packing mode of β-(BEDT-TTF)$_2$CuCl$_2$ are very similar to those of β-(BEDT-TTF)$_2$ICl$_2$ and β-(BEDT-TTF)$_2$BrICl (Emge *et al.*, 1986). We note that Kurmoo, Talham, Day, Howard, Stringer, Obertelli & Friend (1988) report that they found no evidence for the β-phase, which is the subject of this study, either by chemical or electrochemical crystal growth.

The CuCl$_2^-$ anion is linear as required by symmetry. The Cu—Cl distance, 2·098 (3) Å, is in close agreement with that in [N(C$_4$H$_9$)$_2$][CuCl$_2$] (Asplund, Jagner & Nilsson, 1983), α-(BEDT-TTF)$_2$CuCl$_2$ (Geiser *et al.*, 1987) and (BEDT-TTF)CuCl$_2$ (Kawamoto, Tanaka & Tanaka, 1987).

Four-probe conductivity measurements were made on two different single crystals of the same batch of β-(BEDT-TTF)$_2$CuCl$_2$. Fig. 4 shows the resistance of one of these samples in the needle direction (crystallographic *a* axis) in the temperature range of 100 to 290 K. The room-temperature conductivity is approximately $10^{-2}\,\Omega^{-1}$cm^{-1}. Linear dependence of the log *R vs* 1/*T* plot indicates standard semiconductivity behaviour with a relatively small gap of 45 meV.

We would like to thank Professor J. Osteryoung for advice on the electrocrystallization conditions. Support of this work by the National Science Foundation [CHE8711736 (PC) and DMR89-14087 (MJN)] and the Petroleum Research Fund of the American Chemical Society (PRF21392-AC6-C) is gratefully acknowledged.

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Acta Cryst. (1991). C**47**, 2085–2087

Structure of a Binuclear Disulfido–Vanadium Complex, [V$_2$(μ-η^2-S$_2$)$_2$(Et$_2$NCS$_2$)$_4$]

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(*Received* 7 *January* 1991; *accepted* 23 *April* 1991)

Abstract. Di[bis(diethyldithiocarbamato)(μ-η^2-disulfido)vanadium], C$_{20}$H$_{40}$N$_4$S$_{12}$V$_2$, M_r = 823·22, triclinic, $P\bar{1}$, a = 11·071 (7), b = 12·161 (6), c = 6·714 (4) Å, α = 102·62 (4), β = 95·14 (4), γ = 97·17 (5)°, V = 868·8 Å^3, Z = 1, D_x = 1·57 g cm^{-3}, λ(Mo $K\alpha$) 0·71069 Å, μ = 12·4 cm^{-1}, F(000) = 426, room temperature, final R = 0·058 for 1346 unique reflections with $(F_o)^2 > 3\sigma(F_o)^2$. The environment of the V atom in the title compound is of a distorted tetragonal prism geometry. The single V—V bond distance is 2·884 (4)Å.

Introduction. Vanadium compounds are of special interest for their wide range of applications in biological systems, new materials and catalysis. Among sulfido–vanadium complexes reported, only a few

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0108-2701/91/102085-03$03.00

Table 1. *Atomic positional and equivalent isotropic thermal parameters with their e.s.d.'s*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq} (Å^2)
V	0·5493 (2)	0·3947 (2)	0·9451 (3)	2·87 (4)
S(1)	0·5565 (3)	0·5423 (3)	0·7544 (5)	3·53 (7)
S(2)	0·6590 (3)	0·5842 (3)	1·0254 (5)	3·68 (8)
S(11)	0·4567 (4)	0·2787 (3)	0·5978 (5)	3·95 (8)
S(12)	0·4858 (3)	0·1929 (3)	0·9573 (5)	3·83 (8)
S(21)	0·7365 (3)	0·3365 (3)	0·7959 (5)	3·98 (8)
S(22)	0·7090 (3)	0·3745 (3)	1·2232 (5)	4·02 (8)
N(1)	0·379 (1)	0·0608 (8)	0·599 (2)	3·9 (3)
N(2)	0·922 (1)	0·329 (1)	1·079 (2)	5·8 (3)
C(1)	0·431 (1)	0·160 (1)	0·702 (2)	2·4 (2)
C(2)	0·805 (1)	0·345 (1)	1·037 (2)	3·4 (3)
C(11)	0·326 (1)	0·045 (1)	0·375 (2)	3·9 (3)
C(12)	0·197 (1)	0·084 (1)	0·360 (2)	6·4 (5)
C(13)	0·361 (1)	−0·038 (1)	0·705 (2)	5·3 (4)
C(14)	0·227 (2)	−0·052 (1)	0·768 (3)	8·3 (5)
C(21)	0·970 (1)	0·324 (2)	1·306 (2)	7·2 (5)
C(22)	1·089 (2)	0·391 (2)	1·351 (3)	11·3 (7)
C(23)	1·001 (1)	0·318 (2)	0·922 (2)	6·7 (5)
C(24)	1·016 (2)	0·194 (2)	0·845 (4)	12·1 (7)

Table 2. *Selected bond distances* (Å) *and bond angles* (°)

V—V	2·884 (4)	S(11)—C(1)	1·74 (2)
V—S(1)	2·420 (4)	S(12)—C(1)	1·72 (1)
V—S(1′)	2·451 (4)	S(21)—C(2)	1·70 (1)
V—S(2)	2·391 (4)	S(22)—C(2)	1·72 (2)
V—S(2′)	2·374 (5)	N(1)—C(1)	1·29 (1)
V—S(11)	2·500 (4)	N(1)—C(11)	1·52 (2)
V—S(12)	2·489 (4)	N(1)—C(13)	1·52 (2)
V—S(21)	2·495 (4)	N(2)—C(2)	1·35 (2)
V—S(22)	2·528 (5)	N(2)—C(21)	1·59 (2)
S(1)—S(2)	1·984 (5)	N(2)—C(23)	1·43 (2)
V—V—S(1)	54·2 (2)	S(2)—V—S(21)	85·6 (1)
V—V—S(1′)	53·2 (2)	S(2)—V—S(22)	81·3 (1)
V—V—S(2)	52·5 (2)	S(2′)—V—S(11)	81·3 (1)
V—V—S(2′)	53·0 (2)	S(2′)—V—S(12)	85·6 (1)
V—V—S(11)	112·0 (1)	S(2′)—V—S(21)	160·6 (2)
V—V—S(12)	136·1 (2)	S(2′)—V—S(22)	127·3 (2)
V—V—S(21)	135·5 (1)	S(11)—V—S(12)	69·5 (1)
V—V—S(22)	111·9 (1)	S(11)—V—S(21)	79·3 (1)
S(1)—V—S(1′)	107·4 (1)	S(11)—V—S(22)	136·1 (1)
S(1)—V—S(2)	48·7 (1)	S(12)—V—S(21)	88·5 (1)
S(1)—V—S(2′)	87·3 (1)	S(12)—V—S(22)	79·5 (1)
S(1)—V—S(11)	80·1 (1)	S(21)—V—S(22)	69·3 (1)
S(1)—V—S(12)	149·4 (1)	S(11)—C(1)—S(12)	110·8 (6)
S(1)—V—S(21)	88·5 (1)	S(11)—C(1)—N(1)	124·3 (9)
S(1)—V—S(22)	127·2 (1)	S(12)—C(1)—N(1)	124·9 (9)
S(1′)—V—S(2)	86·2 (1)	S(21)—C(2)—S(22)	113·3 (7)
S(1′)—V—S(2′)	48·5 (1)	S(21)—C(2)—N(2)	124 (2)
S(1′)—V—S(11)	127·6 (2)	S(22)—C(2)—N(2)	123 (1)
S(1′)—V—S(12)	89·9 (1)	C(1)—N(1)—C(11)	120 (2)
S(1′)—V—S(21)	150·0 (1)	C(1)—N(1)—C(13)	121 (2)
S(1′)—V—S(22)	81·0 (1)	C(11)—N(1)—C(13)	120 (2)
S(2)—V—S(2′)	105·5 (1)	C(2)—N(2)—C(21)	119 (1)
S(2)—V—S(11)	127·0 (1)	C(2)—N(2)—C(23)	120 (1)
S(2)—V—S(12)	160·8 (1)	C(21)—N(2)—C(23)	121 (1)

binuclear vanadium–dtc (dtc = dialkyldithiocarbamato) compounds (Halbert, Hutchings, Rhodes & Stiefel, 1986) have been characterized.

Experimental. Brown stick-like crystals from acetonitrile solution. Rigaku MSC/AFC5R diffractometer with graphite-monochromated Mo $K\alpha$ radiation, a crystal (0·07 × 0·08 × 0·2 mm) for data collection was mounted on a glass fibre in a random orientation. Lattice parameters determined by least squares from setting angles of 20 reflections. Intensities measured using the ω–2θ scan mode with scan width, $\Delta\omega = (1\cdot36 + 0\cdot35\tan\theta)^\circ$. 3214 reflections with $2\theta \leq 50^\circ$, $0 < h < 13$, $-14 < k < 14$, $-7 < l < 7$, 1346 with $F_o^2 > 3\sigma(F_o^2)$ included in the structure determination. An empirical absorption correction was applied (Walker & Stuart, 1983). Relative transmission coefficients range from 0·938 to 0·996 with an average value of 0·967. Structure solved by direct methods. Seven atoms located on an E map. The remaining atoms found in succeeding difference Fourier syntheses. All non-H atoms refined anisotropically by full-matrix least-squares (on F) technique, the function minimized being $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o^2) + P(F_o^2) + Q]^{-1}$ with $P = 0\cdot010$ and $Q = 3\cdot0$ (Killean & Lawrence, 1969). Final $R = 0\cdot058$, $wR = 0\cdot065$, $S = 1\cdot132$, $(\Delta/\sigma)_{max} = 0\cdot05$ included 172 variables. Max. and min. heights in final difference Fourier map 0·80 and $-0\cdot69$ e Å^{-3}, respectively. Scattering factors were taken from Cromer & Waber (1974). Calculations carried out on a VAX 11/785 computer with *SDP* (Frenz, 1978). Table 1 contains the positional and equivalent isotropic thermal parameters with their standard deviations, while selected bond distances and bond angles are listed in Table 2.* Fig. 1. shows the molecular structure and atomic labelling scheme for $V_2(\mu\text{-}\eta^2\text{-}S_2)_2(Et_2NCS_2)_4$.

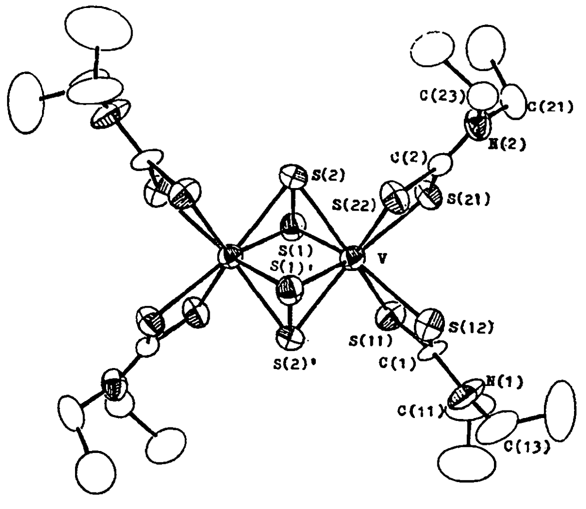

Fig. 1. Molecular structure and atomic labelling of $V_2(\mu\text{-}\eta^2\text{-}S_2)_2(Et_2NCS_2)_4$.

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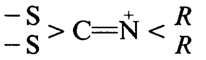
* Lists of structure factors, anisotropic thermal parameters and full bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54190 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. There is a crystallographic centre of symmetry in the molecule. The two V atoms are bridged by two (μ-η^2-S_2) groups. The other coordination sites of each V atom are occupied by two bidentate dithiocarbamato ligands. The arrangement of the ligands is simply described as two distorted hexahedra that share a parallelogram and each has its other five faces strongly twisted. The bond distance of 2·884 (4) Å for V—V, which indicates a direct metal–metal interaction, is consistent with those of diamagnetic complexes (Duraj, Andras & Kibala, 1990; Halbert, Hutchings, Rhodes & Stiefel, 1986), and is much longer than the distance of 2·4 Å postulated for a d^2—d^2 double bond (Dorfman & Holm, 1983). The average V—S_b (bridge) distance (2·409 Å) is obviously shorter than the average value (2·503 Å) for V—S_t (terminal). The S(1)—S(2) distance of 1·984 (5) Å is not significantly different from those in other similar compounds (Bolinger & Rauchfuss, 1982; Bolinger, Rauchfuss & Rheingold, 1983; Bolinger, Weatherill, Rauchfuss, Rheingold, Day & Wilson, 1986).

Atoms S(n1), S(n2), C(n), N(n), C(n1) and C(n3) (n = 1,2) are coplanar, which indicates that the dtc ligand coordinates to a V atom in the



$$\begin{matrix}-S\\-S\end{matrix} > C{=}\overset{+}{N} < \begin{matrix}R\\R\end{matrix}$$

form. Although molecular vanadium dimers with S_2 bridges are known, those with a $V_2(\mu\text{-}\eta^2\text{-}S_2)_2$ core that have been hitherto structurally characterized are found in the mineral patronite $(VS_4)_n$, $V_2(\mu\text{-}\eta^2\text{-}S_2)_2(Bu_2NCS_2)_4$ (Halbert, Hutchings, Rhodes & Stiefel, 1986) and $V_2(\mu\text{-}\eta^2\text{-}S_2)_2(S_2CCH_3)_4$ (Duraj, Andras & Kibala, 1990).

The generous financial support of NNSF, NSFCAS and FNSF is greatly appreciated.

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Acta Cryst. (1991). C**47**, 2087–2090

Structure of Benzyltriphenylphosphonium Imidazolebis(*o*-mercaptophenolato)manganese(III) Acetonitrile Solvate

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(*Received* 7 *January* 1991; *accepted* 23 *April* 1991)

Abstract. $C_{25}H_{22}P^+.[Mn(C_6H_4OS)_2(C_3H_4N_2)]^-.C_2H_3N$, $M_r = 765{\cdot}82$, monoclinic, $P2_1/n$, $a = 16{\cdot}221\,(4)$, $b = 9{\cdot}705\,(2)$, $c = 24{\cdot}457\,(5)$ Å, $\beta = 94{\cdot}96\,(1)°$, $V = 3835$ Å^3, $Z = 4$, $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 5{\cdot}1$ cm^{-1}, $F(000) = 1592$, $T = 296$ K, final $R = 0{\cdot}054$ and $wR = 0{\cdot}064$ for 2570 observed reflections with $F > 3\sigma(F)$. The Mn^{III} ion is in a distorted square-pyramidal S_2O_2N coordination environment.

Introduction. On the basis of chemical and spectroscopic evidence, the acid phosphatase from sweet potato appears to contain a mononuclear manganese(III) site with thiolate (cystein), phenolate (tyrosine) (Sugiura, Kawabe, Tanaka, Fujimoto & Ohara, 1981) and imidazole (histidine) (Fujimoto, Murakami & Ohara, 1981) ligands. These discoveries have stimulated research into manganese chemistry, especially in Mn^{III}–thiolate chemistry (Bashkin, Huffman & Christou, 1986; Christou & Huffman, 1983; Costa, Dorfman, Hagen & Holm, 1983; Seela,

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0108-2701/91/102087-04$03.00