Preparation, *X*-Ray Crystal Structure, and Properties of $[V(S_2)_2(terpy)]$:† Intramolecular Coupling of the Sulphide Ligands of $[VS_4]^{3-}$

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The reaction of $[NH_4]_3[VS_4]$ with 2,2′:6′,2″-terpyridine (terpy) in methanol gives the novel vanadium compound $[V(S_2)_2(terpy)]$, the crystal structure of which has been determined by *X*-ray diffraction. Its formation is probably the simplest example of intramolecular coupling of sulphide ligands in a tetrathiometalate anion.

From the reaction between $[Cl_3Fe_3(\mu_3\text{-}S)_4V(dmf)_3]^-$ (dmf = *N,N*-dimethylformamide) and 2,2′:6′,2″-terpyridine (terpy) we obtained as a minor product black crystalline needles which single-crystal *X*-ray analysis showed to be $[V(S_2)_2(terpy)]$, Figure 1. A brief description of the structure is given below together with some of the physical properties of this new molecule (Table 1).

Results and Discussion

We sought a rational route to $[V(S_2)_2(terpy)]$ and found that reaction (1) afforded the desired product in moderate yield (see Experimental section).

$$[NH_4]_3[VS_4] \xrightarrow{MeOH,\ terpy} [V(S_2)_2(terpy)] \qquad (1)$$

The reaction of a tetrathiometalate with a pyridine is novel and the formation of the bis-disulphide represents perhaps the simplest example of intramolecular sulphide ligand coupling, equation (2): neither is S lost from the co-ordination sphere[1]

$$[MS_4]^{n-} + L \xrightarrow{-ne^-} [M(S_2)_2L] \qquad (2)$$

nor do dimeric products[2,3] result from the so-called 'induced internal redox process'.[3] The oxidising agent is probably proton (available from the ammonium counter ions).

Preliminary studies show $[V(S_2)_2(terpy)]$ to be a reactive species, particularly towards electrophiles. For example, the complex reacts in dmf with acetyl chloride and we have isolated a crystalline product which we are presently characterising.

The ease of its synthesis from readily available starting materials, its evident redox chemistry (see Table 1), and the little that we know about its reactivity suggest that $[V(S_2)_2(terpy)]$ might be a useful compound for developing the range of V–S chemistry, a topic of some current interest.[4]

Description of the Crystal and Molecular Structure.—The crystal contains discrete $[V(S_2)_2(terpy)]$ molecules. In the complex molecule (Figure 1), the V atom is co-ordinated in a distorted pentagonal-bipyramidal arrangement, with the almost planar terpy ligand lying in meridional mode so that its two outer N atoms occupy the axial sites of the bipyramid, and the centre N atom is in one of the equatorial sites. The two disulphide ligands lie in the equatorial plane such that the overall symmetry in the molecule approaches *mm*2.

Table 1. Some physical properties of $[V(S_2)_2(terpy)]$

M.p. (°C)	210 (decomp.)
ν(S–S)/cm^{-1}	530, 555
$\lambda_{max.}$/nm^a	314 (28 100), 326 (9 490), 382 (5 180), 634 (640)
Redox potentials^b	
$^1E^{\circ c}$	−1.01
$^2E^{\circ}$ (at −50 °C)^c	−1.64
$E_p^{\text{irreversible}\ d}$	+0.31

^{a} ε/dm^3 mol^{-1} cm^{-1} given in parentheses. ^{b} Determined by cyclic voltammetry at a Pt electrode in dmf containing 0.2 mol dm^{-3} $[NBu_4][BF_4]$. Values (V) relative to saturated calomel electrode. ^{c} Reduction; successive one-electron processes. ^{d} Oxidation; two-electron step.

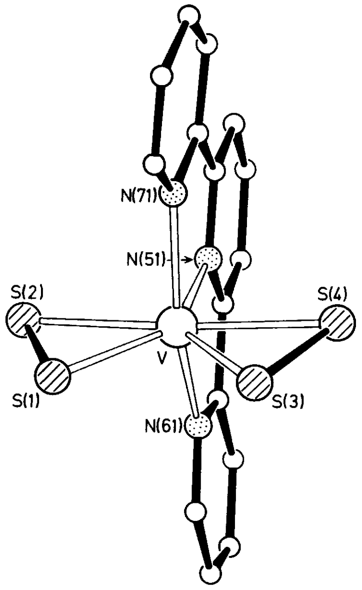

Figure 1. View of the complex molecule $[V(S_2)_2(terpy)]$ with the principal atoms labelled

The V–S distances are not equal; the longer bonds [2.438(1) and 2.448(1) Å, Table 2] are virtually opposite each other, S(2)–V–S(4) 171.6°, whilst the shorter bonds [2.239(1) and 2.313(1) Å] lying adjacent in the equatorial plane are themselves quite different in length, and have no bond directly opposite them on the V atom. Inequalities, to varying degrees, have been noted in some (but not all) other disulphide complexes. In the seven-co-ordinate complexes $[\{MoS_5(\eta\text{-}C_5Me_5)\}_2]$[5] and $[MoO(S_2)_2(mtox)]^{2-}$ (mtox = monothio-oxalate),[6] where the arrangements of pairs of disulphide ligands are very similar to those in our crystal, and in $[WS(S_2)(S_2CNBu^i{}_2)_2]$,[1] where the

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† Bis(disulphido)(2,2′:6′,2″-terpyridine-*NN′N″*)vanadium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Molecular dimensions [bond lengths (Å) and angles (°)], with estimated standard deviations in parentheses; those for angles about the V and S atoms which are <0.05° are not quoted

(*a*) About the V atom							
V–S(1)	2.313(1)	V–S(3)	2.239(1)	V–N(51)	2.083(2)	V–N(71)	2.118(2)
V–S(2)	2.438(1)	V–S(4)	2.448(1)	V–N(61)	2.112(2)		
S(1)–V–S(2)	50.9	S(1)–V–N(51)	138.2(1)	S(2)–V–N(61)	88.4(1)	S(2)–V–N(71)	90.7(1)
S(1)–V–S(3)	86.7	S(2)–V–N(51)	87.4(1)	S(3)–V–N(61)	99.8(1)	S(3)–V–N(71)	100.6(1)
S(2)–V–S(3)	137.4	S(3)–V–N(51)	135.2(1)	S(4)–V–N(61)	88.7(1)	S(4)–V–N(71)	87.9(1)
S(1)–V–S(4)	137.6	S(4)–V–N(51)	84.2(1)	N(51)–V–N(61)	75.2(1)	N(51)–V–N(71)	75.3(1)
S(2)–V–S(4)	171.6	S(1)–V–N(61)	102.2(1)	S(1)–V–N(71)	100.0(1)	N(61)–V–N(71)	150.5(1)
S(3)–V–S(4)	51.0						
(*b*) In the ligands							
S(1)–S(2)	2.043(1)	C(53)–C(54)	1.382(4)	N(61)–C(66)	1.353(3)	N(71)–C(76)	1.346(3)
S(3)–S(4)	2.025(1)	C(54)–C(55)	1.371(4)	C(62)–C(63)	1.381(4)	C(72)–C(73)	1.392(4)
N(51)–C(52)	1.346(3)	C(55)–C(56)	1.385(4)	C(63)–C(64)	1.374(4)	C(73)–C(74)	1.372(4)
N(51)–C(56)	1.352(3)	C(56)–C(72)	1.471(4)	C(64)–C(65)	1.375(4)	C(74)–C(75)	1.370(4)
C(52)–C(53)	1.387(4)	N(61)–C(62)	1.358(3)	C(65)–C(66)	1.383(4)	C(75)–C(76)	1.386(4)
C(52)–C(62)	1.471(4)			N(71)–C(72)	1.357(3)		
V–S(1)–S(2)	67.7	C(53)–C(52)–C(62)	126.4(3)	C(62)–N(61)–C(66)	118.1(2)	V–N(71)–C(76)	124.1(2)
V–S(2)–S(1)	61.4	C(52)–C(53)–C(54)	118.8(3)	C(52)–C(62)–N(61)	114.1(2)	C(72)–N(71)–C(76)	118.4(2)
V–S(3)–S(4)	69.8	C(53)–C(54)–C(55)	120.6(3)	C(52)–C(62)–C(63)	123.9(3)	C(56)–C(72)–N(71)	114.3(2)
V–S(4)–S(3)	59.2	C(54)–C(55)–C(56)	118.8(3)	N(61)–C(62)–C(63)	122.0(3)	C(56)–C(72)–C(73)	123.9(2)
V–N(51)–C(52)	119.6(2)	N(51)–C(56)–C(55)	120.5(3)	C(62)–C(63)–C(64)	119.2(3)	N(71)–C(72)–C(73)	121.8(3)
V–N(51)–C(56)	119.4(2)	N(51)–C(56)–C(72)	113.3(2)	C(63)–C(64)–C(65)	119.5(3)	C(72)–C(73)–C(74)	118.9(3)
C(52)–N(51)–C(56)	120.9(2)	C(55)–C(56)–C(72)	126.2(2)	C(64)–C(65)–C(66)	119.2(3)	C(73)–C(74)–C(75)	119.7(3)
N(51)–C(52)–C(53)	120.3(3)	V–N(61)–C(62)	117.7(2)	N(61)–C(66)–C(65)	122.0(3)	C(74)–C(75)–C(76)	119.4(3)
N(51)–C(52)–C(62)	113.3(2)	V–N(61)–C(66)	124.2(2)	V–N(71)–C(72)	117.3(2)	N(71)–C(76)–C(75)	121.9(3)

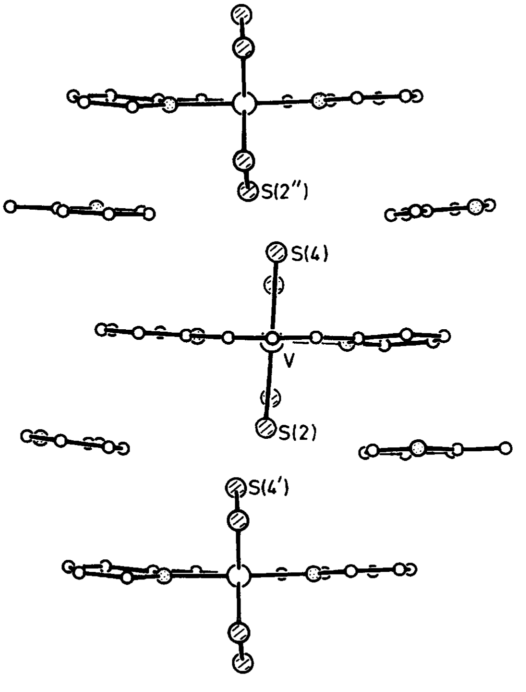

Figure 2. Packing of the molecules of [V(S_2)$_2$(terpy)], showing the stacking of the outer pyridine rings with pyridine rings of neighbouring molecules, and the nearly collinear arrangement of pairs of disulphide ligands

disulphide ligand is in the equatorial plane with a bidentate $S_2CNBu^i_2$ ligand and one S atom of the second $S_2CNBu^i_2$ ligand, differences in the M–S bonds (*ca.* 0.02—0.07 Å) are all rather less than in our molecule (0.125 and 0.209 Å) but all show the same pattern of longer and shorter bonds in the equatorial plane. The S–S bonds in our molecule [2.025(1) and 2.043(1) Å] lie within the range of normal values.

The terpyridyl ligand is under considerable strain; many of the angles in the chelate rings are much reduced from the ideal values of *ca.* 120°, so that the V–N bond lengths approach normal values. The outer, axial V–N bonds are 2.112(2) and 2.118(2) Å. However, the central bond, in the equatorial plane [2.083(2) Å] is shorter than most V–N(pyridine) bonds reported, *e.g.* 2.10(3) Å in [V(bipy)$_3$],[7] 2.189(2) Å in [VCl_2(py)$_4$],[8] and 2.183(3) and 2.192(4) Å in [VCl_2(NSNSN)(py)] (bipy = 2,2′-bipyridine, py = pyridine).[9] The tridentate dipicolinate ligand in [V{$C_5H_3N(COO)_2$-2,6}(NH_2O)(H_2O)O] has a V–N bond of 2.064(3) Å and shows similar strain in its chelate rings as it, too, binds in a meridional conformation.[10]

In our crystal, the molecules are stacked; the outer pyridine rings each have virtually parallel, neighbouring rings approximately 3.3 Å above and below them (Figure 2). In the gaps between the stacks of overlapping rings, the disulphide ligands of adjacent molecules lie in pairs in an almost collinear arrangement; the S(2) ··· S(4′) distance is 3.319(1) Å, considerably less than the sum of van der Waals radii (3.7 Å).

Experimental

The complex [V(S_2)$_2$(terpy)] was prepared from [NH_4]$_3$[VS_4] by reflux under N_2 in methanol with one equivalent of terpy for 24 h; the black product was filtered off (crude yield 50—60%) and recrystallised from dmf–MeOH as green-black needles, overall yield 25%.

Crystal Structure of [V(S_2)$_2$(terpy)].—*Crystal data.* $C_{15}H_{11}N_3S_4V$, M = 412.5, orthorhombic, space group *Pbcn* (no. 60), a = 13.089(3), b = 17.581(2), c = 14.292(3) Å, U = 3 288.9 Å^3, Z = 8, D_c = 1.666 g cm^{-3}, $F(000)$ = 1 672, μ(Mo-K_α) = 10.7 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Table 3. Final fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
V	3 587.3(3)	1 627.0(2)	4 662.5(3)	C(62)	3 672(2)	3 234(2)	3 973(2)
S(1)	2 373.2(6)	822.8(4)	4 027.1(5)	C(63)	3 724(2)	3 847(2)	3 371(2)
S(2)	1 732.9(6)	1 753.9(4)	4 649.1(5)	C(64)	3 777(2)	3 719(2)	2 424(2)
S(3)	4 759.6(6)	831.7(5)	4 074.8(6)	C(65)	3 777(2)	2 984(2)	2 094(2)
S(4)	5 450.4(6)	1 682.1(5)	4 791.2(5)	C(66)	3 723(2)	2 388(2)	2 724(2)
N(51)	3 631(2)	2 627(1)	5 442(1)	N(71)	3 549(2)	1 263(1)	6 074(2)
C(52)	3 645(2)	3 303(2)	4 999(2)	C(72)	3 650(2)	1 804(2)	6 745(2)
C(53)	3 637(3)	3 975(2)	5 508(2)	C(73)	3 746(2)	1 617(2)	7 688(2)
C(54)	3 641(3)	3 936(2)	6 474(2)	C(74)	3 723(2)	865(2)	7 943(2)
C(55)	3 669(2)	3 246(2)	6 920(2)	C(75)	3 601(2)	316(2)	7 272(2)
C(56)	3 655(2)	2 588(2)	6 386(2)	C(76)	3 513(2)	529(2)	6 341(2)
N(61)	3 660(2)	2 506(1)	3 658(2)				

Crystals are air-stable needles, very dark green in colour. One was mounted on a glass fibre and, after preliminary *X*-ray photographic examination, was put on an Enraf-Nonius CAD4 diffractometer (with graphite monochromator) for measurement of accurate cell dimensions (by refinement from the settings of 25 centred reflections having $\theta = 10$—$12°$) and diffraction intensities (to $\theta_{max.} = 25°$). During processing of the intensity data, corrections were made for slight, steady deterioration of the crystal (*ca.* 6.0% overall), Lorentz-polarisation effects and negative intensities (by Bayesian statistical methods). 2 875 Unique reflections [748 with $I < 2\sigma(I)$] were then read into the program SHELX.[11]

The structure was determined from the automatic direct-methods routine EEES,[11] and refined by full-matrix least-squares methods to convergence at $R = 0.048$, $R' = 0.047$ for all data, weighted $w = [\sigma^2(F) + 0.000\,451\,F^2]^{-1}$. Hydrogen atoms were included in the terpyridyl ligand in idealised positions but with independent isotropic thermal parameters. All other atoms were refined anisotropically. A final difference map showed the highest peaks at *ca.* 0.43 e Å^{-3}.

Scattering factors for C, H, N, S, and V atoms were taken from ref. 12; programs for this analysis are listed in Table 4 of ref. 13 and were run on the VAX 11/750 computer at the Glasshouse Crops Research Institute, Littlehampton. Final atomic co-ordinates are given in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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