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Tetrabutylammonium bis[4,4′-dimethyl-2,2′-(3,7-dimethyl-1*H*-4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolato]-vanadium(III) acetonitrile tetrasolvate

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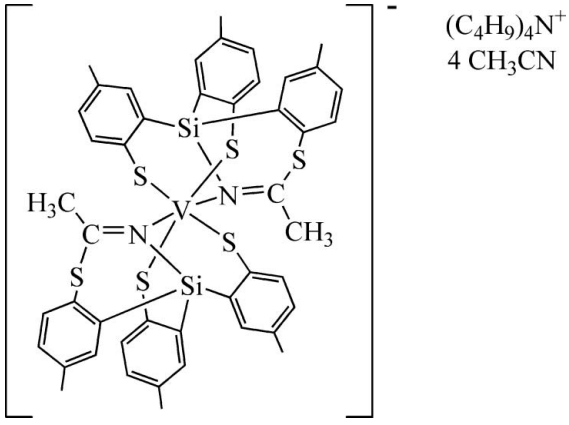
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; R factor = 0.053; wR factor = 0.144; data-to-parameter ratio = 22.3.

In the title compound, $[N(C_4H_9)_4][V(C_{23}H_{21}NS_3Si)_2]\cdot 4CH_3CN$, the V^{III} atom (site symmetry $\overline{1}$) is coordinated by two *N*,*S*,*S*′-tridentate 4,4′-dimethyl-2,2′-(3,7-dimethyl-1*H*-4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolate ligands in a distorted *trans*-VN_2S_4 octahedral geometry. The complete cation is generated by crystallographic twofold symmetry, with the V atom lying on the rotation axis. The unusual ligand arose from nucleophilic attack on the coordinated nitrile by the thiolate precursor and reduction of nitrile to the imidate.

Related literature

For background to vanadium thiolate chemistry, see: Rehder (2008); Crans *et al.* (2004); Eady (2003); Janas & Sobota (2005); Ye *et al.* (2010); Tsai *et al.* (2007). For further mechanistic information, see: Block *et al.* (1989). For related structures, see: Zhu *et al.* (1997, 2002).



Experimental

Crystal data

$(C_{16}H_{36}N)[V(C_{23}H_{21}NS_3Si)_2]\cdot 4C_2H_3N$
M_r = 1328.97
Monoclinic, $C2/c$
a = 27.0867 (16) Å
b = 14.6525 (9) Å
c = 22.0590 (13) Å
β = 126.359 (1)°
V = 7050.5 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 200 K
0.50 × 0.50 × 0.40 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.490, T_{max} = 1.000
26980 measured reflections
8840 independent reflections
5635 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.144
S = 1.05
8840 reflections
396 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å).

V1—N1	2.188 (2)	V1—S2	2.4617 (7)
V1—S1	2.4161 (6)		

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5425).

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supplementary materials

Acta Cryst. (2010). E**66**, m844 [**doi:10.1107/S1600536810022014**]

Tetrabutylammonium bis[4,4'-dimethyl-2,2'-(3,7-dimethyl-1*H*-4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolato]vanadium(III) acetonitrile tetrasolvate

Y.-F. Tsai, H.-F. Hsu, K.-F. Hsu and J.-C. Wang

Comment

Vanadium thiolate chemistry has been drawing much attention due to its biological relevance as well as its medical application (Rehder, 2008; Crans *et al.*, 2004). For example, alternative nitrogenase is proposed to contain a [Fe_7VS_9] cofactor, where V site likely binds to three sulfides, His442 and homocitrate (Eady, 2003). To elucidate the role of vanadium in the enzyme, it is essential to understand fundamental chemistry of vanadium, particularly in a S-rich ligation environment (Janas & Sobota, 2005). Thus, we have been exploring the reactions of vanadium ion with thiolato containing ligands (Ye *et al.*, 2010; Tsai *et al.*, 2007). At this work, the reaction of [VCl_3THF_3] with H_3L1 [H_3L1 = HSi(5-Me–C_6H_4-2-SH)$_3$] and three equivalents of nBu-Li in CH_3CN generated a deep purple solution. The addition of the cation, [$N(C_4H_9)_4$]Br, to the reaction mixture yielded a crystalline solid of the title compound (**I**).

The molecular structure of the anion in (**I**) is shown in Fig 1. It consists a V^{III} ion coordinated to two L2 ligands [L2 = Si{CH_3(5-Me– C_6H_4-2-S)CN} (5-Me–C_6H_4-2-S)$_2$]. L2 ligand has a S2N donor set that contains two benzenethiolates and one thioimidate group. The formation of a thioimidate group in L2 ligand upon the reaction is likely a consequence of nucleophilic attack on the coordinated nitrile by thiolate and reduction of nitrile to the imidate. Similar chemistry was demonstrated in a rhenium complex with thiolate ligands (Block *et al* ., 1989). The V^{III} ion lies on the inversion centre and forms a normal octahedral geometry with a S4N2 ligation environment, four S atoms from thiolate groups and two N atoms from thioimidate groups. Two N donor atoms of thioimidate groups are in *trans* positions.

The bond lengths and bond angles in compound (**I**) are shown in Table 1. The V—S distances of 2.416 (1) Å and 2.462 (1) Å are close to those of reported six-coordinate V^{III} thiolate complexes (Ye *et al.*, 2010; Zhu *et al.*, 2002; Zhu *et al.*, 1997).

The packing diagrams of compound (**I**) are shown in Fig 2. There is no interaction observed between molecules. The methyl groups on the phenyl rings of the ligands probably prevent the occurrence of inter-molecular π-π stacking interactions. The shortest distance between centers of two phenyl rings is 5.181 (2) Å.

Experimental

A THF solution of $VCl_3(THF)_3$ (0.094 g, 0.25 mmol) was added to a acetonitrile solution (10 ml) of HSi(5-Me–C_6H_4-2-SH)$_3$ (0.202 g, 0.51 mmol) and n-BuLi (0.098 g, 1.53 mmol) to generate a deep purple solution. The solution was concentrated and layered with [$N(C_4H_9)_4$]Br (0.080 g, 0.25 mmol) in acetonitrile solution (5 ml). After one week, deep purple blocks of (I) were obtained.

Refinement

H atoms were generated geometrically, with *C*—H_{methyl} = 0.96 Å; *C*—H_{aryl} = 0.93 Å; $U_{iso}H_{methyl}$ = 1.5U_{eq}(C_{methyl}); $U_{iso}H_{aryl}$ = 1.2U_{eq}(C_{aryl}). In case of the CH_3 group, the positional parameters of the hydrogens were constrained by the SHELXL-97 command to the idealized tetrahedral geometry by the command AFIX 137 (Sheldrick, 2008).

Figures

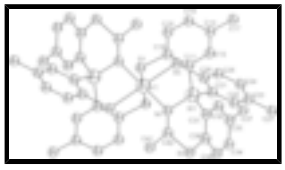


Fig. 1. The anion in (I) with displacement ellipsoids drawn at the 35 % probability level. Unlabelled atoms are generated by the symmetry operation (1–x, –y, 1–z).

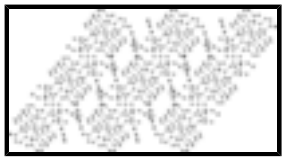


Fig. 2. The packing diagram of (I): A view of the sheet parallel to the ac plane, H atoms have been omitted for clarity.

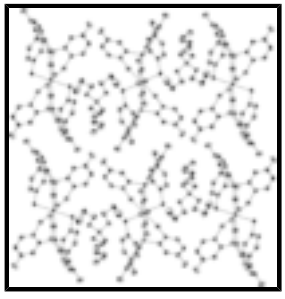


Fig. 3. View of the packing in (I) approximately down the a axis, acetonitrile molecules and H atoms have been omitted for clarity.

Tetrabutylammonium bis[4,4'-dimethyl-2,2'-(3,7-dimethyl-1*H*- 4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolato]vanadium(III) acetonitrile tetrasolvate

Crystal data

$(C_{16}H_{36}N)[V(C_{23}H_{21}NS_3Si)_2]\cdot 4C_2H_3N$	$F(000)$ = 2824
M_r = 1328.97	D_x = 1.252 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 5232 reflections
a = 27.0867 (16) Å	θ = 2.3–28.1°
b = 14.6525 (9) Å	μ = 0.40 mm^{-1}
c = 22.0590 (13) Å	*T* = 200 K
β = 126.359 (1)°	Block, deep purple
V = 7050.5 (7) Å^3	0.50 × 0.50 × 0.40 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector	8840 independent reflections

diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2004)

T_{min} = 0.490, T_{max} = 1.000

26980 measured reflections

5635 reflections with $I > 2\sigma(I)$

R_{int} = 0.063

θ_{max} = 28.4°, θ_{min} = 1.7°

$h = -33 \rightarrow 36$

$k = -19 \rightarrow 19$

$l = -28 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.053

$wR(F^2)$ = 0.144

S = 1.05

8840 reflections

396 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 1.1431P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.66 e Å^{-3}

$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
V1	0.5000	0.0000	0.5000	0.02112 (15)
Si1	0.47274 (3)	0.21699 (5)	0.46284 (4)	0.02117 (16)
S1	0.57178 (3)	0.05741 (5)	0.47806 (4)	0.02504 (16)
S2	0.53127 (3)	0.09662 (5)	0.60866 (4)	0.02710 (16)
S3	0.32852 (3)	0.19171 (5)	0.31598 (4)	0.03403 (18)
N1	0.43811 (10)	0.10819 (14)	0.42448 (12)	0.0222 (5)
N2	0.5000	0.1548 (2)	0.2500	0.0255 (7)
N3	0.2424 (3)	0.3201 (5)	0.3810 (3)	0.182 (4)
N4	0.2660 (2)	0.5583 (4)	0.1270 (3)	0.125 (2)

C11	0.55730 (12)	0.23091 (18)	0.51487 (14)	0.0237 (5)
C12	0.58127 (12)	0.31516 (19)	0.55119 (15)	0.0271 (6)
H12A	0.5547	0.3575	0.5489	0.033*
C13	0.64280 (13)	0.3384 (2)	0.59036 (16)	0.0294 (6)
C14	0.68221 (13)	0.2732 (2)	0.59387 (16)	0.0316 (6)
H14A	0.7236	0.2868	0.6193	0.038*
C15	0.66030 (13)	0.1887 (2)	0.55997 (16)	0.0298 (6)
H15A	0.6874	0.1460	0.5637	0.036*
C16	0.59806 (12)	0.16615 (18)	0.52012 (14)	0.0242 (5)
C17	0.66594 (14)	0.4308 (2)	0.62743 (18)	0.0395 (7)
H17A	0.6356	0.4595	0.6304	0.059*
H17B	0.6737	0.4681	0.5982	0.059*
H17C	0.7032	0.4232	0.6772	0.059*
C21	0.45354 (12)	0.24289 (18)	0.52897 (15)	0.0232 (5)
C22	0.41580 (12)	0.31461 (19)	0.52041 (16)	0.0274 (6)
H22A	0.3971	0.3513	0.4778	0.033*
C23	0.40540 (13)	0.3326 (2)	0.57407 (17)	0.0320 (7)
C24	0.43478 (14)	0.2781 (2)	0.63787 (17)	0.0346 (7)
H24A	0.4294	0.2902	0.6750	0.042*
C25	0.47203 (14)	0.20590 (19)	0.64746 (16)	0.0308 (6)
H25A	0.4908	0.1699	0.6905	0.037*
C26	0.48153 (13)	0.18693 (18)	0.59321 (15)	0.0253 (6)
C27	0.36400 (16)	0.4096 (2)	0.5628 (2)	0.0491 (9)
H27A	0.3652	0.4161	0.6070	0.074*
H27B	0.3228	0.3966	0.5202	0.074*
H27C	0.3776	0.4653	0.5541	0.074*
C31	0.43356 (12)	0.29874 (18)	0.38172 (15)	0.0235 (5)
C32	0.46213 (13)	0.37586 (18)	0.37750 (16)	0.0276 (6)
H32A	0.5037	0.3847	0.4153	0.033*
C33	0.43175 (14)	0.43956 (19)	0.31998 (17)	0.0322 (6)
C34	0.36973 (15)	0.4254 (2)	0.26367 (17)	0.0359 (7)
H34A	0.3481	0.4678	0.2250	0.043*
C35	0.33984 (14)	0.3497 (2)	0.26423 (16)	0.0336 (7)
H35A	0.2985	0.3406	0.2256	0.040*
C36	0.37176 (13)	0.28682 (19)	0.32289 (15)	0.0278 (6)
C37	0.46425 (16)	0.5222 (2)	0.3187 (2)	0.0464 (8)
H37A	0.5077	0.5119	0.3508	0.070*
H37B	0.4547	0.5745	0.3362	0.070*
H37C	0.4510	0.5329	0.2682	0.070*
C41	0.34431 (13)	0.01434 (19)	0.34091 (16)	0.0304 (6)
H41A	0.3674	−0.0339	0.3763	0.046*
H41B	0.3359	−0.0011	0.2933	0.046*
H41C	0.3064	0.0224	0.3348	0.046*
C42	0.38056 (12)	0.10112 (18)	0.36956 (15)	0.0256 (6)
C51	0.68030 (15)	0.3592 (2)	0.43581 (19)	0.0455 (8)
H51A	0.6921	0.4068	0.4720	0.068*
H51B	0.6849	0.3804	0.3983	0.068*
H51C	0.7059	0.3068	0.4607	0.068*
C52	0.61384 (14)	0.3336 (2)	0.39858 (17)	0.0337 (7)

H52A	0.6092	0.3133	0.4368	0.040*
H52B	0.5883	0.3871	0.3745	0.040*
C53	0.59212 (15)	0.2588 (2)	0.34048 (17)	0.0363 (7)
H53A	0.6235	0.2122	0.3602	0.044*
H53B	0.5855	0.2840	0.2956	0.044*
C54	0.53288 (13)	0.21578 (19)	0.31999 (15)	0.0289 (6)
H54A	0.5051	0.2642	0.3119	0.035*
H54B	0.5420	0.1797	0.3624	0.035*
C55	0.31405 (18)	0.0422 (3)	0.1459 (2)	0.0661 (11)
H55A	0.2820	0.0107	0.1438	0.099*
H55B	0.3003	0.0574	0.0958	0.099*
H55C	0.3243	0.0972	0.1748	0.099*
C56	0.36886 (16)	−0.0172 (2)	0.18187 (19)	0.0450 (8)
H56A	0.3578	−0.0732	0.1531	0.054*
H56B	0.3819	−0.0332	0.2320	0.054*
C57	0.42201 (15)	0.0271 (2)	0.18751 (18)	0.0384 (7)
H57A	0.4069	0.0578	0.1405	0.046*
H57B	0.4507	−0.0197	0.1956	0.046*
C58	0.45487 (14)	0.09565 (19)	0.25166 (16)	0.0302 (6)
H58A	0.4247	0.1346	0.2490	0.036*
H58B	0.4766	0.0630	0.2991	0.036*
C61	0.1622 (2)	0.2502 (4)	0.2518 (2)	0.0830 (15)
H61A	0.1721	0.2621	0.2173	0.124*
H61B	0.1229	0.2761	0.2324	0.124*
H61C	0.1611	0.1855	0.2577	0.124*
C62	0.2073 (3)	0.2900 (4)	0.3223 (3)	0.106 (2)
C63	0.18371 (17)	0.6328 (3)	0.0028 (2)	0.0598 (10)
H63A	0.1721	0.6895	0.0129	0.090*
H63B	0.1487	0.5934	−0.0250	0.090*
H63C	0.1990	0.6443	−0.0261	0.090*
C64	0.22959 (19)	0.5909 (3)	0.0711 (3)	0.0625 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0260 (3)	0.0229 (3)	0.0141 (3)	0.0032 (3)	0.0117 (3)	0.0016 (2)
Si1	0.0233 (4)	0.0242 (4)	0.0162 (3)	0.0026 (3)	0.0117 (3)	0.0012 (3)
S1	0.0306 (4)	0.0265 (3)	0.0223 (3)	0.0039 (3)	0.0181 (3)	0.0017 (3)
S2	0.0351 (4)	0.0260 (4)	0.0160 (3)	0.0032 (3)	0.0129 (3)	0.0003 (3)
S3	0.0243 (4)	0.0312 (4)	0.0345 (4)	0.0040 (3)	0.0108 (3)	0.0033 (3)
N1	0.0252 (12)	0.0269 (12)	0.0144 (10)	0.0021 (9)	0.0116 (10)	0.0003 (9)
N2	0.0369 (19)	0.0229 (16)	0.0215 (16)	0.000	0.0198 (15)	0.000
N3	0.119 (5)	0.178 (6)	0.110 (4)	0.088 (4)	−0.009 (4)	−0.069 (4)
N4	0.099 (3)	0.198 (6)	0.102 (4)	0.087 (4)	0.073 (3)	0.093 (4)
C11	0.0256 (14)	0.0292 (14)	0.0162 (13)	0.0025 (11)	0.0124 (11)	0.0034 (11)
C12	0.0289 (15)	0.0309 (15)	0.0209 (13)	0.0012 (11)	0.0144 (12)	0.0000 (11)
C13	0.0311 (15)	0.0346 (16)	0.0215 (14)	−0.0039 (12)	0.0151 (13)	−0.0008 (12)
C14	0.0260 (15)	0.0408 (17)	0.0239 (14)	−0.0023 (12)	0.0126 (13)	0.0037 (13)

C15	0.0288 (15)	0.0338 (16)	0.0263 (15)	0.0077 (12)	0.0160 (13)	0.0083 (12)
C16	0.0266 (14)	0.0298 (14)	0.0160 (13)	0.0022 (11)	0.0126 (12)	0.0041 (11)
C17	0.0369 (18)	0.0411 (18)	0.0369 (18)	−0.0092 (14)	0.0199 (15)	−0.0101 (15)
C21	0.0239 (14)	0.0263 (14)	0.0209 (13)	−0.0046 (10)	0.0141 (12)	−0.0034 (11)
C22	0.0271 (14)	0.0278 (14)	0.0275 (15)	−0.0012 (11)	0.0162 (13)	−0.0039 (12)
C23	0.0341 (16)	0.0327 (16)	0.0370 (17)	−0.0072 (12)	0.0253 (15)	−0.0137 (13)
C24	0.0466 (19)	0.0355 (16)	0.0354 (17)	−0.0084 (13)	0.0319 (16)	−0.0125 (13)
C25	0.0436 (17)	0.0271 (15)	0.0258 (15)	−0.0093 (12)	0.0229 (14)	−0.0054 (12)
C26	0.0322 (15)	0.0238 (14)	0.0238 (14)	−0.0052 (11)	0.0186 (13)	−0.0060 (11)
C27	0.050 (2)	0.050 (2)	0.056 (2)	0.0040 (16)	0.036 (2)	−0.0153 (18)
C31	0.0277 (14)	0.0261 (14)	0.0188 (13)	0.0050 (11)	0.0149 (12)	0.0001 (11)
C32	0.0318 (15)	0.0284 (15)	0.0248 (14)	0.0047 (11)	0.0179 (13)	0.0002 (11)
C33	0.0439 (18)	0.0263 (15)	0.0272 (15)	0.0069 (13)	0.0215 (14)	0.0028 (12)
C34	0.0473 (19)	0.0285 (16)	0.0236 (15)	0.0116 (13)	0.0164 (15)	0.0064 (12)
C35	0.0324 (16)	0.0293 (16)	0.0239 (15)	0.0079 (12)	0.0084 (13)	0.0001 (12)
C36	0.0319 (15)	0.0270 (14)	0.0232 (14)	0.0052 (11)	0.0156 (13)	0.0004 (11)
C37	0.052 (2)	0.0323 (17)	0.051 (2)	0.0036 (15)	0.0284 (18)	0.0137 (16)
C41	0.0319 (16)	0.0314 (16)	0.0246 (15)	−0.0008 (12)	0.0149 (13)	−0.0018 (12)
C42	0.0286 (15)	0.0304 (15)	0.0192 (13)	0.0030 (11)	0.0149 (12)	−0.0006 (11)
C51	0.047 (2)	0.0407 (19)	0.0371 (18)	0.0006 (15)	0.0188 (17)	0.0009 (15)
C52	0.0411 (18)	0.0249 (15)	0.0301 (16)	−0.0016 (12)	0.0184 (15)	−0.0026 (12)
C53	0.0438 (18)	0.0357 (17)	0.0312 (16)	−0.0070 (13)	0.0233 (15)	−0.0050 (13)
C54	0.0394 (17)	0.0278 (15)	0.0221 (14)	0.0005 (12)	0.0196 (13)	−0.0033 (11)
C55	0.049 (2)	0.084 (3)	0.060 (3)	−0.003 (2)	0.030 (2)	0.006 (2)
C56	0.052 (2)	0.051 (2)	0.0305 (17)	−0.0151 (16)	0.0235 (17)	−0.0018 (15)
C57	0.053 (2)	0.0337 (16)	0.0347 (17)	−0.0107 (14)	0.0294 (17)	−0.0064 (14)
C58	0.0423 (17)	0.0268 (14)	0.0285 (15)	−0.0020 (12)	0.0248 (14)	0.0015 (12)
C61	0.064 (3)	0.118 (4)	0.039 (2)	0.026 (3)	0.015 (2)	−0.011 (3)
C62	0.080 (4)	0.124 (5)	0.062 (3)	0.056 (3)	0.014 (3)	−0.027 (3)
C63	0.049 (2)	0.065 (3)	0.057 (2)	0.0072 (19)	0.027 (2)	0.011 (2)
C64	0.058 (3)	0.081 (3)	0.061 (3)	0.027 (2)	0.042 (2)	0.027 (2)

Geometric parameters (Å, °)

V1—N1^{i}	2.188 (2)	C31—C32	1.404 (4)
V1—N1	2.188 (2)	C32—C33	1.386 (4)
V1—S1^{i}	2.4161 (6)	C32—H32A	0.9300
V1—S1	2.4161 (6)	C33—C34	1.391 (4)
V1—S2	2.4617 (7)	C33—C37	1.508 (4)
V1—S2^{i}	2.4617 (7)	C34—C35	1.378 (4)
Si1—N1	1.788 (2)	C34—H34A	0.9300
Si1—C21	1.855 (3)	C35—C36	1.395 (4)
Si1—C11	1.868 (3)	C35—H35A	0.9300
Si1—C31	1.874 (3)	C37—H37A	0.9600
S1—C16	1.767 (3)	C37—H37B	0.9600
S2—C26	1.771 (3)	C37—H37C	0.9600
S3—C36	1.768 (3)	C41—C42	1.498 (4)
S3—C42	1.781 (3)	C41—H41A	0.9600

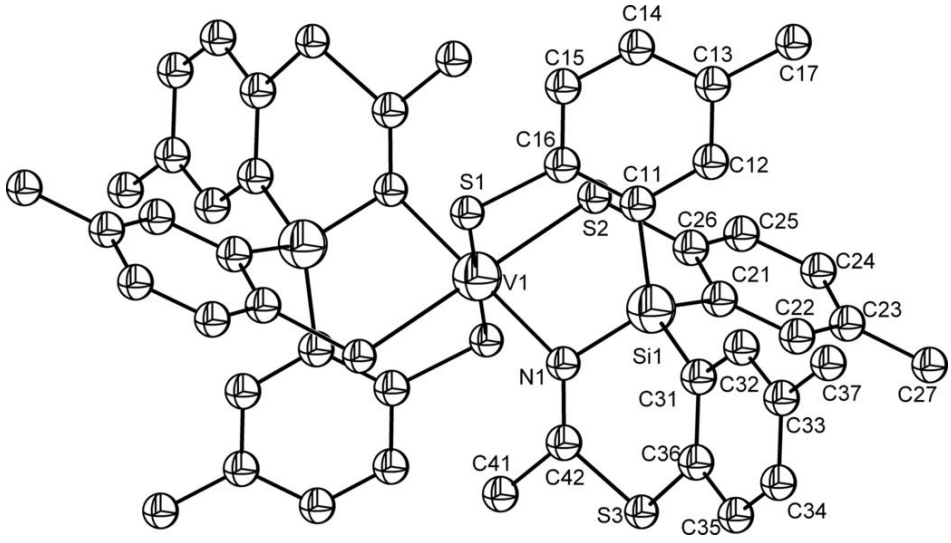
N1—C42	1.292 (3)	C41—H41B	0.9600
N2—C58	1.516 (3)	C41—H41C	0.9600
N2—C58^{ii}	1.516 (3)	C51—C52	1.518 (4)
N2—C54	1.532 (3)	C51—H51A	0.9600
N2—C54^{ii}	1.532 (3)	C51—H51B	0.9600
N3—C62	1.148 (6)	C51—H51C	0.9600
N4—C64	1.131 (5)	C52—C53	1.515 (4)
C11—C12	1.404 (4)	C52—H52A	0.9700
C11—C16	1.407 (4)	C52—H52B	0.9700
C12—C13	1.390 (4)	C53—C54	1.522 (4)
C12—H12A	0.9300	C53—H53A	0.9700
C13—C14	1.400 (4)	C53—H53B	0.9700
C13—C17	1.511 (4)	C54—H54A	0.9700
C14—C15	1.386 (4)	C54—H54B	0.9700
C14—H14A	0.9300	C55—C56	1.482 (5)
C15—C16	1.402 (4)	C55—H55A	0.9600
C15—H15A	0.9300	C55—H55B	0.9600
C17—H17A	0.9600	C55—H55C	0.9600
C17—H17B	0.9600	C56—C57	1.515 (4)
C17—H17C	0.9600	C56—H56A	0.9700
C21—C22	1.399 (4)	C56—H56B	0.9700
C21—C26	1.407 (4)	C57—C58	1.520 (4)
C22—C23	1.395 (4)	C57—H57A	0.9700
C22—H22A	0.9300	C57—H57B	0.9700
C23—C24	1.387 (4)	C58—H58A	0.9700
C23—C27	1.504 (4)	C58—H58B	0.9700
C24—C25	1.389 (4)	C61—C62	1.413 (7)
C24—H24A	0.9300	C61—H61A	0.9600
C25—C26	1.393 (4)	C61—H61B	0.9600
C25—H25A	0.9300	C61—H61C	0.9600
C27—H27A	0.9600	C63—C64	1.404 (5)
C27—H27B	0.9600	C63—H63A	0.9600
C27—H27C	0.9600	C63—H63B	0.9600
C31—C36	1.393 (4)	C63—H63C	0.9600
N1^{i}—V1—N1	180.0	C32—C33—C37	121.5 (3)
N1^{i}—V1—S1^{i}	86.54 (6)	C34—C33—C37	120.8 (3)
N1—V1—S1^{i}	93.46 (6)	C35—C34—C33	121.1 (3)
N1^{i}—V1—S1	93.46 (6)	C35—C34—H34A	119.4
N1—V1—S1	86.54 (6)	C33—C34—H34A	119.4
S1^{i}—V1—S1	180.0	C34—C35—C36	119.7 (3)
N1^{i}—V1—S2	90.53 (6)	C34—C35—H35A	120.1
N1—V1—S2	89.47 (6)	C36—C35—H35A	120.1
S1^{i}—V1—S2	81.86 (2)	C31—C36—C35	121.5 (3)
S1—V1—S2	98.14 (2)	C31—C36—S3	123.2 (2)
N1^{i}—V1—S2^{i}	89.47 (6)	C35—C36—S3	115.2 (2)
N1—V1—S2^{i}	90.53 (6)	C33—C37—H37A	109.5

S1^{i}—V1—S2^{i}	98.14 (2)	C33—C37—H37B	109.5
S1—V1—S2^{i}	81.86 (2)	H37A—C37—H37B	109.5
S2—V1—S2^{i}	180.0	C33—C37—H37C	109.5
N1—Si1—C21	103.98 (11)	H37A—C37—H37C	109.5
N1—Si1—C11	119.77 (11)	H37B—C37—H37C	109.5
C21—Si1—C11	107.92 (12)	C42—C41—H41A	109.5
N1—Si1—C31	106.07 (11)	C42—C41—H41B	109.5
C21—Si1—C31	110.86 (12)	H41A—C41—H41B	109.5
C11—Si1—C31	108.12 (12)	C42—C41—H41C	109.5
C16—S1—V1	109.28 (8)	H41A—C41—H41C	109.5
C26—S2—V1	117.31 (9)	H41B—C41—H41C	109.5
C36—S3—C42	107.89 (13)	N1—C42—C41	126.0 (2)
C42—N1—Si1	121.20 (19)	N1—C42—S3	127.1 (2)
C42—N1—V1	127.58 (18)	C41—C42—S3	106.85 (19)
Si1—N1—V1	109.60 (11)	C52—C51—H51A	109.5
C58—N2—C58^{ii}	110.3 (3)	C52—C51—H51B	109.5
C58—N2—C54	107.73 (15)	H51A—C51—H51B	109.5
C58^{ii}—N2—C54	111.25 (15)	C52—C51—H51C	109.5
C58—N2—C54^{ii}	111.25 (15)	H51A—C51—H51C	109.5
C58^{ii}—N2—C54^{ii}	107.73 (15)	H51B—C51—H51C	109.5
C54—N2—C54^{ii}	108.6 (3)	C53—C52—C51	112.2 (3)
C12—C11—C16	118.1 (2)	C53—C52—H52A	109.2
C12—C11—Si1	115.51 (19)	C51—C52—H52A	109.2
C16—C11—Si1	126.4 (2)	C53—C52—H52B	109.2
C13—C12—C11	123.3 (3)	C51—C52—H52B	109.2
C13—C12—H12A	118.4	H52A—C52—H52B	107.9
C11—C12—H12A	118.4	C52—C53—C54	111.3 (2)
C12—C13—C14	117.4 (3)	C52—C53—H53A	109.4
C12—C13—C17	121.0 (3)	C54—C53—H53A	109.4
C14—C13—C17	121.5 (3)	C52—C53—H53B	109.4
C15—C14—C13	120.8 (3)	C54—C53—H53B	109.4
C15—C14—H14A	119.6	H53A—C53—H53B	108.0
C13—C14—H14A	119.6	C53—C54—N2	114.9 (2)
C14—C15—C16	121.3 (3)	C53—C54—H54A	108.5
C14—C15—H15A	119.3	N2—C54—H54A	108.5
C16—C15—H15A	119.3	C53—C54—H54B	108.5
C15—C16—C11	119.1 (3)	N2—C54—H54B	108.5
C15—C16—S1	120.1 (2)	H54A—C54—H54B	107.5
C11—C16—S1	120.8 (2)	C56—C55—H55A	109.5
C13—C17—H17A	109.5	C56—C55—H55B	109.5
C13—C17—H17B	109.5	H55A—C55—H55B	109.5
H17A—C17—H17B	109.5	C56—C55—H55C	109.5
C13—C17—H17C	109.5	H55A—C55—H55C	109.5
H17A—C17—H17C	109.5	H55B—C55—H55C	109.5
H17B—C17—H17C	109.5	C55—C56—C57	113.2 (3)
C22—C21—C26	119.2 (2)	C55—C56—H56A	108.9
C22—C21—Si1	124.8 (2)	C57—C56—H56A	108.9

C26—C21—Si1	115.95 (19)	C55—C56—H56B	108.9
C23—C22—C21	121.8 (3)	C57—C56—H56B	108.9
C23—C22—H22A	119.1	H56A—C56—H56B	107.7
C21—C22—H22A	119.1	C56—C57—C58	111.3 (3)
C24—C23—C22	118.0 (3)	C56—C57—H57A	109.4
C24—C23—C27	121.5 (3)	C58—C57—H57A	109.4
C22—C23—C27	120.5 (3)	C56—C57—H57B	109.4
C23—C24—C25	121.4 (3)	C58—C57—H57B	109.4
C23—C24—H24A	119.3	H57A—C57—H57B	108.0
C25—C24—H24A	119.3	N2—C58—C57	113.0 (2)
C24—C25—C26	120.6 (3)	N2—C58—H58A	109.0
C24—C25—H25A	119.7	C57—C58—H58A	109.0
C26—C25—H25A	119.7	N2—C58—H58B	109.0
C25—C26—C21	119.0 (2)	C57—C58—H58B	109.0
C25—C26—S2	119.4 (2)	H58A—C58—H58B	107.8
C21—C26—S2	121.55 (19)	C62—C61—H61A	109.5
C23—C27—H27A	109.5	C62—C61—H61B	109.5
C23—C27—H27B	109.5	H61A—C61—H61B	109.5
H27A—C27—H27B	109.5	C62—C61—H61C	109.5
C23—C27—H27C	109.5	H61A—C61—H61C	109.5
H27A—C27—H27C	109.5	H61B—C61—H61C	109.5
H27B—C27—H27C	109.5	N3—C62—C61	176.4 (9)
C36—C31—C32	116.4 (2)	C64—C63—H63A	109.5
C36—C31—Si1	119.8 (2)	C64—C63—H63B	109.5
C32—C31—Si1	123.7 (2)	H63A—C63—H63B	109.5
C33—C32—C31	123.5 (3)	C64—C63—H63C	109.5
C33—C32—H32A	118.3	H63A—C63—H63C	109.5
C31—C32—H32A	118.3	H63B—C63—H63C	109.5
C32—C33—C34	117.7 (3)	N4—C64—C63	178.3 (5)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*+1, *y*, −*z*+1/2.

Fig. 1


C14
C15
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C17
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S1
C11
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C26
C25
C24
C21
V1
C22
C23
Si1
N1
C31
C32
C37
C27
C33
C36
C41
C42
S3
C35
C34

Fig. 2

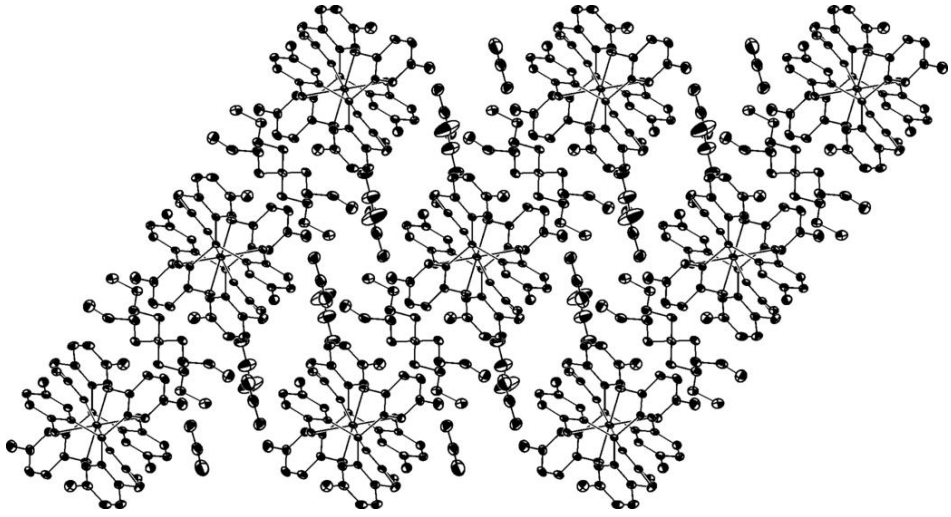

Fig. 3