

A Vanadium-Containing Iron–Sulfur Cluster with a $V_2Fe_2S_4$ Cubane-like Core. Synthesis, Structure, and Characterization of $(Et_4N)[V_2Fe_2S_4(Me_2dtc)_5]$

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A cubane-type cluster $(Et_4N)[V_2Fe_2S_4(Me_2dtc)_5]$ (**1**) has been synthesized from an assembly system $VS_4^{3-}/FeCl_2/Me_2dtc^-/PhS^-$ in acetonitrile ($Me_2dtc^- =$ dimethyldithiocarbamate). The compound **1**·2CH₃CN crystallizes in the monoclinic space group $P2_1/c$ (No. 14), with $a = 12.174(3)$ Å, $b = 22.135(4)$ Å, $c = 19.712(5)$ Å, $\beta = 105.43(2)^\circ$, $V = 5120.3$ Å³, $\rho_{calcd} = 1.50$ g/cm³, and $Z = 4$. The structure was solved from 6336 unique reflections ($I > 3\sigma(I)$) and refined by a full-matrix least-squares method to $R = 0.053$. The cluster anion contains a cubane-like $[V_2Fe_2S_4]^{4+}$ core, in which the V–V, Fe–Fe, and V–Fe(mean) distances of the V_2Fe_2 tetrahedron are 2.745–(2), 2.681(1), and 2.780(6) Å, respectively. The Mössbauer effect and the structural parameters indicate that the oxidation states of the Fe and V atoms in the $[V_2Fe_2S_4]^{4+}$ core are both +3. The ¹H NMR shows the paramagnetism of the cluster. The chemical shift of ⁵¹V NMR was observed at –391 ppm. The FAB-MS behavior of the cluster indicates the bond breaking of the cluster core.

Introduction

Immense interest in vanadium-containing heterometallic sulfur complexes in recent years has stemmed from their important role in some metalloenzymes,¹ including V nitrogenase.² They are also of interest to inorganic chemists since such vanadium heterometallic complexes have until recently been little investigated. We have reported a series of Mo/Fe/S³ and Mo/Cu/S⁴ clusters (M = Mo, W) containing R₂dtc ligands obtained from

the $MoS_4^{2-}/FeCl_2/R_2dtc^-$ and $MoS_4^{2-}/CuCl/R_2dtc^-$ systems, respectively, and have extended our research to include VS_4^{3-} . Tetrathiovanadate anion has proved to be a useful starting point for the preparation of poly- and heterometallic sulfide clusters in the self-assembly reaction systems illustrated in Scheme 1. Several kinds of heterometallic V/Cu/S⁹ and V/Ag/S^{9a,10} clusters with R₂dtc⁻ ligands have been prepared successfully from the $VS_4^{3-}/CuCl/R_2dtc^-/PhS^-$ and $VS_4^{3-}/Ag(PPh_3)_2Cl/R_2dtc^-/PhS^-$ self-assembly systems, respectively. However, few reports on the V/Fe/S cluster compounds have been found to date. Holm et al. have reported a series of linear^{8a} and cubane-like^{8b–d} V/Fe/S clusters and a $VFe_4S_6(PEt_3)_4X$ ($X = Cl, SR$) cluster¹¹ which contains a cuboidal Fe_4S_3 fragment for simulating the active center of the V nitrogenase. Rauchfuss et al. have also prepared several V/Fe/S clusters,¹² one of which is a $V_2Fe_2S_4$ cubane-like cluster.^{12a} This paper reports the preparation, structure, and spectroscopic characterizations of a new $V_2Fe_2S_4$ cluster $(Et_4N)[V_2Fe_2S_4(Me_2dtc)_5]$ as our successive study on the VS_4^{3-} reaction system.

Experimental Section

All manipulations were carried out under a dinitrogen atmosphere, and a Schlenk apparatus was used throughout the experimental process. The solvents were dried with molecular sieves and degassed prior to use. Reagents Et₄NCl and anhydrous FeCl₂ were commercially

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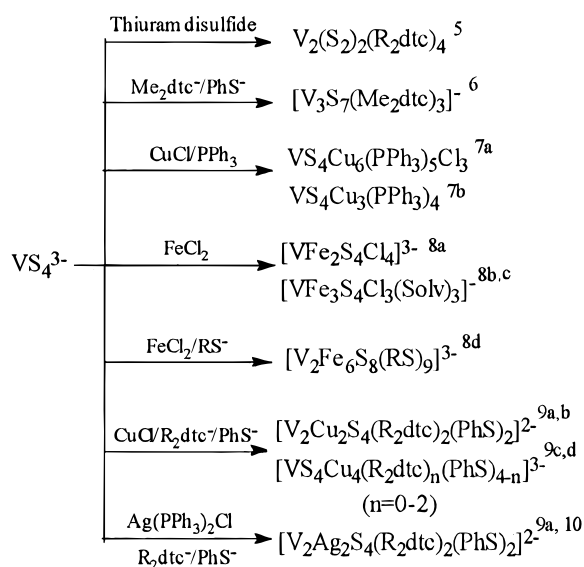
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Scheme 1. The Reactions in the VS_4^{3-} System**Table 1.** Summary of Crystallographic Data for $(\text{Et}_4\text{N})[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{NCS}_2)_5] \cdot 2\text{CH}_3\text{CN}$

formula	$\text{C}_{27}\text{H}_{58}\text{Fe}_2\text{N}_8\text{S}_{14}\text{V}_2$
fw	1155.27
a , Å	12.174(3)
b , Å	22.135(4)
c , Å	19.712(5)
β , deg	105.43(2)
V , Å ³	5120.3
Z	4
space group	$P2_1/c$ (No. 14)
ρ_{calcd} , g/cm ³	1.50
μ , cm ⁻¹	14.8
T , °C	23 ± 1
λ , Å	0.710 69
R^a	0.053
R_w^b	0.075

$$^a R = \sum |F_o - F_c| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}.$$

available and used without further purification. Compounds $(\text{NH}_4)_3\text{VS}_4$ ^{8a} and PhSNa ¹³ were obtained according to literature methods. Me_2dtcNa was prepared in good yield by reaction of equimolar amounts of Me_2NH , NaOH , and CS_2 in aqueous solution (at about 5–10 °C) as previously described.¹⁴

Synthesis of $(\text{Et}_4\text{N})[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{dtc})_5]$ (I). A mixture of $(\text{NH}_4)_3\text{VS}_4$ (0.67 g, 2.9 mmol), FeCl_2 (1.09 g, 8.6 mmol), Me_2dtcNa (1.64 g, 11.5 mmol), and Et_4NCl (1.90 g, 11.5 mmol) in 100 mL of CH_3CN was stirred at room temperature for 24 h. After the undissolved material was filtered off, the dark brown-red solution was allowed to stand in a refrigerator for separation of the inorganic salt. After filtration, the filtrate was again kept in the refrigerator for several days to give black rectangular crystals, which were collected, washed with $\text{CH}_3\text{CN}/(\text{CH}_3)_2\text{CO}$ (1:1), and dried in vacuo to afford 0.52 g (16.7%, based on V) of product. Anal. Calcd for $\text{C}_{23}\text{H}_{50}\text{Fe}_2\text{N}_6\text{S}_{14}\text{V}_2$: C, 25.7; H, 4.7; Fe, 10.4; N, 7.8; S, 41.8; V, 9.5. Found: C, 24.0; H, 4.35; Fe, 10.35; N, 7.04; S, 40.11; V, 10.17. IR (KBr, cm⁻¹): 314, 360 (V–S, Fe–S), 441 (V– μ_3 -S), 975 (C–S), 1135 (N–C), 1503 (C=N). ¹H NMR (DMSO- d_6): δ 1.15 (CH_3 , Et_4N), 3.20 (CH_2 , Et_4N), 47.90 (α -H, Me_2dtcFe), 19.92, 9.61 (α -H, Me_2dtcV) ppm. ⁵¹V NMR (DMSO- d_6): δ –391 ppm.

Data Collection and Reduction. The title compound was recrystallized from $\text{CH}_3\text{CN}/\text{DMF}$, affording a black rectangular crystal with approximate dimensions of 0.85 × 0.55 × 0.60 mm, which was taken

out from the solution and coated immediately with epoxy resin and sealed in a glass capillary. Data collection was performed with Mo $K\alpha$ radiation ($\lambda = 0.710 69$ Å) on a MSC/Rigaku diffractometer equipped with a graphite monochromator at 23 ± 1 °C using ω – 2θ scan technique. From the systematic absences of $h0l$ ($l = 2n$), $0k0$ ($k = 2n$), and subsequent least-squares refinement, the space group was determined to be $P2_1/c$ (No. 14). A total of 9748 reflections were collected, of which 9279 were unique. The reflections were corrected for Lorentz polarization effects, linear decay, and empirical absorption (ψ scan). Intensities of equivalent reflections were averaged. An empirical absorption correction using the program DIFABS¹⁵ was made after structure refinement with isotropic thermal parameters.

The crystal data and intensity collection are listed in Table 1.

Structure Solution and Refinement. The structure was solved by direct methods with the MULTAN-83 program followed by successive difference Fourier syntheses. The structure was refined in full-matrix least-squares using anisotropic thermal parameters for all the non-hydrogen atoms except the solvent molecules. All hydrogen atoms were geometrically located and added to the structure factor calculations, but their positions were not refined. Two carbon atoms, C(81) and C(82), in one of the two solvent molecules CH_3CN were statistically distributed at two positions, respectively, having an occupancy of 0.5 for each position, and the acetonitrile molecule with C(81) and C(82) was refined rigidly. The function minimized was $\sum w(|F_o| - |F_c|)^2$, and the weight w is defined as per the Killean and Lawrence method with terms of 0.020 and 1.0.¹⁶ Atomic scattering factors were taken from Cromer and Waber.¹⁷ The final cycle of refinement included 444 variable parameters for 6336 reflections with $I > 3.0\sigma(I)$ and converged to 0.18 σ with unweighted and weighted agreement factors of

$$R_1 = \sum |F_o - F_c| / \sum |F_o| = 0.053$$

$$R_2 = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2} = 0.075$$

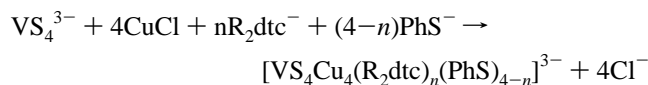
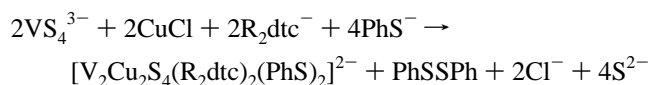
The standard deviation of an observation of unit weight was 1.90. The highest peak in the final difference Fourier had a height of 1.04 e/Å³, and the minimum negative peak, 0.16 e/Å³. All calculations were performed on a COMPAQ PL4/50 computer using the MoEM/PC program.¹⁸

Other Physical Measurements. The IR spectrum was recorded on an Bio-Rad FTS-40 model spectrophotometer. The ¹H and ⁵¹V NMR spectra were recorded on a Bruker-Am 500 spectrometer with TMS and VOCl_3 as standards, respectively. The Mössbauer spectrum was measured at liquid-nitrogen temperature on a constant-acceleration spectrometer using 50 mCi of ⁵⁷Co in a Pd matrix held at 21 ± 1 °C as the source. The mass spectroscopic measurement was performed on a Finnigan MAT-8230 GL/MS/DS mass spectrometer in FAB mode at a resolution of 1000, FAB mode parameters: target gas of Ar with pressure of 1 Pa, discharge voltage 8 kV, discharge current 2 mA, m -nitrobenzyl alcohol (NBA) matrix. Elemental analyses were carried out by the Analytical Chemistry Group of this Institute.

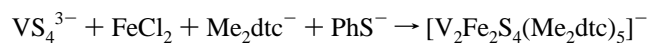
Results and Discussion

Synthesis. After a series of $\text{MS}_4^{2-}/\text{FeCl}_2$ (or CuCl)/ $R_2\text{dtc}^-$ reaction systems^{3,4} ($M = \text{Mo}, \text{W}$) have been extensively investigated in our group, a new $VS_4^{3-}/\text{CuCl}/R_2\text{dtc}^-/\text{PhS}^-$ reaction system has also been used to extend our research and has afforded two types of V/Cu/S clusters, one of which is a $V_2Cu_2S_4$ cubane-like cluster,^{9a,b} and the other is a VCu_4 planar cluster.^{9c,d} Both of the clusters contain $R_2\text{dtc}^-$ and PhS^- mixed ligands.

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In this work, when FeCl_2 is used as the heterometal instead of CuCl , a $\text{V}_2\text{Fe}_2\text{S}_4$ single cubane cluster is separated as shown in the following reaction:



In contrast with the $\text{VS}_4^{3-}/\text{CuCl}/\text{R}_2\text{dtc}^-/\text{PhS}^-$ reaction system,^{9a} which produces the cluster of mixed ligands, the present V/Fe/S system affords a cluster product containing only a Me_2dtc^- ligand. This indicates that the benzenethiolate only acts as a reducing agent together with FeCl_2 to reduce V(V) to V(III) and also explains that the bidentate Me_2dtc^- ligand has obvious superiority in coordinating to the Fe atom over the monodentate PhS^- ligand, since the chelating coordination will satisfy a stable five-coordinate geometry of the Fe site in the cuboidal core. Interestingly, even though a bridging coordination of Me_2dtc^- can occur between any two of the four metal atoms (V and Fe), in the cubane skeleton two vanadium atoms are bridged selectively by a Me_2dtc^- ligand, resulting in more stable six-coordination of the V sites than that of the Fe site(s).

It is noteworthy that the Me_2dtc^- ligand exhibits its distinct behavior in all the mentioned reaction systems from the other R_2dtc ligands. An unexpected compound having a special structure was usually obtained when using Me_2dtc^- to replace the other R_2dtc ligands. For example, in the $\text{MS}_4^{2-}/\text{CuCl}/\text{R}_2\text{dtc}^-$ system ($\text{M} = \text{Mo}, \text{W}$), the use of Me_2dtc^- has led to a hetero heptanuclear cluster $[\text{M}_2\text{Cu}_5\text{S}_8(\text{Me}_2\text{dtc})_3]^{2-}$ ^{4b,c} consisting of two defective cubane units, MCu_2S_3 and MCu_3S_3 , while other R_2dtc ligands lead to an MCu_3 planar cluster $[\text{MCu}_3\text{S}_4(\text{R}_2\text{dtc})_3]^{2-}$ ^{4a,d,e}. In a $\text{VS}_4^{3-}/\text{CuCl}/\text{Me}_2\text{dtc}^-/\text{PhS}^-$ system, besides $[\text{V}_2\text{Cu}_2\text{S}_4(\text{Me}_2\text{dtc})_2(\text{PhS})_2]^{2-}$,^{9b} we have also obtained a new trinuclear cluster $[\text{V}_3\text{S}_7(\text{Me}_2\text{dtc})_3]^-$.^{6a} As a similar case, in this work the reaction system using Me_2dtc^- results in the $\text{V}_2\text{Fe}_2\text{S}_4$ cubane-like cluster which has not yet been observed when using the other R_2dtc ligands. These interesting results may be attributed to the smaller steric effect and the stronger $\sigma-\pi$ conjugation effect of the methyl group than those of other alkyl groups in R_2dtc ligand, which give rise to the stabilization of the cluster containing Me_2dtcM units and lead to a variety of cluster structures.

Structure. The crystal structure of $1 \cdot 2\text{CH}_3\text{CN}$ consists of a discrete anion and Et_4N^+ cation and two solvent molecules in an asymmetric unit. The cation and the solvent molecules have their expected structures and will not be considered further. An ORTEP projection of the anion is depicted in Figure 1, and the selected bond distances and angles are shown in Tables 2 and 3, respectively.

The anion contains a $\text{V}_2\text{Fe}_2\text{S}_4$ distorted cubane core which consists of two rhombic units V_2S_2 and Fe_2S_2 by the combination of V–S and Fe–S bonds between them. None of the six rhombic units of the $\text{V}_2\text{Fe}_2\text{S}_4$ core is planar; however, the six pairs of opposite edges form six nearly perfect planes of which plane V(1)S(1)V(2)S(4) can extend to involve S(51), S(52), C(50), and N(50) atoms with the largest deviation of 0.05 Å from their least-squares plane. The anion has an ideal C_{2v} symmetry, but is not crystallographically imposed, with a C_{2v} axis passing through the N(50)–C(50) bond and the centers of the V_2S_2 and Fe_2S_2 rhombic units. Each metal atom is chelated

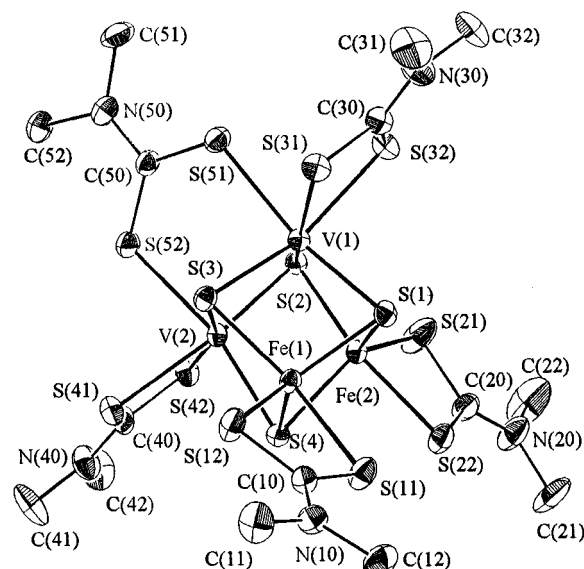


Figure 1. ORTEP diagrams showing 50% probability ellipsoids for the anion $[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{dtc})_5]^-$ with numbering scheme.

Table 2. Selected Bond Distances (Å) for $[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{CNS}_2)_5]^-$

V(1)–V(2)	2.745(2)	Fe(1)–Fe(2)	2.681(1)
V(1)–Fe(1)	2.780(1)	V(1)–Fe(2)	2.798(2)
V(2)–Fe(1)	2.769(2)	V(2)–Fe(2)	2.775(1)
	mean ^a (V–Fe)		2.780(6)
V(1)–S(1)	2.266(2)	V(2)–S(2)	2.286(2)
V(1)–S(2)	2.281(2)	V(2)–S(3)	2.271(2)
V(1)–S(3)	2.272(2)	V(2)–S(4)	2.264(2)
	mean		2.273(4)
V(1)–S(31)	2.512(3)	V(1)–S(32)	2.518(3)
V(2)–S(41)	2.498(3)	V(2)–S(42)	2.519(3)
V(1)–S(51)	2.552(2)	V(2)–S(52)	2.536(3)
	mean		2.523(8)
Fe(1)–S(1)	2.238(2)	Fe(2)–S(1)	2.234(2)
Fe(1)–S(3)	2.247(3)	Fe(2)–S(2)	2.252(3)
Fe(1)–S(4)	2.232(2)	Fe(2)–S(4)	2.238(2)
	mean		2.240(3)
Fe(1)–S(11)	2.342(2)	Fe(2)–S(21)	2.294(2)
Fe(1)–S(12)	2.286(2)	Fe(2)–S(22)	2.361(2)
	mean		2.321(18)
S(11)–C(10)	1.697(8)	S(12)–C(10)	1.723(8)
S(21)–C(20)	1.717(9)	S(22)–C(20)	1.696(7)
S(31)–C(30)	1.721(7)	S(32)–C(30)	1.726(9)
S(41)–C(40)	1.716(9)	S(42)–C(40)	1.714(7)
S(51)–C(50)	1.707(8)	S(52)–C(50)	1.718(8)
	mean		1.714(4)
N(10)–C(10)	1.29(2)	N(40)–C(40)	1.32(2)
N(20)–C(20)	1.319(9)	N(50)–C(50)	1.35(1)
N(30)–C(30)	1.32(2)	mean	1.32(1)

^a In this and succeeding tables the standard deviation of the mean value is estimated from $\sigma = [\sum_{i=1}^N (x_i - \bar{X})^2 / N(n - 1)]^{1/2}$.

by a Me_2dtc^- ligand while the fifth Me_2dtc^- is bridged between the two V atoms to make a distorted octahedral site for each V atom. The two five-coordinate Fe atoms have distorted trigonal bipyramidal geometry with S(3), S(11) and S(2), S(22) locating on the respective apical positions. There are three types of intermetallic interactions in the $\text{V}_2\text{Fe}_2\text{S}_4$ core. The first one is the Fe–Fe distance of 2.681(1) Å, which is the shortest among those seen in some cubane cluster compounds containing R_2dtcFe groups shown in Table 4 and is comparable with those found in some complexes^{3a,b,19} with an Fe(III)–Fe(III) bond (2.671–2.712 Å) despite the different coordination number in some of these complexes. The second type of metal–metal bond is V–V with a distance of 2.745(2) Å, which is shorter than those seen in other $\text{V}_2\text{M}_2\text{S}_4$ clusters ($\text{M} = \text{Fe}, 2.95$;^{12a} Cu, 2.787(4),^{9a} 2.823(5),^{9b} 2.774(4);^{6b} Ag, 2.793(1);^{9a} V, 2.873(3)²⁰ and 2.854(5)²⁰ Å) and is comparable with certain complexes

Table 3. Selected Bond Angles (deg) in $[V_2Fe_2S_4(Me_2CNS)_5]^-$

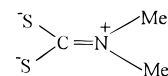
S(1)–V(1)–S(2)	100.17(8)	S(2)–V(2)–S(3)	105.02(8)
S(1)–V(1)–S(3)	101.01(7)	S(2)–V(2)–S(4)	101.20(7)
S(2)–V(1)–S(3)	105.15(8)	S(3)–V(2)–S(4)	101.04(8)
S(1)–V(1)–S(31)	89.66(8)	S(2)–V(2)–S(41)	160.40(9)
S(1)–V(1)–S(32)	89.44(7)	S(2)–V(2)–S(42)	93.91(7)
S(1)–V(1)–S(51)	167.25(8)	S(2)–V(2)–S(52)	86.78(8)
S(2)–V(1)–S(31)	159.99(8)	S(3)–V(2)–S(41)	88.78(7)
S(2)–V(1)–S(32)	92.78(7)	S(3)–V(2)–S(42)	157.36(7)
S(2)–V(1)–S(51)	86.52(8)	S(3)–V(2)–S(52)	88.54(8)
S(3)–V(1)–S(31)	89.80(7)	S(4)–V(2)–S(41)	89.43(7)
S(3)–V(1)–S(32)	157.10(9)	S(4)–V(2)–S(42)	87.02(8)
S(3)–V(1)–S(51)	87.53(7)	S(4)–V(2)–S(52)	165.34(9)
S(31)–V(1)–S(32)	69.75(7)	S(41)–V(2)–S(42)	70.01(7)
S(31)–V(1)–S(51)	80.84(8)	S(41)–V(2)–S(52)	79.61(7)
S(32)–V(1)–S(51)	79.33(7)	S(42)–V(2)–S(52)	80.12(8)
S(1)–Fe(1)–S(3)	102.66(7)	S(1)–Fe(2)–S(2)	102.07(9)
S(1)–Fe(1)–S(4)	105.25(8)	S(1)–Fe(2)–S(4)	105.18(8)
S(3)–Fe(1)–S(4)	102.81(9)	S(2)–Fe(2)–S(4)	103.09(7)
S(1)–Fe(1)–S(11)	91.68(8)	S(1)–Fe(2)–S(21)	131.87(8)
S(1)–Fe(1)–S(12)	125.4(1)	S(1)–Fe(2)–S(22)	87.87(9)
S(3)–Fe(1)–S(11)	157.90(8)	S(2)–Fe(2)–S(21)	84.09(8)
S(3)–Fe(1)–S(12)	83.48(8)	S(2)–Fe(2)–S(22)	157.29(7)
S(4)–Fe(1)–S(11)	89.24(8)	S(4)–Fe(2)–S(21)	119.98(9)
S(4)–Fe(1)–S(12)	126.5(2)	S(4)–Fe(2)–S(22)	93.72(8)
S(11)–Fe(1)–S(12)	74.50(8)	S(21)–Fe(2)–S(22)	74.23(8)
Fe(1)–S(1)–Fe(2)	73.65(7)	Fe(2)–S(2)–V(1)	76.22(7)
Fe(1)–S(1)–V(1)	76.24(7)	Fe(2)–S(2)–V(2)	75.39(6)
Fe(2)–S(1)–V(1)	76.88(8)	V(1)–S(2)–V(2)	73.88(6)
Fe(1)–S(3)–V(1)	75.94(6)	Fe(1)–S(4)–Fe(2)	73.70(7)
V(1)–S(3)–V(2)	74.33(6)	Fe(2)–S(4)–V(2)	76.10(6)

containing a V–V single bond, such as (*i*-PrCp)₂V₂S₄ (2.610(1) Å),²¹ V₂(S₂)₂(S₂CMe)₄ (2.800(2) Å),²² [V₂(S₂)₂(CS₃)₄]⁴⁻ (2.872(6) Å),²³ V₂(S₂)₂(*i*-Bu₂dtc)₄ (2.851 Å),⁵ and V₂(S₂)₂(Et₂-dtc)₄ (2.884(4) Å).²⁴ The V–Fe distances, being the third type of M–M bond in the cubane cluster, have a mean distance of 2.780(6) Å, which is slightly longer than those in several V/Fe/S compounds.^{8c,d,12a} It is believed that the four metal atoms contain six M–M bonds forming a V₂Fe₂ tetrahedron in the V₂Fe₂S₄ cuboidal core.

The M–S_{dtc} and M–S_{core} distances are sensitive to the oxidation state of the metal atom. The appropriate available comparison of Fe–S_{dtc} and Fe–S_{core} bond lengths in some related five-coordinate Fe/R₂dtc⁻ compounds is summarized in Table 4. The Fe–S_{dtc} distances in **1** range from 2.286(2) to 2.361(2) Å with a mean value of 2.321(18) Å, which fall in with the ranges of the Fe–S_{dtc} distances found in other compounds containing five-coordinate Fe(III) atoms, but are significantly shorter than those in some complexes in which the oxidation states of the Fe atoms are all lower than +3. The Fe–μ₃-S distances in the V₂Fe₂S₄ core also show a feature

similar to the Fe–S_{dtc} bonds when compared with those in some related compounds. So it is reasonable to consider that the Fe atoms in **1** have the formal oxidation state of +3. The V–S_{dtc} bond length of 2.523(8) Å (av) is obviously longer than those of all the complexes^{5,6a,9a,b,24,31,32} in which the V atoms have oxidation states being higher than +3. Therefore, the oxidation states of the metal atoms in complex **1** can be deduced to be 2V(III) + 2Fe(III).

Infrared Spectrum. The bands near 1500 and 1000 cm⁻¹ are very characteristic for the C–N and C–S stretching vibrations of the R₂dtc ligand.³² For compound **1**, the strong absorption at 1518 cm⁻¹ is assigned to the stretching vibration of the C=N bond with a considerable double-bond character in the canonical form.



This is consistent with the bond distances of the C(n0)–N(n0) (*n* = 1–5) (Table 2) of 1.29–1.35 Å.

In the low-frequency region, the absorptions at 330–360 cm⁻¹ are assigned to Fe–S_{dtc} and V–S_{dtc} vibrations, respectively.³² In the region 400–500 cm⁻¹ where the M–μ₃-S vibrations are expected,³³ the band at 440 cm⁻¹ can be assigned to the V–μ₃-S vibration, which is consistent with that of [V₃S₇(Me₂dtc)₃]⁻ (ν_{V-S}, 442 cm⁻¹)⁶ and shifts to low frequency in comparison with the data of VS₄³⁻ (ν_{V-S}, 476 cm⁻¹).^{8a}

NMR Spectrum. There are three types of Me₂dtc groups in the cluster, one of which coordinates to the Fe site, the second to the V site, and the third bridges between the two V atoms. The corresponding three signals at 47.9, 19.2, and 9.6 ppm in the ¹H spectrum (Figure 2a) can tentatively be assigned to the chemical shifts of the three kinds of N(CH₃)₂, respectively. In comparison with the free ligand Me₂dtcNa (3.5 ppm, DMSO-*d*₆), the proton chemical shifts of N(CH₃)₂ obviously move downfield, indicating the paramagnetism of the cluster. The measurement of bulk magnetic susceptibility shows that complex **1** has μ_{eff} = 1.8 μ_B at 300 K, implying the probability of a low-spin state of Fe(III). The signal at 47.9 ppm associated to the Me₂dtcFe is consistent with that in MFe₃S₄(Me₂dtc)₅ (δ_{α-H}: M = Mo, 45.7 ppm; M = W, 46.3 ppm),^{3a} containing three Fe(III) atoms of low-spin state (*S* = 1/2).³⁴ Owing to the chelating and bridging coordinations, the ¹H NMR shifts of Me₂-dtcV appear at 19.2 and 9.6 ppm, which are comparable to those of the compounds V(MePh(dtC))₃ (δ_{α-H}: 13.47 ppm)³⁵ and [V₃S₇(Me₂dtc)₃]⁻ (δ_{α-H}: 10.67, 8.72 ppm).^{6a}

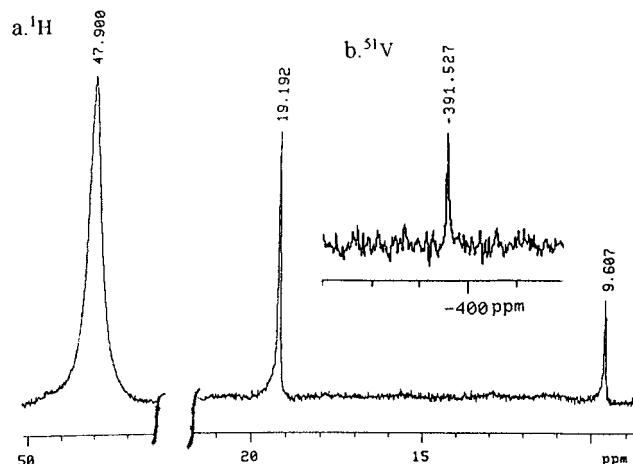
Under anaerobic conditions, it was observed that the ¹H NMR spectrum of the measured solution would change after several

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Table 4. Summary and Comparison of the Structural Parameters of Five-Coordinate Fe Sites in Some Cubane-Type Cluster Compounds with R_2dtc^- Ligand

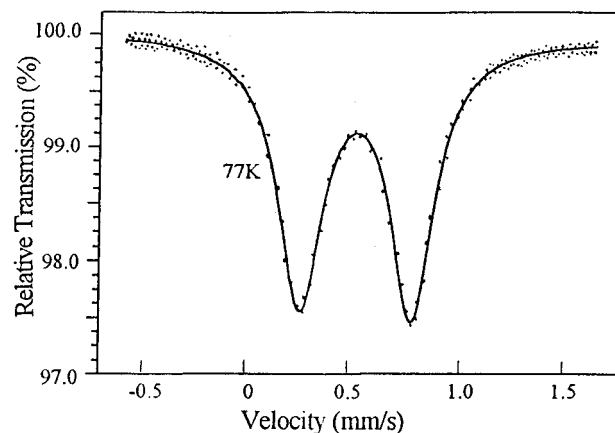
compd	oxidation state of Fe	Fe-S _{dtc} ^a (Å)	Fe-μ ₃ -S ^a (Å)	Fe-Fe ^a (Å)	ref
[V ₂ Fe ₂ S ₄ (Me ₂ dtc) ₅] ⁻	+3	2.321(18)	2.240(3)	2.681(2)	this work
MoFe ₃ S ₄ (R ₂ dtc) ₅	+3	2.308(7)	2.223(16)	2.706(18)	3a
WFe ₃ S ₄ (C ₄ H ₈ dtc) ₅	+3	2.34(4)	2.227(12)	2.718(3)	3b
Fe ₄ S ₄ (C ₅ H ₁₀ dtc) ₄	+3	2.283(2)	2.238(7)	2.87(9)	25
Mo ₂ Fe ₂ S ₄ (Et ₂ dtc) ₅	<+3	2.38(5)	2.256(11)	2.784(3)	26
[Fe ₄ S ₄ (Et ₂ dtc) ₄] ⁻	+2.75	2.397(1)	2.289(21)	2.92(5)	27
[Fe ₄ S ₄ (Et ₂ dtc) ₄] ²⁻	+2.5	2.50(2)	2.29(2)	2.90(4)	28
[Fe ₄ S ₄ (PhS) ₂ (Et ₂ dtc) ₂] ²⁻	+2.5	2.49(6)	2.31(5)	3.053(3)	29
[Fe ₄ S ₄ Cl ₂ (Et ₂ dtc) ₂] ²⁻	+2.5	2.50(8)	2.33(4)	3.045(4)	29

^a Average value.**Figure 2.** ¹H and ⁵¹V NMR spectra of (Et₄N)[V₂Fe₂S₄(Me₂dtc)₅] in DMSO-*d*₆ solution at room temperature.

hours. A new absorption peak appeared at 67.2 ppm assigned to the signal of Fe(Me₂dtc)₃.^{3a} This proposes that complex **1** is not stable in DMSO-*d*₆ solution and the skeleton of V₂Fe₂S₄ would undergo a degradation process affording Fe(Me₂dtc)₃.

An absorption of ⁵¹V NMR was observed at -391 ppm (Figure 2b). The general features of the ⁵¹V NMR shift depend strongly upon the oxidation state and coordination environment (ligand electronegativity and coordination number, etc.).^{23,36} Compared to VS₄³⁻ (δ 1388 ppm)^{36b,37} and [VS₄Cu₄(R₂dtc)_{*n*}(PhS)_{4-*n*}]³⁻ (δ 663, 670 ppm),^{9d} the vanadium(III) in **1** has a lower oxidation state and a larger shielding effect caused by six sulfur atoms coordinating directly to the metal atom, so the ⁵¹V absorption peak occurring upfield seems to be reasonable.

Mössbauer Spectrum. The solid Mössbauer spectrum of cluster **1** at liquid-nitrogen temperature is shown in Figure 3. Only one type of Fe atom with a quadrupole splitting of 0.23 mm/s and an isomer shift of 0.42 mm/s was observed. The Mössbauer parameters obtained by least-squares fitting with the experimental absorption spectrum are shown in Table 5, together with the data of a number of related complexes containing a well-defined Fe(mean) oxidation state in a five-coordination environment with an R₂dtc⁻ ligand. The value of the isomer shift (IS) observed for the Fe sites in **1** is very close to those found for the five-coordinate Fe(III) in MFe₃S₄(R₂dtc)₅^{3a} (M = Mo, W, Fe, R₂ = Me₂, Et₂, C₄H₈). The IS values for the five-coordinate Fe sites in some other compounds with a lower oxidation level than +3 are all significantly larger than that of cluster **1**. We, therefore, can also conclude that the Fe sites of

**Figure 3.** Mössbauer spectrum of (Et₄N)[V₂Fe₂S₄(Me₂dtc)₅] at liquid-nitrogen temperature. Solid line represents the least-squares fits for the experimental data.**Table 5.** Isomer Shifts (IS, mm/s) at 77 K for [V₂Fe₂S₄(Me₂dtc)₅]⁻ and Related Compounds for Five-Coordinate Fe Sites

compd	oxidation state of Fe	IS ^a	ref
[V ₂ Fe ₂ S ₄ (Me ₂ dtc) ₅] ⁻	+3(2.93) ^b	0.42	this work
MoFe ₃ S ₄ (Me ₂ dtc) ₅	+3(3.06)	0.35	3a
MoFe ₃ S ₄ (C ₄ H ₈ dtc) ₅	+3(3.01)	0.38	3a
MoFe ₃ S ₄ (Et ₂ dtc) ₅	+3(3.05)	0.36	3a
WFe ₃ S ₄ (Me ₂ dtc) ₅	+3(2.99)	0.39	3a
WFe ₃ S ₄ (C ₄ H ₈ dtc) ₅	+3(2.99)	0.39	3a
Fe ₄ S ₄ (Et ₂ dtc) ₄	+3(2.95)	0.41	3a
[MoFe ₃ S ₄ (Et ₂ dtc) ₅] ⁻	+2.67(2.69)	0.54	3a
[Fe ₄ S ₄ (PhS) ₂ (Et ₂ dtc) ₂] ²⁻	+2.5(2.49)	0.64	29
[Fe ₄ S ₄ Cl ₂ (Et ₂ dtc) ₂] ²⁻	+2.5(2.53)	0.62	29
[Fe(Et ₂ dtc) ₂] ₂	+2(1.98)	0.90	38

^a Relative to Fe metal at room temperature. ^b The data in the parentheses are deduced according to the equation IS = 1.902 - 0.506X.

1 have found formal oxidation state of +3, consistent with the result from the structure data.

It is also noticed that the isomer shifts of a series of Fe complexes and clusters containing Fe atom(s) in a similar coordination environment should follow an empirical linear relationship, IS = *a* - *b*X, where *a* and *b* are constants and X is the mean oxidation state of Fe atom. On the basis of a regression on the isomer shift data of Table 5, we present the following equation to evaluate the Fe(mean) oxidation state (X) in five-coordination FeS₅ sites containing R₂dtc⁻ ligand(s),

$$IS = 1.902 - 0.506X$$

and deduce the mean oxidation state of the Fe atoms in cluster **1** as X = 2.93. A similar formula for the four-coordination Fe in tetrahedral FeS₄ sites has been presented by Holm and co-workers previously.^{8d,11b,39}

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Mass Spectrum. Fast atom bombardment mass spectrometry (FAB-MS) has been used to analyze a series of $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{SEt}, \text{SPh}$)⁴⁰ and $\text{MFe}_3\text{S}_4(\text{R}_2\text{dtc})_5$ ($\text{M} = \text{Mo}, \text{W}$)⁴¹ cubane clusters. The FAB-MS data of the cluster **1** have been obtained by using *m*-nitrobenzyl alcohol as a matrix. The main fragment ions containing metal and their relative abundances referring to Et_4N^+ (m/z 130) are listed in Table 6. It is deduced that the breakdown of the cluster skeleton is the major cleavage process indicated by the occurrence of the following fragment ions: $[\text{Fe}_2\text{S}_2(\text{Me}_2\text{dtc})_2]^+$ (m/z 416), $[\text{FeS}_2\text{V}(\text{Me}_2\text{dtc})_2]^+$ (m/z 411), $[\text{V}_2\text{S}_2(\text{Me}_2\text{dtc})_2]^+$ (m/z 406), $[\text{Fe}(\text{Me}_2\text{dtc})_3]^+$ (m/z 416), and $[\text{Fe}(\text{Me}_2\text{dtc})_2]^{2+}$ (m/z 296). The latter two ions are generated by a recombination, which has been reported for $\text{MoFe}_3\text{S}_4(\text{R}_2\text{-dtc})_5$ complexes,⁴¹ of fragment species formed by the core breaking. A similar reaction involving the matrix molecule has also been reported in the literature.⁴⁰

The peak of the cluster ion $[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{dtc})_5]^+$ (m/z 942) is unobserved in the FAB-MS, showing its low stability. However, the process of losing the Me_2dtc ligand stepwise to get a series of ion species $[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{dtc})_n]^+$ ($n = 4, m/z$ 822; $n = 3, m/z$ 702; $n = 2, m/z$ 580) was observed, though the abundances of the species are very low. The species ions $[\text{V}_2\text{-Fe}_2\text{S}_4(\text{Me}_2\text{dtc})_3(\text{CS}_2)]^+$ (m/z 778) and $[\text{V}_2\text{Fe}_2\text{S}_4(\text{CS}_2)]^+$ (m/z 418)

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Table 6. The Main Metal-Containing Fragment Ions and Their Relative Abundance in the Positive Ion FAB Mass Spectrum of Cluster $[\text{V}_2\text{Fe}_2\text{S}_4(\text{Me}_2\text{dtc})_5]^-$ Using Matrix NBA

ion	<i>m/z</i>	abundance
$[(\text{Et}_4\text{N})(\text{V}_2\text{Fe}_2\text{S}_4\text{L}_5)]^+{}^a$	1072	unobsd
$[\text{V}_2\text{Fe}_2\text{S}_4\text{L}_5]^+$	942	unobsd
$\{(\text{Et}_4\text{N})[(\text{V}_2\text{Fe}_2\text{S}_4\text{L}_3)(\text{S}_2\text{CN})]\}^+$	922	0.05
$[\text{V}_2\text{Fe}_2\text{S}_4\text{L}_5]^+$	822	0.24
$[\text{V}_2\text{Fe}_2\text{S}_4\text{L}_3(\text{S}_2\text{C})]^+$	778	0.07
$[\text{V}_2\text{Fe}_2\text{S}_4\text{L}_3]^+$	702	0.17
$[\text{V}_2\text{Fe}_2\text{S}_4\text{L}_2]^+$	582	0.19
$[\text{V}_2\text{Fe}_2\text{S}_4\text{L}]^+$	462	0.05
$[\text{V}_2\text{Fe}_2\text{S}_4(\text{S}_2\text{C})]^+$	418	0.59
$[\text{V}_2\text{Fe}_2\text{S}_4]^+$	342	0.07
$[\text{FeS}_2\text{L}_2]^+, \text{FeL}_3^+$	416	1.44
$[\text{VS}_2\text{FeL}_2]^+$	411	0.10
$[\text{V}_2\text{S}_2\text{L}_2]^+$	406	0.05
FeL_2^+	296	8.47
Et_4N^+	130	100

^a L = Me_2NCS_2 .

may occur from the loss of Me_2N from one Me_2dtc ligand ligating to Fe atom.

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Supporting Information Available: Tables of crystallographic data, atomic coordinate parameters, bond angles and bond lengths, and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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