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Structure of a $V_2Cu_2S_4$ Cubane-Like Cluster $(Et_4N)_2[V_2Cu_2S_4(S_2CNMe_2)_2(SPh)_2]$

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Abstract

The title compound, bis(tetraethylammonium) bis-(*N*,*N*-dimethyldithiocarbamato)-$1\kappa^2S,S';2\kappa^2S,S'$-bis(phenylthiolato)-$3\kappa S,4\kappa S$-tetra-$\mu_3$-sulfido-$1{:}2{:}3\kappa^3S;1{:}2{:}4\kappa^3S;1{:}3{:}4\kappa^3S;2{:}3{:}4\kappa^3S$-*tetrahedro*-dicopperdivanadium, is a cubane-like cluster containing a $V_2Cu_2(\mu_3\text{-}S)_4$ distorted-cubic core. Each V atom is chelated by a dimethyldithiocarbamate group and each Cu atom is bonded to a phenylthiolate group.

Comment

Heterometallic thiocubane clusters have attracted attention due to their relevance and importance to a wide variety of chemical, industrial and biological systems. Among the V-containing heteronuclear thiocubanes only a few complexes, with VFe_3S_4 (Kovacs & Holm, 1987) and $V_2Fe_2S_4$ (Rauchfuss, Weatherill, Wilson & Zebrowski, 1983) cores, have been structurally characterized. We have recently reported $V_2Cu_2S_4$ and $V_2Ag_2S_4$ cubane clusters and determined the structures of $(Et_4N)_2[V_2M_2S_4(OC_4H_8NCS_2)_2(PhS)_2]$ (M = Cu, Ag; Yang, Liu, Huang, Kang & Lu, 1992). Here, we report the crystal structure of a compound containing a $V_2Cu_2S_4$ cubic core which was obtained from an assembly reaction system including $(NH_4)_3VS_4$, CuCl, $Me_2NCSSNa$ and C_6H_5SNa in the molar ratio 1:3:4:4 in dimethylformamide (DMF). This compound was crystallized from $DMF/CH_3CN/(CH_3)_2CO$ solution to give single black crystals used for X-ray diffraction.

The title compound contains well separated tetraethylammonium cations and $[V_2Cu_2S_4(S_2CNMe_2)_2(SPh)_2]^{2-}$ anions. There is a distorted cubic $V_2Cu_2S_4$ core in the anion. A crystallographically imposed C_2 axis passes through the centers of both the V—S(1)—V′—S(1′) and Cu—S(2)—Cu′—S(2′) units. Each V atom is chelated by a dimethyldithiocarbamate group and coordinated by three μ_3-S atoms in a distorted square pyramidal site which is out of the equatorial plane toward the apical S(2) atom. Each Cu atom is coordinated by three μ_3-S atoms and a terminal phenylthiolate group in a distorted tetrahedral site. The metal bond distances of 2.803 (5) Å for V···V and 2.762 (2) to 2.791 (3) Å for V···Cu, which indicate direct intermetallic contacts, are comparable to those in other V–S dimers (Duraj, Andras & Kibala, 1990: Halbert, Hutchings, Rhodes & Stiefel, 1986) and V–Cu–S clusters (Müller, Schimanski & Bögge, 1987; Scattergood, Bonney, Slater, Garner & Clegg, 1987). In comparison with $[V_2Cu_2S_4(S_2CNC_4H_8O)_2(SPh)_2]^{2-}$, the anion of the title complex shows the same structural features of the core with similar bond distances and angles. The non-H atoms in the dimethyldithiocarbamate group are coplanar. The C(20)—N(20) bond distance of 1.28 (2) Å indicates a C=N double bond, strongly indicating that the dimethyldithiocarbamate group coordinates to a V atom in the form $(Me)_2N^+{=}C(S^-)_2$ rather than $(Me)_2N{—}C(S_2)^-$. The four C atoms in the tetraethylammonium cation, C(31), C(33), C(35) and C(37), are disordered and have the occupancies given in Table 1.

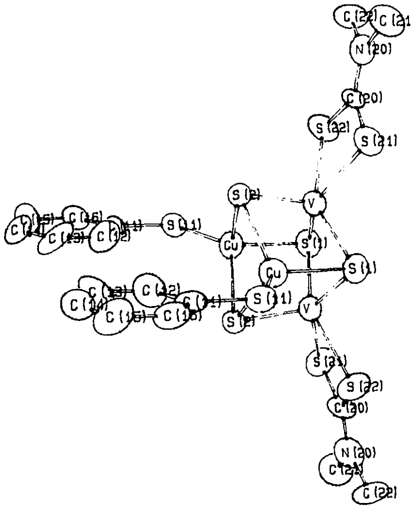

Fig. 1. Structure and atomic labelling of the $[V_2Cu_2S_4(S_2CNMe_2)_2(SPh)_2]^{2-}$ anion.

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Experimental

Crystal data

$2C_8H_{20}N.[Cu_2V_2(C_3H_6NS_2)_2(C_6H_5S)_2S_4]$
$M_r = 1076.5$
Monoclinic
$C2/c$
$a = 20.088$ (9) Å
$b = 13.895$ (4) Å
$c = 17.751$ (12) Å
$\beta = 105.07$ (4)°
$V = 4784.3$ Å^3
$Z = 4$

$D_x = 1.49$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 0$–25°
$\mu = 1.70$ mm^{-1}
$T = 296$ (1) K
Cubic
0.4 × 0.35 × 0.3 mm
Black

Data collection

MSC/Rigaku diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{\min} = 0.771$, $T_{\max} = 0.986$
4542 measured reflections
1829 independent reflections
1411 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.041$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 17$
$l = -21 \rightarrow 21$
3 standard reflections monitored every 250 reflections intensity variation: insignificant

Refinement

Refinement on F^2
Final $R(F) = 0.067$
$wR(F^2) = 0.074$
$S = 1.33$
1411 reflections
231 parameters
H-atom parameters not refined

$w = [\sigma^2(F_o)^2 + 0.02(F_o)^2 - 1.0]^{-1}$
$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.62$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

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

	x	y	z	$B_{\rm eq}$
Cu	0.4139 (1)	0.3310 (2)	0.7328 (1)	4.26 (5)
V	0.5074 (1)	0.2076 (2)	0.8307 (2)	3.38 (7)
S(1)	0.4115 (2)	0.1686 (3)	0.7341 (3)	4.0 (1)
S(2)	0.5061 (2)	0.3606 (3)	0.8463 (3)	3.6 (1)
S(11)	0.3116 (2)	0.4040 (3)	0.7028 (3)	4.1 (1)
S(21)	0.4475 (2)	0.1439 (3)	0.9234 (3)	4.8 (1)
S(22)	0.5925 (2)	0.1539 (4)	0.9473 (3)	4.9 (1)
N(20)	0.5359 (7)	0.118 (1)	1.0623 (8)	4.9 (4)
N(30)	0.3187 (7)	0.481 (1)	0.4475 (8)	4.9 (4)
C(11)	0.3223 (8)	0.529 (1)	0.7011 (8)	3.6 (4)
C(12)	0.3880 (9)	0.577 (1)	0.715 (1)	5.5 (5)
C(13)	0.391 (1)	0.674 (1)	0.715 (1)	8.0 (7)
C(14)	0.332 (1)	0.728 (1)	0.703 (1)	8.8 (7)
C(15)	0.269 (1)	0.689 (1)	0.689 (1)	8.3 (7)
C(16)	0.264 (1)	0.589 (1)	0.688 (1)	5.5 (5)
C(20)	0.5249 (8)	0.135 (1)	0.9894 (9)	4.1 (4)
C(21)	0.478 (1)	0.108 (1)	1.100 (1)	6.4 (6)
C(22)	0.604 (1)	0.108 (1)	1.117 (1)	6.2 (6)
C(31)	0.261 (1)	0.531 (6)	0.395 (2)	6.4 (8)*
C(31*a*)	0.266 (3)	0.511 (5)	0.505 (4)	7 (2)†
C(32)	0.207 (1)	0.562 (2)	0.450 (1)	8.8 (7)
C(33)	0.361 (1)	0.537 (2)	0.521 (1)	4.6 (6)*
C(33*a*)	0.319 (4)	0.579 (5)	0.415 (4)	10 (2)†
C(34)	0.374 (1)	0.643 (1)	0.495 (1)	9.1 (7)
C(35)	0.302 (1)	0.381 (2)	0.479 (1)	4.6 (6)*
C(35*a*)	0.270 (3)	0.420 (4)	0.376 (3)	5 (1)†
C(36)	0.2642 (9)	0.315 (1)	0.407 (1)	6.0 (5)
C(37)	0.372 (1)	0.459 (2)	0.393 (1)	4.5 (6)*
C(37*a*)	0.380 (3)	0.437 (4)	0.495 (3)	5 (1)†
C(38)	0.4344 (9)	0.404 (2)	0.436 (1)	6.3 (6)

* Refined isotropically, occupancy of 0.67.
† Refined isotropically, occupancy of 0.33.

Table 2. *Geometric parameters* (Å, °)

Cu—Cu′	3.351 (5)	N(30)—C(33)	1.57 (3)
Cu—V	2.791 (3)	N(30)—C(33*a*)	1.48 (8)
Cu—V′	2.762 (3)	N(30)—C(35)	1.56 (3)
V—V′	2.803 (5)	N(30)—C(35*a*)	1.62 (5)
Cu—S(1)	2.257 (5)	N(30)—C(37)	1.64 (3)
Cu—S(2)	2.390 (5)	N(30)—C(37*a*)	1.43 (6)
Cu—S(2)′	2.427 (5)	C(11)—C(12)	1.44 (2)
Cu—S(11)	2.229 (5)	C(11)—C(16)	1.41 (3)
V—S(1)	2.285 (5)	C(12)—C(13)	1.35 (2)
V—S(1)′	2.290 (6)	C(13)—C(14)	1.37 (3)
V—S(2)	2.145 (5)	C(14)—C(15)	1.34 (3)
V—S(21)	2.443 (5)	C(15)—C(16)	1.40 (3)
V—S(22)	2.434 (5)	C(31)—C(32)	1.69 (3)
S(11)—C(11)	1.76 (2)	C(31*a*)—C(32)	1.51 (6)
S(21)—C(20)	1.69 (2)	C(33)—C(34)	1.59 (3)
S(22)—C(20)	1.73 (2)	C(33*a*)—C(34)	1.79 (8)
N(20)—C(20)	1.28 (2)	C(35)—C(36)	1.60 (3)
N(20)—C(21)	1.49 (3)	C(35*a*)—C(36)	1.58 (5)
N(20)—C(22)	1.47 (3)	C(37)—C(38)	1.50 (3)
N(30)—C(31)	1.47 (3)	C(37*a*)—C(38)	1.77 (6)
N(30)—C(31*a*)	1.72 (6)		
S(1)—Cu—S(2)	100.2 (2)	Cu—S(1)—V	75.8 (2)
S(1)—Cu—S(2)′	101.2 (2)	Cu—S(1)—V′	74.8 (2)
S(1)—Cu—S(11)	115.9 (2)	V—S(1)—V′	75.5 (2)
S(2)—Cu—S(2)′	88.5 (2)	Cu—S(2)—Cu′	88.1 (2)
S(2)—Cu—S(11)	125.9 (2)	Cu—S(2)—V	75.7 (2)
S(2)′—Cu—S(11)	119.5 (2)	Cu′—S(2)—V	74.0 (2)
S(1)—V—S(1)′	97.9 (2)	Cu—S(11)—C(11)	110.3 (7)
S(1)—V—S(2)	107.2 (2)	V—S(21)—C(20)	88.1 (6)
S(1)—V—S(21)	87.3 (2)	V—S(22)—C(20)	87.5 (6)
S(1)—V—S(22)	146.5 (2)	C(20)—N(20)—C(21)	121 (2)
S(1)′—V—S(2)	109.5 (2)	C(20)—N(20)—C(22)	125 (2)
S(1)′—V—S(21)	142.4 (2)	C(21)—N(20)—C(22)	114 (2)
S(1)′—V—S(22)	85.5 (2)	S(21)—C(20)—S(22)	112 (1)
S(2)—V—S(21)	104.3 (2)	S(21)—C(20)—N(20)	127 (1)
S(2)—V—S(22)	103.0 (2)	S(22)—C(20)—N(20)	121 (1)
S(21)—V—S(22)	71.1 (2)		

Program used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program used to refine structure: *LSFM* (B. A. Frenz & Associates Inc., 1985). Molecular graphics: *ORTEP* (Johnson, 1976).

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Lists of structure factors, anisotropic and refined thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71159 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1048]

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Ring Cleavage of Imidazole to Oxamide by Reaction with Dioxygen in the Presence of a Cu^{I}-Amine Complex. Structure of μ-Oxamidato-bis[(1,4,7-trimethyl-1,4,7-triazacyclononane)copper(II)] Triiodide Iodide

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Abstract

An oxamidato group in a *trans* conformation bridges two trimethyltriazacyclononane moieties. Each Cu atom is fivefold coordinated by four N and one O atoms. The N and O atoms of the oxamidato ligand are disordered over two sites giving two different *trans* conformations. The cations are packed along [100] with iodide and triiodide anions between them. The I_3^- ions are disordered and have asymmetric I—I bond lengths.

Comment

This work stems from our interest in the polynuclear complexes of copper(II) with multi-atom bridging ligands (Chaudhuri *et al.*, 1992; Chaudhuri & Oder, 1990). In this paper we present the isolation, although in very low yield, and characterization of an oxamidato-bridged binuclear copper(II) complex, which results from the oxidation of an imidazolate ring, presumably by dioxygen in the presence of a Cu^{I}-amine unit. Activation of oxygen by Cu^{I} complexes is of particular interest as a model for a number of copper proteins, such as haemocyanin, tyrosinase and ascorbate oxidase. Imidazole itself is reasonably resistant to oxidation (Katritzky & Rees, 1984), being attacked only by strong oxidizing agents such as MnO_4^- and various peracids. These reactions usually result in ring degradation, leading to ammonia or ammonia derivatives and aliphatic carbonyl compounds, while hydrogen peroxide has been reported to oxidize some imidazoles to oxamide.

The structure consists of dinuclear $[(L\mathrm{Cu})_2(\mathrm{oxam})]^{2+}$ cations (L = trimethyltriazacyclononane and oxam = oxamidato), and both I^- and I_3^- anions. The geometrical centre of the oxamide which bridges the two CuL moieties is situated on a crystallographic inversion centre. The Cu atoms reach distorted square-pyramidal configurations with three N and one O ligand atoms in the equatorial plane with bond distances of Cu—N(L) = 2.039 (9) and 2.039 (8) Å, and Cu—N,O(oxam) = 1.993 (7) and 1.998 (6) Å. A fourth N atom from the L ligand completes the coordination in the axial position with a distinctly longer Cu—N(1) bond length of 2.255 (10) Å. This geometry has been observed previously in other square-pyramidal L complexes of copper(II) (Chaudhuri *et al.*, 1991, 1992). The N_3O coordination plane around the copper and the plane of the oxamidato group form a dihedral angle of 8.6°. The distance between the two copper centres is 5.229 (2) Å which is in the range of other reported dicopper oxamidato structures: 5.189 (2) (Bencini, Di Vaira, Fabretti, Gatteschi & Zanchini, 1984), 5.192 (2) (Okawa, Matsumoto, Koikawa, Takeda & Kida, 1990) and 5.290 (1) Å (Lloret, Julve, Faus, Journaux, Philoche-Levisalles & Jeannin, 1989). In these structures, the copper has four, five and sixfold coordination.

During refinement the anisotropic displacement parameters of the oxamidato N and O atoms indicated positional disorder which was successfully treated by a split model with half occupation of positions $X1$ and $X2$ with both N and O atoms. This leads to two indistinguishable *trans* conformations of the oxamide. The disorder is also reflected by the equal Cu—X (X = N, O) bond lengths of 1.993 (7) and 1.998 (6) Å. In the structures of Bencini *et al.* (1984) and Lloret *et al.* (1989), with unambiguous N and O positions, the Cu—N bonds are clearly shorter [1.899 (6) and 1.924 (3) Å, respectively] than the Cu—O