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Short Communication

The first triangular $V_3S_7^{2+}$ complex. Synthesis and structure of $(Et_4N)[V_3S_7(Me_2dtc)_3]\cdot CH_3CN$

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Abstract

A triangular $V_3S_7^{2+}$ complex $(Et_4N)[V_3S_7(Me_2dtc)_3]\cdot CH_3CN$ has been obtained from a complicated reaction system containing $(NH_4)_3VS_4$ as a starting material. The complex crystallizes in the triclinic, space group $P\bar{1}$ with crystal data: $a=13.027(2)$, $b=13.180(5)$, $c=12.554(4)$ Å, $\alpha=97.00(3)$, $\beta=116.21(2)$, $\gamma=95.28(3)°$, $V=1893.5(5)$ Å^3, $Z=2$, $R=0.043$ and $R_w=0.054$ for 4501 reflections with $I>3\sigma(I)$. The anion $[V_3S_7(Me_2dtc)_3]^-$ is isostructural (exclusive of R groups in the ligand), but not isoelectronic with its Mo analogue $[Mo_3S_7(Et_2dtc)_3]^+$, and has a lower mean oxidation state $(+3\frac{1}{3})$ of vanadium than that observed in $[V_3S_4(edt)_3]^{3-}$. The structural parameters show the identity of three V atoms, implying an electronic delocalization. The ^{1}H NMR spectrum exhibits two types of methyl resonances of the ligand at 10.69 and 8.72 ppm with an intensity ratio of 1:1.

Introduction

The chemistry of vanadium bound to sulfide and sulfur-based ligands (RS^-, ethane-1,2-dithiolate (edt), etc.) has raised considerable interest [1, 2]. Illuminating comparisons between V/S and Mo/S (or W/S) chemistry have promoted the development of an extensive study on V/S chemistry. There are several recent reports [3–6] of trinuclear, triangular clusters of Mo(W) comprising M_3E_4 or M_3E_7 (M = Mo, W; E = S, Se) cores. However, the study on the corresponding V_3 cluster is rare. Only one example, $(Et_4N)_3[V_3S_4(edt)_3]$, has been prepared by Christou and co-workers [7], while the V_3S_7 cluster has not yet been reported in the literature. We have been interested in research on V-containing clusters in which dialkyldithiocarbamates (R_2dtc) exist as the ligand and have obtained $V_2(S_2)_2(Et_2dtc)_4$ [8], $[V_2Cu_2S_4(R_2dtc)_2(PhS)_2]^{2-}$ [9] and $[V_2Ag_2S_4(R_2dtc)_2(PhS)_2]^{2-}$ [9]. Noticing that $[Mo_3S_7(Et_2dtc)_3]^+$ [5] and $M_3Se_7(Et_2dtc)_4$ [4] (M = Mo, W) have been obtained and structurally characterized recently, herein we report the synthesis and structure of the V analogue $(Et_4N)[V_3S_7(Me_2dtc)_3]\cdot CH_3CN$, which is the first example containing a V_3S_7 core and an R_2dtc ligand.

Experimental

Synthesis of $(Et_4N)[V_3S_7(Me_2dtc)_3]\cdot CH_3CN$ (1)

A mixture of $(NH_4)_3VS_4$ (0.6 g, 2.57 mmol), CuCl (0.51 g, 5.14 mmol), PhSNa (0.68 g, 5.14 mmol), Me_2dtcNa (0.74 g, 5.4 mmol) and Et_4NCl (0.86 g, 5.14 mmol) in 100 ml of DMF was stirred for 24 h. The deep brown solution was filtered and concentrated in vacuum. The subsequent careful addition of acetonitrile/acetone produced a large amount of dark red microcrystals, which were collected by filtration as the major product, shown to be the $V_2Cu_2S_4$ cubane-like cluster $(Et_4N)_2[V_2Cu_2S_4(Me_2dtc)_2(PhS)_2]$ [10]. After removing the precipitates which were continuously deposited, the filtrate was stored in a freezer for several weeks. The resulting black crystals were collected by filtration, washed with acetone, and dried in vacuum. Yield is *c.* 3% based on $(NH_4)_3VS_4$ used. *Anal.* Calc. for $C_{19}H_{41}N_5S_{13}V_3$: C, 25.10; H, 4.54; N, 7.70. Found: C, 25.33; H, 4.57; N, 7.56%.

IR spectrum (KBr pellet, cm^{-1}) 354, 442, 553, 986, 1510.

Crystal data and structure determination

A black leaflet crystal of **1** with dimensions 0.8×0.4×0.3 mm was mounted on a glass fiber. Data were collected on a MSC/Rigaku diffractometer with Mo Kα radiation ($\lambda=0.71069$ Å) at 23 ± 1 °C using the ω–2θ mode. The crystal data, intensity collection and structure refinement parameters are listed in Table 1. A total of 6986 reflections was collected, of which 4876 were unique. LP and empirical absorption corrections were applied to the data. The structure was solved by direct methods. Using 431 reflections and 4135 relationships, a total of 32 phase sets was produced. From an E-map, 16 atoms including V and S atoms in the core and M_2dtc groups were located. The remaining atoms were found in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to structure factor calculations but not refined. The struc-

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TABLE 1. Crystallographic data for $(Et_4N)[V_3S_7(S_2CNMe_2)_3]\cdot CH_3CN$

Formula	$C_{19}H_{41}N_5S_{13}V_3$
Formula weight	909.23
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	13.027(3)
b (Å)	13.180(5)
c (Å)	12.554(4)
α (°)	97.00(3)
β (°)	116.21(2)
γ (°)	95.28(3)
V (Å^3)	1893.5
Z	2
D_{calc} ($g\ cm^{-3}$)	1.59
Dimensions (mm)	$0.3\times0.4\times0.35$
Diffractometer	MSC/Rigaku
Radiation and wavelength	Mo Kα ($\lambda=0.71069$ Å)
Scan mode	ω–2θ. $V_{min}=16$°/min
$2\theta_{max}$ (°)	50
μ (cm^{-1})	14.1
Temperature (°C)	23 ± 1
Total reflections	6985
Independent reflections	4501 ($I>3\sigma(I)$)
R	0.043
R_w	0.054

ture was refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The final cycle of refinement included 341 variable parameters for 4501 reflections with $I>3\sigma(I)$ and converged to

$$R=\Sigma|F_o-F_c|/\Sigma F_o=0.043 \quad \text{and}$$

$$R_w=[\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{1/2}=0.054.$$

The standard deviation of an observation of unit weight was 1.44. The highest peak in the final difference Fourier map is 0.89 e/Å^3. All calculations were performed on a VAX/785 computer using the SDP program. The atomic coordinates and thermal parameters are listed in Table 2; the selected bond lengths and angles in Tables 3 and 4, respectively.

Other physical measurements

The IR spectrum was recorded on an FTS-40 spectrophotometer. The UV–Vis spectrum was recorded on a Shimadzu UV-300 spectrophotometer. The ^1H NMR spectrum was recorded on an FT-80A spectrometer with Me_4Si as internal standard. Chemical shifts are reported in ppm, with a positive sign for a resonance appearing downfield from Me_4Si. Cyclic voltammograms were recorded on a CV-1B cyclic voltammeter with an SCE reference electrode, Pt plate working electrode and Pt auxiliary electrode. The supporting electrolyte was Bu_4NClO_4.

TABLE 2. Positional parameters and their e.s.d.s for $(Et_4N)[V_3S_7(S_2CNMe_2)_3]\cdot MeCN$

Atom	x	y	z	B (Å^2)[a]
V(1)	0.23031(7)	0.37381(7)	0.34872(8)	2.14(2)
V(2)	0.34037(7)	0.20532(7)	0.35590(7)	2.04(2)
V(3)	0.36315(7)	0.31842(7)	0.56686(7)	1.90(2)
S	0.1909(1)	0.2199(1)	0.4104(1)	2.29(3)
S(1)	0.2476(1)	0.4596(1)	0.5440(1)	2.74(3)
S(2)	0.3886(1)	0.4830(1)	0.5160(1)	2.50(3)
S(3)	0.5193(1)	0.2868(1)	0.5246(1)	2.47(3)
S(4)	0.4456(1)	0.1583(1)	0.5549(1)	2.67(3)
S(5)	0.3639(1)	0.3514(1)	0.2697(1)	2.73(3)
S(6)	0.2085(1)	0.2575(1)	0.1677(1)	2.98(3)
S(11)	0.0167(1)	0.3701(1)	0.2483(1)	3.57(4)
S(12)	0.1832(1)	0.5288(1)	0.2489(1)	3.35(4)
S(21)	0.4463(1)	0.1159(1)	0.2596(1)	3.33(4)
S(22)	0.2480(1)	0.0207(1)	0.2742(1)	3.20(4)
S(31)	0.2907(1)	0.2590(1)	0.7041(1)	3.01(3)
S(32)	0.5076(1)	0.3906(1)	0.7815(1)	3.02(3)
N(10)	−0.0469(5)	0.5261(4)	0.1262(5)	4.6(1)
N(20)	0.3598(5)	−0.0862(4)	0.1737(5)	4.0(1)
N(30)	0.4392(4)	0.3240(4)	0.9375(4)	3.9(1)
N(40)	0.1351(4)	−0.2003(4)	0.5071(4)	3.1(1)
C(10)	0.0398(5)	0.4808(5)	0.1980(5)	3.1(1)
C(11)	−0.0246(7)	0.6194(6)	0.0837(6)	5.5(2)
C(12)	−0.1689(7)	0.4837(7)	0.0874(8)	6.4(3)
C(20)	0.3518(5)	0.0039(5)	0.2278(5)	2.8(1)
C(21)	0.4471(6)	−0.0965(6)	0.1328(6)	4.9(2)
C(22)	0.2848(7)	−0.1810(6)	0.1576(7)	5.5(2)
C(30)	0.4154(5)	0.3251(4)	0.8239(5)	2.5(1)
C(31)	0.3600(7)	0.2623(7)	0.9682(6)	5.8(2)
C(32)	0.5505(7)	0.3770(7)	1.0389(6)	5.3(2)
C(41)	0.1160(8)	−0.1877(8)	0.3769(8)	3.7(2)
C(42)	0.0043(7)	−0.1336(7)	0.3173(8)	6.4(3)
C(43)	0.0349(8)	−0.2689(8)	0.5024(8)	3.9(2)
C(44)	0.0003(6)	−0.3753(5)	0.4276(7)	4.9(2)
C(45)	0.2481(7)	−0.2502(7)	0.5548(8)	3.5(2)
C(46)	0.2865(9)	−0.2718(9)	0.6825(9)	4.7(3)
C(47)	0.1538(9)	−0.0965(9)	0.5830(9)	5.0(3)
C(48)	0.2574(8)	−0.0189(6)	0.5860(9)	6.8(3)
N(50)	0.235(1)	−0.020(1)	−0.119(1)	9.7(3)*
C(51)	0.1563(9)	−0.0454(9)	−0.104(1)	6.5(3)*
C(52)	−0.063(1)	0.073(1)	0.087(1)	7.5(3)*

[a] Starred atoms were refined isotropically.

Results and discussion

Complex **1** crystallizes in triclinic, space group $P\bar{1}$ and contains discrete cations, anions and CH_3CN solvate molecules. An ORTEP projection of anion **1** is shown in Fig. 1. The anion of **1** contains a V_3 triangle capped by a μ_3-S atom with V–V distances in the narrow range, 2.742(1)–2.754(1) Å. Each V–V edge of the triangle is bridged by an S_2 group. Three S_2 groups consist of two types of sulfur atoms. Three equatorial atoms S(1), S(4) and S(6) deviate from the V_3 plane by not more than 0.16 Å, and three other sulfur atoms, S(2), S(3) and S(5), occupy axial positions opposite to the μ_3-S atom. The V–S bond distances for the axial S atoms

TABLE 3. Selected bond distances in (Å) for $(Et_4N)[V_3S_7(S_2CNMe_2)_3]\cdot MeCN$

V(1)–V(2)	2.742(1)	V(2)–S(6)	2.457(2)
V(1)–V(3)	2.750(1)	V(2)–S(21)	2.485(2)
V(2)–V(3)	2.754(1)	V(2)–S(22)	2.487(2)
V(1)–S	2.349(1)	V(3)–S	2.351(2)
V(1)–S(1)	2.476(2)	V(3)–S(1)	2.465(1)
V(1)–S(2)	2.371(2)	V(3)–S(2)	2.369(1)
V(1)–S(5)	2.376(2)	V(3)–S(3)	2.377(2)
V(1)–S(6)	2.469(2)	V(3)–S(4)	2.472(1)
V(1)–S(11)	2.490(2)	V(3)–S(31)	2.471(2)
V(1)–S(12)	2.510(2)	V(3)–S(32)	2.506(2)
V(2)–S	2.348(1)	S(1)–S(2)	2.021(2)
V(2)–S(3)	2.387(2)	S(3)–S(4)	2.030(2)
V(2)–S(4)	2.452(2)	S(5)–S(6)	2.033(3)
V(2)–S(5)	2.379(2)		

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4. Selected bond angles in (°) for $(Et_4N)[V_3S_7(S_2CNMe_2)_3]\cdot MeCN$

V(2)–V(1)–V(3)	60.21(3)	S(4)–V(2)–S(5)	133.98(6)
V(1)–V(2)–V(3)	60.04(3)	S(4)–V(2)–S(6)	169.90(6)
V(1)–V(3)–V(2)	59.75(3)	S(4)–V(2)–S(21)	96.53(5)
S–V(1)–S(1)	84.44(5)	S(4)–V(2)–S(22)	88.63(5)
S–V(1)–S(2)	108.23(5)	S(5)–V(2)–S(6)	49.66(5)
S–V(1)–S(5)	108.68(5)	S(5)–V(2)–S(21)	88.07(5)
S–V(1)–S(6)	84.73(5)	S(5)–V(2)–S(22)	134.93(6)
S–V(1)–S(11)	86.18(5)	S(6)–V(2)–S(21)	92.94(5)
S–V(1)–S(12)	156.21(6)	S(6)–V(2)–S(22)	91.32(5)
S(1)–V(1)–S(2)	49.22(5)	S(21)–V(2)–S(22)	70.11(5)
S(1)–V(1)–S(5)	134.31(6)	S–V(3)–S(1)	84.65(6)
S(1)–V(1)–S(6)	169.13(6)	S–V(3)–S(2)	108.25(5)
S(1)–V(1)–S(11)	91.43(5)	S–V(3)–S(3)	108.46(5)
S(1)–V(1)–S(12)	94.88(5)	S–V(3)–S(4)	84.37(5)
S(2)–V(1)–S(5)	85.49(5)	S–V(3)–S(31)	85.56(6)
S(2)–V(1)–S(6)	134.60(6)	S–V(3)–S(32)	155.80(6)
S(2)–V(1)–S(11)	134.19(6)	S(1)–V(3)–S(2)	49.38(5)
S(2)–V(1)–S(12)	88.63(5)	S(1)–V(3)–S(3)	134.16(5)
S(5)–V(1)–S(6)	49.55(5)	S(1)–V(3)–S(4)	168.95(6)
S(5)–V(1)–S(11)	131.87(6)	S(1)–V(3)–S(31)	88.76(6)
S(5)–V(1)–S(12)	88.80(5)	S(1)–V(3)–S(32)	95.33(5)
S(6)–V(1)–S(11)	88.75(6)	S(2)–V(3)–S(3)	85.16(5)
S(6)–V(1)–S(12)	95.39(5)	S(2)–V(3)–S(4)	134.09(5)
S(11)–V(1)–S(12)	70.06(5)	S(2)–V(3)–S(31)	132.23(6)
S–V(2)–S(3)	108.26(5)	S(2)–V(3)–S(32)	89.43(5)
S–V(2)–S(4)	84.89(6)	S(3)–V(3)–S(4)	49.42(5)
S–V(2)–S(5)	108.61(5)	S(3)–V(3)–S(31)	134.71(6)
S–V(2)–S(6)	85.04(6)	S(3)–V(3)–S(32)	88.92(5)
S–V(2)–S(21)	155.42(7)	S(4)–V(3)–S(31)	91.66(5)
S–V(2)–S(22)	85.42(5)	S(4)–V(3)–S(32)	95.22(5)
S(3)–V(2)–S(4)	49.56(5)	S(31)–V(3)–S(32)	70.25(6)
S(3)–V(2)–S(5)	84.74(5)	V(1)–S–V(2)	71.43(4)
S(3)–V(2)–S(6)	134.03(6)	V(1)–S–V(3)	71.61(5)
S(3)–V(2)–S(21)	90.73(5)	V(2)–S–V(3)	71.78(4)
S(3)–V(2)–S(22)	132.46(6)		

Numbers in parentheses are e.s.d.s in the least significant digits.

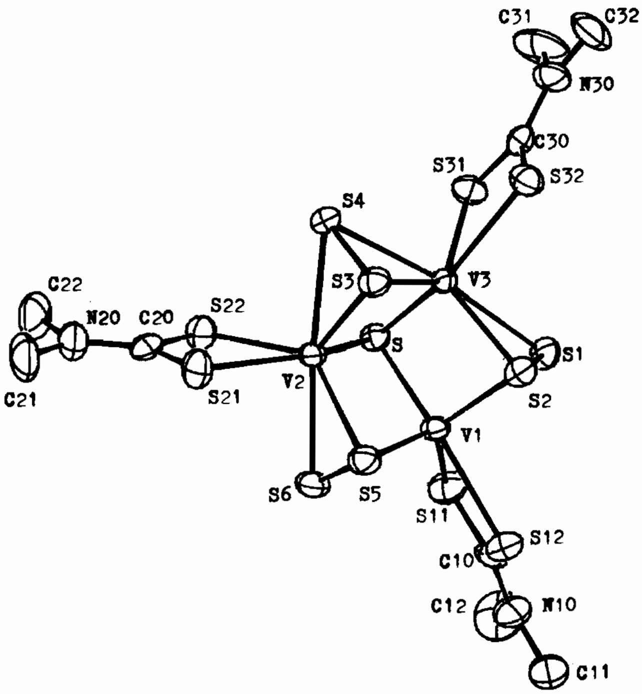
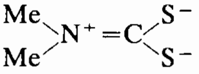


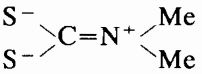
Fig. 1. Structure of $[V_3S_7(S_2CNMe_2)_3]^-$ with numbering scheme for non-hydrogen atoms and the 50% probability ellipsoids.

(mean 2.377 Å) are shorter obviously than those for the equatorial ones (mean 2.466 Å). The axial S, μ_3-S and three V atoms make an incomplete V_3S_4 cubic structure. Each V atom is chelated by an Me_2dtc group in a planar



mode which is oriented approximately perpendicular to the V_3 triangle. The V_3S_{13} fragment of the anion has idealized C_{3v} symmetry but is not crystallographically imposed. In comparison with the Mo analogue $[Mo_3S_7(Et_2dtc)_3]^+$, the anion of **1** is isostructural, if the R group in R_2dtc is excluded, but is not isoelectronic. Also, the structural parameters in Tables 3 and 4 show that the anion is better described as electronically delocalized with an average metal oxidation state of $+3\frac{1}{3}$ which is lower than that in $[V_3S_4(edt)_3]^{3-}$ ($+3\frac{2}{3}$). Meanwhile, all V–S distances in **1** are longer than those in $[V_3S_4(edt)_3]^{3-}$. This variation of bond lengths could be attributed to the differences of both the oxidation state and the coordination environment of the vanadium atoms in the two V_3 complexes.

The IR spectrum of **1** contains a strong absorption at 1519 cm^{-1} assigned to the stretching vibration of the C=N bond of the canonical form



which shifts evidently to a higher frequency region than that in Me_2dtcNa (1485 cm^{-1}) [11]. This indicates an important contribution of the C=N double bond and is consistent with the data of the bond distances (1.331(1)–1.343(7) Å) in the structure. The C–S stretching frequencies of the Me_2dtc group are found at 985 cm^{-1} and the NC_2 frequencies at 1136 cm^{-1}. In the low frequency region, the $V{-}S_{dtc}$ vibrations are found at 354 cm^{-1} as a sharp band, the $V{-}\mu_3{-}S$ vibrations at 442 cm^{-1}, and the S–S vibrations at 554 cm^{-1}. These assignments are consistent with those generally reported in the literature [12] and verify the structure of the anion.

The electronic spectrum of **1** in DMSO solution shows two principal absorptions at 280 and 345(sh) nm. The former is attributed to a ligand transition (π–π^*) and the latter is considered as either an n–π^* transition or a charge transfer (ligand → d-orbital) [12]. Similar to the Mo_3 trimer $[Mo_3S_7(Et_2dtc)_3]^+$ [5], no significant absorbance has been observed above 450 nm for this V_3 trimer.

The ^1H NMR spectrum of **1** in DMSO-d_6 is depicted in Fig. 2. There are two types of CH_3 groups in the vanadium trimer since the C=N double bond restricts free rotation around the bond. Thus it is reasonable to allow the observation of two distinct methyl signals at 10.69 and 8.72 ppm, respectively, with the intensity ratio of 1:1. In comparison with free Me_2dtc, the resonance of which is at *c*. 3.50 ppm, the proton chemical shifts of the Me_2dtc ligands in **1** move obviously downfield due to the effect from the paramagnetic center which has one unpaired electron being delocalized among three vanadium atoms. The mean metal oxidation state $(+3\frac{1}{3})$, the measurement of bulk magnetic susceptibility of **1** showing $\mu_{eff} = 1.76\ \mu_B$ at 301 K and the identity of three vanadium atoms in the structural feature support and explain the result of the ^1H NMR spectrum. Brief exposure of the solution used for measuring the ^1H NMR spectrum to air for a long time (beyond one week) did not cause any variation of the spectrum. This observation indicates that complex **1** is very stable even in solution.

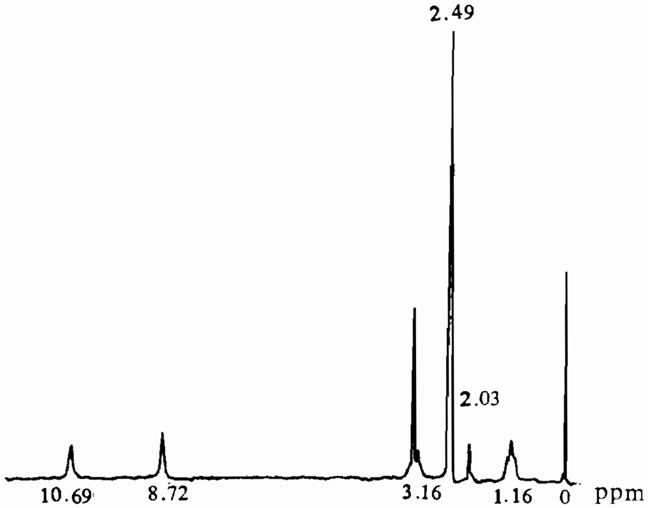


Fig. 2. ^1H NMR spectrum of **1** in DMSO-d_6 solution at room temperature. DMSO, 2.49; CH_3CN, 2.03; $CH_3(Et_4N)$, 1.16; CH_2-(Et_4N), 3.26; $CH_3(Me_2dtc)$, 8.72, 10.69 ppm.

Complex **1** displays rich redox behavior with two reversible one-electron processes as shown in Fig. 3. We consider that complex **1** is a member of the three-component electron-transfer series of the following equation:

$$[V_3S_7(Me_2dtc)_3]^0 \underset{0.04\ V}{\overset{-0.06\ V}{\rightleftharpoons}} [V_3S_7(Me_2dtc)_3]^- \underset{-0.97\ V}{\overset{-1.09\ V}{\rightleftharpoons}} [V_3S_7(Me_2dtc)_3]^{2-}$$

where $[V_3S_7(Me_2dtc)_3]^{2-}$ is isoelectronic with $[Mo_3S_7(Et_2dtc)_3]^+$, while $[V_3S_7(Me_2dtc)_3]^0$ is a V_3 trimer having the same metal oxidation state $(+3\frac{2}{3})$ as $[V_3S_4(edt)_3]^{3-}$ which has also been reported as possessing rich redox chemistry [7].

As aforementioned, complex **1** was obtained as a by-product from a complicated reaction system including VS_4^{3-}, CuCl, Me_2dtc^-, PhS^- and counter ion, in which the major product was $[V_2Cu_2S_4(Me_2dtc)_2(PhS)_2]^{2-}$. It is difficult to discuss the possible reactions occurring in the system in detail. However, the fact that VS_4^{3-} undergoes reduction to form the vanadium trimer is unambiguous. Stiefel and co-workers [13] suggested a induced internal redox reaction to explain the formation of vanadium(IV) dimer $V_2(S_2)_2(i\text{-}Bu_2dtc)_4$ from a reaction of VS_4^{3-} with thiuram disulfide. The reduction of V(V) to V(IV) corresponds to the oxidation of bound sulfide to disulfide. This redox may also occur in our reaction system, since we have separated and structurally characterized a V(IV) dimer $V_2(S_2)_2(Et_2dtc)_4$ [8] from a similar complicated system. In the presence of reducing agents PhS^- and Me_2dtc^-, the further reduction of V(V) to V(IV) or V(III) could lead to the triangular disulfide bridging V_3S_7 trimer. Nevertheless, we are trying to obtain the V_3S_7/R_2dtc or V_3S_4/R_2dtc trimers in which the vanadium atoms lie in various oxidation

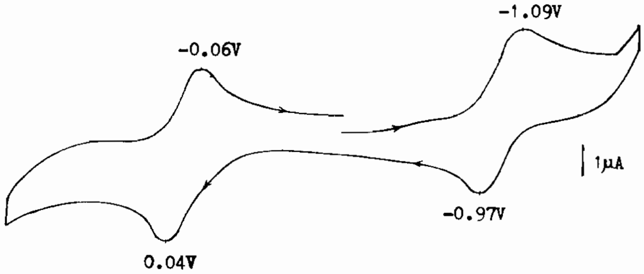


Fig. 3. Cyclic voltammogram of complex **1** in DMSO at 150 mV/s.

states, from a simpler reaction system including VS_4^{3-} as the sole metal source.

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