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Tris(*N*,*N*-diethyldithiocarbamato-*S*,*S*′)-vanadium(III)

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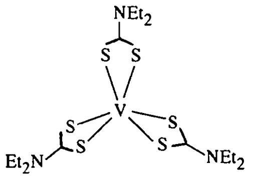
Abstract

In the title compound, $[V(C_5H_{10}NS_2)_3]$, three diethyldithiocarbamate (Et_2dtc^-) ligands chelate to the V atom, with an average S—V—S bite angle of 72.77 (4)°, forming a screw-propeller structure centered on the V atom. The average V—S bond distance is 2.434 (1) Å.

Comment

Reported studies on tris(dialkyldithiocarbamate)vanadium(III) complexes are rare. One complex, $[V(Bu_2dtc)_3]$, (2), was structurally characterized by X-ray diffraction and the title compound, (1), was considered to be isomorphous with $[Fe(Et_2dtc)_3]$ determined by X-ray powder diffraction (Porter, Novick & Murray, 1994). This view is supported by the fact that (1) and $[Fe(Et_2dtc)_3]$ [$P2_1/c$, a = 14.29 (1), b = 10.37 (1), c = 17.87 (1) Å, β = 116.6 (1)°, V = 2367.3 (1) Å^3; Leipoldt & Coppens, 1973] have similar cell dimensions.



(1)

The V atom in (1) has very distorted octahedral coordination geometry, indicated by the S—V—S bond angles which appear to fall into four categories: (i) the ligand bite angles [72.61 (4)–73.01 (4)°], (ii) the *trans* angles [153.65 (5)–158.94 (5)°], (iii) angles in the range 90.34 (4)–96.33 (5)° and (iv) angles in the range 104.54 (5)–107.75 (5)°. There are three VS_2CN units which form three near perfect planes, with the deviation of each atom from its respective least-squares plane being less than 0.05 Å. Furthermore, each of these planes extends to include two other C atoms linked to the N atom, with deviations less than 0.08 Å from the respective plane, except for the C11 atom (0.29 Å). The dihedral angles between these least-squares planes are 109.14 (4), 101.90 (6) and 106.55 (6)°. The three C atoms around the central V atom (C10, C20 and C30) form a regular triangle, with C—V—C angles close to 120°. All of the above features show that compound (1) (Fig. 1) can be viewed as a screw-propeller structure centered on the V atom, with the VS_2CNC_2 units as the screw leaves.

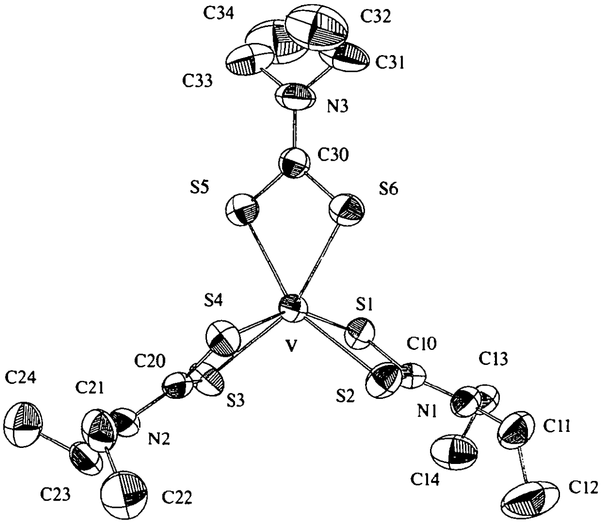


Fig. 1. The crystal structure of $[V(Et_2dtc)_3]$ showing 50% probability displacement ellipsoids.

A comparison of complexes (1) and (2) indicates that both have almost the same structural features, including V—S bond distances [2.423 (1)–2.445 (1) Å for (1) and 2.413–2.449 Å for (2)] and S—V—S bite angles [72.61 (4)–73.01 (4)° for (1) and 72.6–72.8° for (2)], as well as other comparable S—C and C—N distances of the R_2dtc^- ligands. The two $[V(R_2dtc)_3]$ complexes reported may therefore show structural features that are general for tris(dialkyldithiocarbamate) complexes of vanadium(III). Comparison can also be made with those in other similar metal species, such as $[Fe(Et_2dtc)_3]$. It is noted that the V^{III}—S_{dtc} bond distances (mean 2.434 Å) are obviously longer than the Fe^{III}—S_{dtc} distances (mean 2.358 Å). The S—C (1.71–1.72 Å) and C—N (1.32–1.33 Å) distances, however, are in agreement with those of other iron– or cobalt–diethyldithiocarbamate complexes (Leipoldt & Coppens, 1973; Merlino, 1968).

Experimental

The title compound was separated as yellow–brown prismatic crystals from a reaction system of $VS_4^{3-}/Ag(PPh_3)_2^+/Et_2dtc^-$, which was used in an attempt to prepare V/Ag/S heterometallic cluster compounds in CH_3CN at room temperature under an N_2 atmosphere.

Crystal data

$[V(C_5H_{10}NS_2)_3]$
$M_r = 495.75$
Monoclinic
$P2_1/c$
$a = 13.731\ (1)$ Å
$b = 10.294\ (1)$ Å
$c = 17.230\ (1)$ Å
$\beta = 103.06\ (1)°$
$V = 2372.35\ (1)$ Å^3
$Z = 4$
$D_x = 1.39$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 12–13°$
$\mu = 0.92$ mm^{-1}
$T = 293$ K
Prism
0.25 × 0.17 × 0.15 mm
Yellow–brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (Fair, 1990)
$T_{\min} = 0.841$, $T_{\max} = 0.870$
4432 measured reflections
4267 independent reflections

2417 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 12$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 120 min
intensity decay: 0.6%

Refinement

Refinement on F
$R = 0.0393$
$wR = 0.0456$
$S = 1.27$
2417 reflections
226 parameters
H atoms not refined
$w = 1/[\sigma^2(F)]$

$(\Delta/\sigma)_{\max} = 0.0007$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

V—S1	2.434 (1)	S3—C20	1.716 (4)
V—S2	2.434 (1)	S4—C20	1.723 (4)
V—S3	2.423 (1)	S5—C30	1.721 (4)
V—S4	2.436 (1)	S6—C30	1.721 (4)
V—S5	2.445 (1)	N1—C10	1.321 (6)
V—S6	2.433 (1)	N2—C20	1.324 (6)
S1—C10	1.719 (4)	N3—C30	1.327 (6)
S2—C10	1.722 (4)		
S1—V—S2	72.69 (4)	V—S1—C10	86.6 (2)
S1—V—S3	91.44 (5)	V—S2—C10	86.5 (1)
S1—V—S4	153.65 (5)	V—S3—C20	86.6 (1)
S1—V—S5	96.16 (5)	V—S4—C20	86.0 (2)
S1—V—S6	104.54 (5)	V—S5—C30	86.4 (1)
S2—V—S3	107.75 (5)	V—S6—C30	86.8 (1)
S2—V—S4	91.55 (5)	S1—C10—S2	113.9 (2)
S2—V—S5	156.89 (5)	S1—C10—N1	122.8 (3)
S2—V—S6	90.30 (4)	S2—C10—N1	123.3 (3)
S3—V—S4	73.01 (4)	S3—C20—S4	114.4 (2)
S3—V—S5	92.39 (4)	S3—C20—N2	122.5 (3)
S3—V—S6	158.94 (5)	S4—C20—N2	123.1 (3)
S4—V—S5	105.43 (5)	S5—C30—S6	114.1 (2)
S4—V—S6	96.33 (5)	S5—C30—N3	122.6 (3)
S5—V—S6	72.61 (4)	S6—C30—N3	123.3 (3)

The title structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares methods. H atoms were located and added to the structure-factor calculations, but their positions were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cycloboronated Nickelaundecaborane: $[(Ph\overline{COS)_2NiB}_{10}H_8(PPh_3)]$

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Abstract

The title compound 7,8:7,11-di(μ-thiobenzoato-*S*:*O*)-10-(triphenylphosphine-*P*)-8:9-μH-7-nickela-*nido*-undecaborane, $C_{32}H_{33}B_{10}NiO_2PS_2$, has been synthesized and characterized by X-ray diffraction analysis. The cluster is a *nido* eleven-vertex $\{NiB_{10}\}$ cage with the Ni atom in the open NiB_4 face. Cyclizations resulting in two five-membered rings, Ni7—S1—C1—O1—B8 and Ni7—S2—C2—O2—B11, have occurred.