

Communication

Synthesis and characterization of the mononuclear oxovanadium–disulphide compound $[\text{N}(\text{Bu})_4][\text{V}(\text{O})(\text{S}_2)_2\text{bipy}]$

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Summary

The reaction of NH_4VO_3 with S_2^{2-} in ammonia in the presence of 2,2'-bipyridine (bipy) and $[\text{N}(\text{Bu})_4]\text{Br}$ gives the mononuclear compound $[\text{N}(\text{Bu})_4][\text{V}(\text{O})(\text{S}_2)_2\text{bipy}]$ (1) isolated at room temperature in crystalline form. The X-ray crystal structure determination shows that the vanadium(V) centre is ligated by four sulphur atoms and a nitrogen atom of the bipy ligand forming the equatorial plane of pentagonal bipyramid, an oxygen and the remaining nitrogen atom of the bipy occupying the two apices of the bipyramid.

Introduction

Transition metal sulphur compounds have been extensively studied in recent years for their relevance to coordination chemistry, catalysis and bioinorganic chemistry. Part of our interest in thiotungstates has focused on their protonation⁽¹⁾, in order to isolate intermediates and transient species before precipitation of the polymeric amorphous WS_3 . Recently we succeeded in extracting from acidified solutions of WS_4^{2-} the molecular complex $[\text{W}(\text{O})(\text{S}_2)_2\text{bipy}]^{(2)}$, which was also obtained via a different route in the absence of acid⁽³⁾. The geometry of the pyramidal $\text{W}(\text{O})(\text{S}_2)_2$ fragment led us to extend our research to vanadium, which is known to exhibit a similar but fully oxygenated environment⁽⁴⁾.

Experimental

All chemicals and solvents were used as purchased without further purification. I.r. spectra were recorded on an FTIR Nicolet Magna 550 instrument. The products were sampled as KBr pellets. The ^{51}V n.m.r. spectrum (78.94 MHz) was obtained on a Bruker (AC-300) spectrometer using 5 mm diameter sample tubes. Chemical shifts were referenced to external VOCl_3 (0 p.p.m.). Chemical analyses were performed by the Service d'Analyses du CNRS, Solaize, France.

$[\text{NBu}_4][\text{V}(\text{O})(\text{S}_2)_2\text{bipy}]$ (1)

Addition of NH_4VO_3 (0.024 g, 0.2 mmol) and 2,2'-bipyridine (bipy) to a freshly prepared solution of tetrabutylammonium polysulphides gave a dark red solution. After standing at room temperature for 2 weeks, dark purple crystals (1), suitable for X-ray analysis, were collected (yield 60–70%).

I.r.: 3100(w), 3070(w), 3046(w), 3025(w), 3013(sh), 2992(vw), 2960(m), 2938(sh), 2871(m), 1596(m), 1571(vw), 1561(vw), 1480(m), 1471(m), 1441(s), 1417(w), 1383(m), 1348(vw), 1312(m), 1284(w), 1250(vw), 1164(m), 1151(m), 1117(vw), 1105(vw), 1076(vw), 1056(w), 1041(vw), 1019(m), 975(vw), 929(vs), 896(m), 875(sh), 776(s), 731(m), 651(vw), 631(vw), 535(s), 422(vw), 380(m), 358(m), 353(sh).

^{51}V n.m.r. (CH_3CN $\text{C}_3\text{D}_6\text{O}$, 1:1). $\delta = -398$ p.p.m.

$[\text{NH}_4][\text{V}(\text{O})(\text{S}_2)_2\text{bipy}]$ (2)

By a similar route, thin crystals of $[\text{NH}_4][\text{V}(\text{O})(\text{S}_2)_2\text{bipy}]$ (2) were obtained from a solution of $(\text{NH}_4)_2\text{S}_x$.

Found: C, 31.4; H, 3.5; N, 10.9; S, 33.5; V, 13.1; $\text{C}_{10}\text{H}_{12}\text{N}_3\text{S}_4\text{OV}$ calcd: C, 32.5; H, 3.3; N, 11.4; S, 34.7; V, 13.8%.

I.r.: 3139(br), 3021(vw), 1595(m), 1571(vw), 1562(vw), 1487(w), 1469(m), 1440(s), 1396(m), 1307(m), 1167(sh), 1153(w), 1104(vw), 1072(vw), 1058(vw), 1041(vw), 1022(w), 912(s), 802(w), 760(vs), 729(m), 651(w), 631(w), 535(s), 422(w), 381(m), 359(m), 353(sh).

Crystallographic data for (1)

$\text{C}_{26}\text{H}_{44}\text{N}_3\text{S}_4\text{OV}$, fw = 593.84 g mol⁻¹, monoclinic, space group $\text{P}2_1/a$, $a = 12.257(2)$ Å, $b = 14.479(3)$ Å, $c = 17.999(3)$ Å, $\beta = 106.78(2)^\circ$, $V = 3058$ Å³, $Z = 4$, $\mu = 5.99$ cm⁻¹, $D_c = 1.29$ g cm⁻³, $F(000) = 1264$, temperature = 20°C, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, Enraf-Nonius CAD-4 diffractometer, $\omega/2\theta$ scan, scan width $0.8^\circ + 0.345 \tan \theta$, θ -limits 1–25°. A total of 5366 independent reflections were collected, of which 3445 were used ($|F_o|^2 > 3\sigma|F_o|^2$). The structure was solved by direct methods using the SHELX86 programme⁽⁵⁾ and subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically (318 variables). Hydrogen atoms were located in the difference electron density map and their positions refined. The final refinement converged for $R(w) = 0.036(0.037)$.

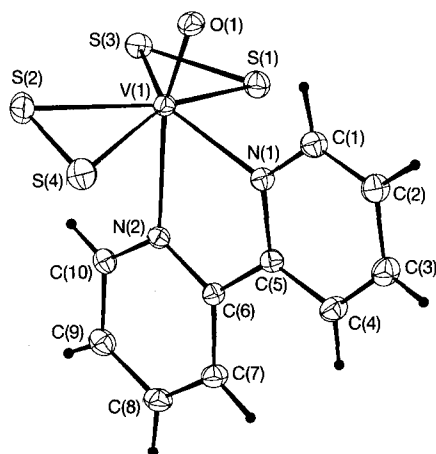
Results and discussion

The geometry of the monoanion (1) represented in Figure 1 can be viewed as a distorted pentagonal bipyramid with two asymmetrically bonded persulphido groups (mean V—S, 2.42 and 2.34 Å) (Table 1), and one nitrogen atom [V—N, 2.156 (3) Å] from the bipy ligand forming the pentagonal plane. The apical positions are occupied by the remaining nitrogen of the bipy and by a terminal oxygen. The vanadium atom is located 0.33 Å above the equatorial S(1)S(2)S(3)S(4)N(1) plane. The angle between the equatorial plane and the planar bipy

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Table 1. Selected interatomic distances (Å) angles (°) for compound (1).

Bond lengths			
V(1)—S(1)	2.425(1)	V(1)—S(2)	2.337(1)
V(1)—S(3)	2.347(1)	V(1)—S(4)	2.417(1)
V(1)—O(1)	1.609(2)	V(1)—N(1)	2.156(3)
V(1)—N(2)	2.278(3)	S(2)—S(4)	2.042(2)
S(1)—S(3)	2.046(1)		
Bond angles			
S(2)—V(1)—S(1)	134.20(4)	S(3)—V(1)—S(1)	50.74(4)
S(3)—V(1)—S(2)	85.17(4)	S(4)—V(1)—S(1)	160.95(4)
S(4)—V(1)—S(2)	50.84(4)	S(4)—V(1)—S(3)	135.03(4)
O(1)—V(1)—S(1)	97.59(9)	O(1)—V(1)—S(2)	103.68(9)
O(1)—V(1)—S(3)	101.51(9)	O(1)—V(1)—S(4)	98.19(9)
N(1)—V(1)—S(1)	85.19(8)	N(1)—V(1)—S(2)	133.36(8)
N(1)—V(1)—S(3)	135.04(8)	N(1)—V(1)—S(4)	83.79(8)
N(1)—V(1)—O(1)	91.5(1)	N(2)—V(1)—S(1)	80.75(7)
N(2)—V(1)—S(2)	89.00(7)	N(2)—V(1)—S(3)	90.50(7)
N(2)—V(1)—S(4)	81.05(7)	N(2)—V(1)—O(1)	163.1(1)
N(2)—V(1)—N(1)	71.6(1)	S(4)—S(2)—V(1)	66.62(4)
S(3)—S(1)—V(1)	62.64(4)	S(2)—S(4)—V(1)	62.54(4)
S(1)—S(3)—V(1)	66.62(4)		

**Figure 1.** Representation of the anion of compound (1) showing the pyramidal environment of vanadium (50% ellipsoids).

ligand containing the vanadium atom (mean deviation 0.08 Å) is 91.4°. This overall arrangement is quite similar to that observed for the molecular $[\text{W}(\text{O})(\text{S}_2)_2\text{phen}]$, $[\text{W}(\text{O})(\text{S}_2)_2\text{bipy}]$ ⁽²⁾ and $[\text{Mo}(\text{O})(\text{S}_2)_2\text{bipy}]$ ⁽³⁾, and for the monoanion $[\text{V}(\text{O})(\text{O}_2)_2\text{bipy}]^-$ ⁽⁴⁾. The i.r. spectrum shows absorptions at 929 cm^{-1} , characteristic of the V=O stretching mode, and at 535 cm^{-1} attributed to the S—S group. In the far-i.r. region, absorptions between 421–353 cm^{-1} were observed which could be assigned to V—S and V—N bonds. The ⁵¹V n.m.r. spectrum shows a signal at –398 p.p.m. which is in agreement with the observations of Christou and coworkers⁽⁶⁾, who reported that vanadyl compounds containing nitrogen ligands are shielded with respect to VOCl_3 (–500 to –700 p.p.m.). The smaller chemical shift of compound (1) compared to Christou's compounds probably results from the presence of persulphido ligands, as observed for $[\text{VO}(\text{OH})(\text{S}_2\text{CNEt}_2)_2]$ ⁽⁶⁾ (–468 p.p.m.) which also contains sulphido ligands.

Note added in proof

Since this work was submitted to *Transition Metal Chemistry*, a related work has appeared in *Inorganic Chemistry*⁽⁷⁾.

Supplementary material

The following tables are available from the authors or from the Cambridge Crystallographic Data Centre: crystallographic data (Table S1), fractional atomic coordinates (Table S2), anisotropic thermal parameters (Table S3), interatomic distances and angles (Table S4), fractional atomic coordinates for hydrogen atoms (Table S5), interatomic distances for hydrogen atoms (Table 6), bond angles for hydrogen atoms (Table S7), mean-plane equations with V-deviations (Table S8), and observed and calculated structure factors for (1) (Table S9).

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