the packing in the *bc* plane. Dotted lines represent the hydrogen-bonding scheme.

hydrogen bonding establishes the role of the bpy in the crystallization of compound **1**.

The ^{51}V NMR spectrum of **1** in D_2O solution exhibits two signals at δ -475 and -414, as expected for two sets of two inequivalent vanadium atoms, V(1),V(4) and V(2),(3), respectively. The values of chemical shifts are in accord with those previously reported for oxothiovanadates.[3]

Footnotes

† $NH_4[VO_3]$ (0.235 g, 2 mmol) was dissolved in a solution of $(NH_4]S_x$ obtained by bubbling H_2S in 25 ml of commercial 25% ammonia in the presence of solid sulfur (0.350 g, 11 mmol). To the resultant red solution was added 4,4′-bipyridine (0.350 g, 2.5 mmol) and single crystals suitable for X-ray determination were obtained after the solution was kept at room temperature for several days.

‡ *Crystal data*: red-brown prisms of **1** are triclinic, space group $P\bar{1}$, with a = 11.197(2), b = 16.544(3), c = 23.609(2) Å, α = 104.06(1), β = 96.80(1), γ = 102.27(1)°, U = 4078(24) Å^3, μ(Mo-Kα) = 9.81 cm^{-1}, Z = 2. Single-crystal X-ray diffraction data were collected at room temperature on a Nonius CAD4 four-circle diffractometer. Empirical absorption correction was applied by using the DIFABS program;[18] 9981 unique reflections of which 4482 with $I > 3\sigma(I)$ were used; the structure was solved by direct methods and refined by full-matrix least-squares procedures[19] to R = 0.045 and R_w = 0.049.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No.1.

References

1 S. L. Castro, J. D. Martin and G. Christou, *Inorg. Chem.*, 1993, **32**, 2978.
2 C. Simonnet-Jégat, F. Robert and F. Sécheresse, *Transition Met. Chem.*, 1994, **19**, 379.
3 S. C. Sendlinger, J. R. Nicholson, E. B. Lobrovsky, J. C. Huffman, D. Rehder and G. Christou, *Inorg. Chem.*, 1993, **32**, 204.
4 D. D. Heinrich, K. Folting, J. C. Huffman, J. G. Reynolds and G. Christou, *Inorg. Chem.*, 1991, **30**, 300.
5 G. Christou, D. D. Heinrich, J. K. Money, J. R. Rambo, J. C. Huffman and K. Folting, *Polyhedron*, 1989, **8**, 1723.
6 J. K. Money, J. R. Nicholson, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1986, **25**, 4074.
7 T. R. Halbert, L. L. Hutchings, R. Rhodes and E. I. Stiefel, *J. Am. Chem. Soc.*, 1986, **108**, 6437.
8 A. Müller, K. Schneider, J. Erfkamp, V. Wittneben, E. Diemann and N. A. Eaton, *Naturwissenschaften*, 1988, **75**, 625.
9 R. R. Eady, *Polyhedron*, 1989, **8**, 1695; B. F. Smith, *Nature (London)*, 1987, **325**, 372.
10 P. C. H. Mitchell, C. E. Scott, J. P. Bonnelle and J. G. Grimblot, *J. Chem. Soc., Faraday Trans.*, 1985, **81**, 1047.
11 F. Lin, R. L. Beddoes, D. Collinson and F. E. Mabbs, *J. Chem. Soc., Chem. Commun.*, 1993, 496.
12 A. I. Hadjikyriacou and D. Coucouvanis, *Inorg. Chem.*, 1989, **28**, 2177.
13 J. M. Manoli, C. Potvin and F. Sécheresse, *Inorg. Chem.*, 1987, **26**, 340.
14 P. K. Chakrabarty, S. Bhattacharya, C. G. Pierpont and R. Bhattacharyya, *Inorg. Chem.*, 1992, **31**, 3573.
15 C. Simonnet-Jégat, N. Jourdan, F. Robert, C. Bois and F. Sécheresse, *Inorg. Chim. Acta*, 1994, **216**, 201.
16 Z. Nianyong, D. Shaowu, W. Xintao and L. Jiaxi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1.
17 S. Schreiner, L. E. Aleandri, D. Kang and J. A. Ibers, *Inorg. Chem.*, 1989, **28**, 392.
18 N. Walker, and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
19 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS, An Advanced Crystallographic Program System, Chemical Crystallographic Laboratory, University of Oxford, 1989.

Received, 25th October 1995; Com. 5/07038D