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Study on an Assembly System Including Tetrathiovanadate. Syntheses and Structural Characterizations of $V_2Cu_2S_4$ Cubane-like Clusters and VS_4Cu_4 Bimetallic Aggregates

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The reaction system $(NH_4)_3VS_4$/CuCl/R_2dtcNa/PhSNa in DMF affords two types of V/Cu/S complexes. One is the VS_4Cu_4 complex $[VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-}$ (R_2 = Et or OC_4H_8; n =0, 1, or 2), the other one is the cubane-like cluster $[V_2Cu_2S_4(R_2dtc)_2(PhS)_2]^{2-}$ (R_2 = Me_2, OC_4H_8). $(Et_4N)_2[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]$ crystallizes in the monoclinic space group *C*2/*c* with $a = 20.219(10)$ Å, $b = 14.972(13)$ Å, $c = 18.027(9)$ Å, $\beta = 109.03(4)°$, $V = 5158.7$ Å^3, and $Z = 4$. With use of 1797 unique data ($I > 3\sigma(I)$) the structure was refined to $R = 0.060$. The dianion contains a $V_2Cu_2S_4$ cuboidal core and a butterfly array of four metal atoms with a V−V single bond. $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)(PhS)_3]$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 16.917(5)$ Å, $b = 25.996(13)$ Å, $c = 14.937(9)$ Å, $V = 6568.5$ Å^3 and $Z = 4$. With use of 2793 unique data ($I > 3\sigma(I)$), the structure was refined to $R = 0.059$. $(Et_4N)_3[VS_4Cu_4(Et_2dtc)(PhS)_3]$ crystallizes in the triclinic space group *P*1 with $a = 10.391(2)$ Å, $b = 12.391(4)$ Å, $c = 12.586(5)$ Å, $\alpha = 78.67(3)°$, $\beta = 82.48(2)°$, $\gamma = 81.59(2)°$, $V = 1563.1$ Å^3, $Z = 1$, and $R = 0.039$ using 4538 reflections ($I > 3\sigma(I)$). $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]$ crystallizes in the orthorhombic space group $Pna2_1$ with $a = 24.333(7)$ Å, $b = 17.648(4)$ Å, $c = 14.822(6)$ Å, $V = 6364.8$ Å^3, $Z = 4$, and $R = 0.058$ using 2857 reflections ($I > 1\sigma(I)$). $(Et_4N)_3[VS_4Cu_4(PhS)_4]$ crystallizes in the orthorhombic space group *Pbnm* with $a = 12.207(2)$ Å, $b = 15.493(3)$ Å, $c = 32.210(5)$ Å, $V = 6092.6$ Å^3, $Z = 4$ and $R = 0.060$ using 1109 reflections ($I > 3\sigma(I)$). All of the VS_4Cu_4 complexes contain a VS_4 tetrahedral core and have a nearly planar VCu_4 array. The overall symmetry of the VS_4Cu_4 unit closely approaches D_{2d}; however, the presence of ligands lowers the symmetry of all the anions. Structural, spectral, and magnetic data indicate that the VS_4Cu_4 complexes contain metal atoms with formal oxidation levels of V(V) + 4Cu(I). ^{51}V NMR spectra exhibit disproportion reactions caused by ligand exchange existing in the DMSO solution. With the variation of the mole ratio of $[VS_4Cu_4(PhS)_4]^{3-}$ to OC_4H_8dtcNa from 1:2 to 1:32 in DMSO solution, the complexes containing dtc ligands were detected by ^{51}V NMR spectra. This affords an evidence of the disproportions for $[VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-}$ (n =1 and 2) in solution. A reaction of $[VS_4Cu_4(PhS)_4]^{3-}$ with a large excess of PPh_3 was performed. A ^{51}V chemical shift appearing downfield from that of $[VS_4Cu_4(PhS)_4]^{3-}$ was observed and was supposed to be associated with a skeletal conversion from VS_4Cu_4 to VS_4Cu_3. Electrochemical studies for both two types of complexes show no reversible redox process and give a support of dissociable property of the coordinated ligand in solution.

Introduction

Studies on thiometalate and related multimetal complexes have been known for a long time. Many reports of such interesting complexes obtained from a reaction system containing thiometalate have shown their considerable versatility in molecular structure. Holm et al.[1] have reported MS_4^{n-}/$FeCl_2$-3/RS^- (M = Mo,W, n = 2; M = V, Nb, n = 3; M = Re, n = 1) reaction systems from which MFe_3S_4 double cubane clusters were synthesized. Christou and Garner[2] have also obtained by similar means several MFe_3S_4 (M = Mo, W) double cubanes. Müller has studied M/Cu/S complexes[3] (M = Mo, W, V, and Re) and reported a number set of compounds having linear, planar, cuboidal, and cage skeletons in which the thiometalate anions have been shown to act as a bidentate ligand to one to five copper(I) atoms and to remain in an unvarying tetrahedral geometry. Similar research in other laboratories has also led to the characterizations of many heterometallic sulfur complexes containing the MS_4 (M = Mo, W, V) moiety, one of which is $VS_4Cu_6(PPh_3)_5Cl_3$,[4e] having the most copper atoms. In Fujian Institute, Fuzhou, China, some worthwhile synthetic and structural information in the chemistry of the heterometallic sulfur complexes has been obtained. Wu and co-workers have recently synthesized several Mo/Cu/S/SR cubane clusters.[5] Our studies on the reaction system consisting of MS_4^{2-} (M = Mo, W), metal halide (metal = Fe, Cu), and R_2dtc^- salt (R_2dtc^- =

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dialkyldithiocarbamate) have reached a fairly advanced level in the last decade. Series of heterometallic sulfur complexes, such as $[MFe_3S_4(R_2dtc)_{5-6}]^{1-,0}$ (cubane-like clusters[6]), $[MCu_3S_4(R_2dtc)_3]^{2-}$ (MCu_3 planar complexes[7]), and $[S_2M_2Cu_5S_6(R_2dtc)_3]^{2-}$ (defective $M_2Cu_5S_6$ double cubane clusters[8]), have been obtained from the system.

As a similar and extensive study to the above $MoS_4{}^{2-}$ (or $WS_4{}^{2-}$) system, we have recently turned our attention to an exploration of the assembly system including $VS_4{}^{3-}$/CuCl/R_2-dtc$^-$. Vanadium-containing heterometallic sulfur complexes are of interest as models of the active sites in metalloenzymes[9] to biomimetic chemists. They are also of interest to inorganic chemists, since the vanadium has until recently been little investigated in such heterometallic sulfur systems. Up to the present, only a few examples have been reported, including V/Fe/S[1c,10] and V/Cu/S[3f,4e,10b] clusters. In recent communications, we have briefly described a variety of V/S/dtc[11] and V/M′/S/dtc (M′ = Cu, Ag)[12] complexes of nuclearity 2−5. The subject of this paper is the preparation of a $V_2Cu_2S_4$ cubane-like cluster and a VS_4Cu_4 bimetallic aggregate from the assembly system and subsequent structural characterizations on these complexes.

Experimental Section

All manipulations were carried out under dinitrogen atmosphere using standard Schlenk techniques. The solvents were purified by conventional methods and were degassed prior to use. Compounds $(NH_4)_3VS_4$[10b] and PhSNa[13] were prepared as reported. Reagents R_2-dtcNa (R_2 = Me_2, Et_2, and OC_4H_8) were synthesized by the reaction of R_2NH, NaOH, and CS_2 in water. CuCl was purchased from Aldrich and used without further purification.

$(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)(PhS)_3]$ (I). To a stirred slurry of $(NH_4)_3VS_4$ (0.66 g, 2.83 mmol) and CuCl (0.84 g, 8.49 mmol) in 30 mL of DMF was added a solution of OC_4H_8dtcNa (2.10 g, 11.34 mmol), PhSNa (1.50 g, 11.35 mmol), and Et_4NCl (1.88 g, 11.35 mmol) in 70 mL of DMF. The resulting solution was stirred at room temperature for 6.5 h. After filtration, the filtrate was concentrated to reduce the volume to 4 mL in vacuo and then filtered to remove the precipitates formed. A $CH_3CN/(CH_3)_2CO$ mixed solvent (30 mL, v/v ratio 1:1) was added to the filtrate. The solution was allowed to stand for 2 days. The precipitates and inorganic salts deposited were filtered out, and small portions of $(CH_3)_2CO$ was added until black crystalline began to separate. The black-red crystals formed after leaving the filtrate for several days at 5 °C were collected, washed with $(CH_3)_2CO$, and dried in vacuo, affording 0.5 g (yield 18% based on Cu) of **I**. Anal. Calcd for $C_{47}H_{83}Cu_4ON_4S_9V$: C, 42.96; H, 6.37; Cu, 19.35; N, 4.26; S, 21.96; V, 3.88. Found: C, 40.65; H, 6.09; Cu, 19.09; N, 4.03; S, 23.92; V, 3.87. IR (KBr, cm^{-1}): 464.6 (s), 546.5 (m), 696.6 (s), 748.2 (s), 782.3 (s), 1002.6 (s), 1021.8 (s), 1471.7 (s), 1574.0 (s). Electronic spectrum in DMSO, λ_{max}, nm (ϵ_M, M^{-1} cm^{-1}): 268 (36 000), 288 (32 000), 350 (15 000), 410 (12 000), 520 (2700). ^1H NMR (DMSO-d_6): δ 1.12 (CH_3, Et_4N), 3.16 (CH_2, Et_4N), 3.59 (NCH_2, dtc), 4.16 (OCH_2, dtc), 6.73 (*p*-H), 6.92 (*m*-H), 7.63 (*o*-H) ppm. ^{13}C NMR (DMSO-d_6): δ 7.10 (CH_3, Et_4N), 50.0 (NC, dtc), 51.6 (CH_2, Et_4N), 65.8 (OC, dtc), 119.8 (*p*-C), 126.9 (*m*-C), 132.1 (*o*-C), 148.6 (SC, PhS), 209.3 (S_2C, dtc) ppm.

$(Et_4N)_3[VS_4Cu_4(Et_2dtc)(PhS)_3]$ (I′). Compound **I′** was prepared by the same procedure as for **I** with the use of Et_2dtcNa (1.47 g, 8.58 mmol) instead of OC_4H_8dtcNa. The yield was 17% (based on Cu). Anal. Calcd for $C_{47}H_{85}Cu_4N_4S_9V$: C, 43.42; H, 6.59; Cu, 19.56; N, 4.31; S, 22.20; V, 3.92. Found: C, 43.03; H, 6.46; Cu, 19.40; N, 4.39; S, 22.22; V, 4.07. IR (KBr, cm^{-1}): 462.8 (s), 665.8 (s), 747.2 (s), 762.0 (s), 998.3 (s), 1022.2 (s), 1474.1 (s), 1574.8 (s). ^1H NMR (DMSO-d_6): δ 1.12 (CH_3, Et_4N), 1.21 (CH_3, dtc), 3.14 (CH_2, Et_4N), 3.89 (CH_2, dtc), 6.71 (*p*-H), 6.91 (*m*-H), 7.63 (*o*-H) ppm. ^{13}C NMR (DMSO-d_6) δ 7.03 (CH_3, Et_4N), 12.31 (CH_3, dtc), 47.14 (CH_2, dtc), 51.41 (CH_2, Et_4N), 119.9 (*p*-C), 126.9 (*m*-C), 132.1 (*o*-C), 148.1 (SC, PhS), 207.1 (CS_2, dtc) ppm.

$(Et_4N)_2[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]$ (II). A mixture of $(NH_4)_3VS_4$ (0.52 g, 2.23 mmol), CuCl (0.67 g, 6.77 mmol), OC_4H_8dtcNa (1.66 g, 8.96 mmol), PhSNa (1.30 g, 9.84 mmol), and Et_4NCl (1.50 g, 9.05 mmol) in 200 mL of DMF was stirred for 20 h. The solution became black-red and brown-red precipitates were observed. After filtration the filtrate was concentrated in vacuo to reduce the volume to 130 mL and then filtered. To the filtrate was added 100 mL of $CH_3CN/(CH_3)_2CO$ (v/v ratio 1:1). The solution was allowed to stay for several days at room temperature, causing the separation of black prismatic crystals which were collected, washed with $(CH_3)_2CO$, and dried in vacuo (yield 0.4 g, 30% based on V). Anal. Calcd for $C_{38}H_{66}Cu_2N_4O_2S_{10}V_2$: C, 39.32; H, 5.73; Cu, 10.95; N, 4.83; S, 27.62; V, 8.78. Found: C, 38.22; H, 5.57; Cu, 14.12; N, 4.67; S, 27.86; V, 8.90. IR (KBr, cm^{-1}): 353.0 (s), 479.4 (s), 540.5 (m), 692.5 (s), 737.2 (s), 778.9 (s), 996.1 (s), 1024.0 (s), 1468.8 (s), 1572 (s). ^1H NMR (DMSO-d_6): δ 1.16 (CH_3, Et_4N), 3.18 (CH_2, Et_4N), 3.68 (NCH_2, dtc), 4.04 (OCH_2, dtc), 6.83 (*p*-H), 7.39 (*m*-H), 7.48 (*o*-H) ppm.

$(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]$ (III). To the above filtrate from which complex **II** had been separated 5−10 mL of $(CH_3)_2CO$ was added. After storage for several days at 4 °C, black hexagonal crystals of **III** were collected (yield 0.42 g, 31% based on Cu). Anal. Calcd for $C_{46}H_{86}Cu_4N_5O_2S_{10}V$: C, 40.42; H, 6.34; Cu, 18.60; N, 5.12; S, 23.45; V, 3.73. Found: C, 39.88; H, 6.29; Cu, 18.30; N, 5.17; S, 23.25; V, 3.91. IR (KBr, cm^{-1}): 465.0 (s), 546.2 (m), 694.7 (s), 747.7 (s), 782.4 (s), 1003.7 (s), 1022.1 (s), 1478.7 (s), 1575.0 (s). Electronic spectrum in DMSO, λ_{max}, nm (ϵ_M, M^{-1} cm^{-1}): 268 (53 000), 290 (sh, 40 000), 340 (17 000), 418 (15 000). ^1H NMR (DMSO-d_6): δ 1.12 (CH_3, Et_4N), 3.15 (CH_2, Et_4N), 3.59 (NCH_2, dtc), 4.16 (OCH_2, dtc), 6.73 (*p*-H), 6.92 (*m*-H), 7.63 (*o*-H) ppm. ^{13}C NMR (DMSO-d_6): δ 7.08 (CH_3, Et_4N), 49.9 (NC, dtc), 51.5 (CH_2, Et_4N), 65.8 (OC, dtc), 119.8 (*p*-C), 126.9 (*m*-C), 132.1 (*o*-C), 148.4 (SC, PhS), 208.7 (CS_2, dtc) ppm.

$(Et_4N)_3[VS_4Cu_4(PhS)_4]$ (IV). To a stirred slurry of $(NH_4)_3VS_4$ (0.66g, 2.83 mmol) and CuCl (0.84g, 8.48 mmol) in 30 mL of DMF was added a solution of PhSNa (1.50g, 11.35 mmol) and Et_4NCl (1.90g, 11.46 mmol) in 70 mL of DMF, and the mixture was stirred for 24 h. The solution became brown-red and was concentrated in vacuo to reduce the volume to 30 mL. After filtration, the filtrate was added with 40 mL of $CH_3CN/(CH_3)_2CO$ (v/v ratio 1:1) and allowed to stay for several days to cause the deposition of black precipitates which were removed by filtration. To the filtrate were added 2 × 20 mL

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Table 1. Crystallographic Data

	I	**I′**	**II**	**III**	**IV**
formula	$C_{47}H_{83}Cu_4N_4OS_9V$	$C_{47}H_{85}Cu_4N_4S_9V$	$C_{38}H_{66}Cu_2N_4O_2S_{10}V_2$	$C_{46}H_{86}Cu_4N_5O_2S_{10}V$	$C_{48}H_{80}Cu_4N_3S_8V$
fw	1313.89	1299.91	1160.58	1366.93	1260.81
space group	$P_12_12_1$ (No. 19)	$P1$ (No. 1)	$C2/c$ (No. 15)	$Pna2_1$ (No. 33)	$Pbnm$ (No. 62)
a, Å	16.917(5)	10.391(2)	20.219(10)	24.333(7)	12.207(2)
b, Å	25.996(13)	12.391(4)	14.972(13)	17.648(4)	15.493(3)
c, Å	14.937(9)	12.586(5)	18.027(9)	14.822(6)	32.210(5)
α, deg	90	78.67(3)	90	90	90
β, deg	90	82.48(2)	109.03(4)	90	90
γ, deg	90	81.59(2)	90	90	90
V, Å^3	6568.5	1563.1	5158.7	6364.8	6092.6
Z	4	1	4	4	4
ϱ_{calcd}, g cm^{-3}	1.33	1.38	1.49	1.41	1.37
μ, cm^{-1}	17.2	18.0	15.8	18.1	18.2
λ, Å	0.710 69	0.710 73	0.710 69	0.710 69	0.710 73
transm factors	0.993−0.426	0.990−0.727	0.997−0.921	0.993−0.800	0.995−0.709
R^a	0.059	0.039	0.060	0.058	0.060
$R_w{}^b$	0.091	0.042	0.068	0.060	0.065

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

Table 2. Selected Positional Parameters and Their Estimated Standard Deviations for $[Et_4N]_3[VS_4(CuSPh)_3(CuS_2CNC_4H_8O)]$

atom	x	y	z	B,[a] Å^2
V	0.9798(2)	−0.0446(2)	0.2949(3)	4.19(9)
Cu(1)	0.9772(2)	0.0212(1)	0.1620(2)	5.13(7)
Cu(2)	0.9232(2)	−0.1143(1)	0.1879(2)	4.57(7)
Cu(3)	0.9868(2)	−0.1067(1)	0.4312(2)	6.47(9)
Cu(4)	1.0379(2)	0.0323(1)	0.3914(2)	5.60(8)
S(1)	1.0208(4)	−0.0602(3)	0.1575(4)	5.0(2)
S(2)	0.8898(4)	−0.1014(3)	0.3311(5)	5.6(2)
S(3)	1.0799(4)	−0.0505(2)	0.3869(5)	5.5(2)
S(4)	0.9297(4)	0.0341(3)	0.3009(4)	5.3(2)
S(11)	0.9795(5)	0.0825(3)	0.0638(5)	7.1(2)
S(21)	0.8621(4)	−0.1683(3)	0.0998(5)	5.3(2)
S(31)	1.0064(7)	−0.1540(4)	0.5504(6)	12.0(3)
S(41)	1.0481(4)	0.0843(3)	0.5225(4)	5.1(2)
S(42)	1.1450(4)	0.0956(3)	0.3616(5)	5.3(2)
O(4)	1.269(1)	0.2154(8)	0.605(1)	10.0(6)*
C(11)	0.991(2)	0.059(1)	−0.049(2)	6.1(7)*
C(12)	0.984(2)	0.008(1)	−0.071(2)	6.2(7)*
C(13)	0.992(2)	−0.011(1)	−0.161(2)	7.9(8)*
C(14)	1.009(2)	0.029(1)	−0.231(2)	7.2(7)*
C(15)	1.015(2)	0.081(1)	−0.206(2)	8.0(8)*
C(16)	1.008(2)	0.104(1)	−0.116(2)	11(1)*
C(21)	0.907(1)	−0.1647(9)	−0.010(2)	4.7(6)*
C(22)	0.854(1)	−0.177(1)	−0.085(2)	6.3(7)*
C(23)	0.885(2)	−0.176(1)	−0.174(2)	7.4(8)*
C(24)	0.965(2)	−0.164(1)	−0.189(2)	8.4(8)*
C(25)	1.015(2)	−0.150(1)	−0.114(2)	7.6(8)*
C(26)	0.983(2)	−0.151(1)	−0.019(2)	6.1(6)*
C(31)	0.934(2)	−0.204(1)	0.566(2)	9.0(9)*
C(32)	0.958(3)	−0.240(2)	0.632(3)	11(1)*
C(33)	0.896(6)	−0.271(3)	0.682(6)	27(4)*
C(34)	0.847(3)	−0.272(2)	0.606(3)	14(1)*
C(35)	0.787(3)	−0.247(2)	0.546(3)	18(2)*
C(36)	0.864(2)	−0.204(1)	0.531(2)	10(1)*
C(40)	1.122(1)	0.1171(9)	0.464(2)	5.1(6)*
N(4)	1.160(1)	0.1550(8)	0.502(1)	6.1(5)*
C(41)	1.222(2)	0.186(1)	0.450(2)	7.6(8)*
C(42)	1.295(2)	0.193(1)	0.519(2)	9.3(9)*
C(43)	1.138(2)	0.176(1)	0.595(2)	9.1(9)*
C(44)	1.212(2)	0.191(1)	0.660(2)	12(1)*

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

portions of $CH_3CN/(CH_3)_2CO$. The resulting solution was placed in the refrigerator for ~3 days to cause the separation of black cubic crystals which were collected, washed with $(CH_3)_2CO$, and dried in vacuo, affording 0.5g (19% based on Cu) of **IV**. Anal. Calcd for $C_{48}H_{80}Cu_4N_3S_8V$: C, 45.72; H, 6.40; Cu, 20.16; N, 3.33; S, 20.34; V, 4.04. Found: N, 46.69; H, 6.64; Cu, 20.93; N, 4.26; S, 20.09; V, 4.23. IR (KBr, cm^{-1}): 353.0 (s), 479.4 (s), 540.5 (m), 695.2 (s), 737.2 (s), 778.9 (s), 996.1 (s), 1024.0 (s), 1468.8 (s), 1572.0 (s). Electronic spectrum in DMSO, λ_{max}, nm (ϵ_M, M^{-1} cm^{-1}): 265(sh, 34 000), 288 (57 000), 360 (19 000), 420 (sh, 11 000), 540 (1800). ^{1}H NMR (DMSO-d_6): δ 1.02 (CH_3, Et_4N), 3.05 (CH_2, Et_4N), 6.75 (*p*-H), 6.92 (*m*-H), 7.64 (*o*-H) ppm. ^{13}C NMR (DMSO-d$_6$): δ 7.08 (CH_3, Et_4N), 51.5 (CH_2, Et_4N), 120.1 (*p*-C), 127.0 (*m*-C), 132.0 (*o*-C), 147.8 (SC, PhS) ppm.

$(Et_4N)_2[V_2Cu_2S_4(Me_2dtc)_2(PhS)_2]$ (V). A mixture of $(NH_4)_3VS_4$ (0.60 g, 2.57 mmol), CuCl (0.51 g, 5.15 mmol), Me_2dtcNa (0.74 g, 5.17 mmol), PhSNa (0.68 g, 5.15 mmol), and Et_4NCl (0.86 g, 5.17 mmol) in 100 mL of DMF was stirred for 20h. After concentration in vacuo to reduce the volume to 30 mL, the cloudy mixture was filtered. To the filtrate was added 40 mL of $CH_3CN/(CH_3)_2CO$ (v/v ratio 1:1). The resulting solution was allowed to stand for 3 days to cause the separation of dark-red microcrystals which were collected, washed with $(CH_3)_2CO$, and dried in vacuo, affording 0.31g (22% based on V) of **V**. The crystal structure of **V** has been reported.[12c] IR (KBr, cm^{-1}): 359.2 (m), 480.7 (s), 695.7 (s), 740.0 (s), 779.1 (s), 994.6 (m), 1022.0 (m), 1467.9 (s), 1524.5 (s), 1571.3 (s).

X-ray Crystallography and Structure Solution. (a) **Data Collection and Reduction.** Data were collected at 23 ± 1 °C on an MSC/Rigaku diffractometer for **I**, **II**, and **III** and on an Enraf-Nonius CAD4 diffractometer for **IV** and **I′**. A single crystal carefully chosen for each compound was coated with epoxy resin and mounted on a glass fiber. Graphite-monochromitized Mo Kα radiation was used for data collection and cell dimension measurements. Intensity data for all crystals were obtained with use of a $\omega - 2\theta$ scan technique. Throughout the data collection three standard reflections were monitored every 250 reflections to monitor crystal and instrumental stability. *LP* corrections and a empirical absorption correction based on a series of ψ-scans were applied to the data. After structure refinement with isotropic thermal parameters, an empirical absorption correction using the DIFABS program[14] was made for all complexes. Crystal parameters are listed in Table 1.

(b) **Determination of Structures.** All calculations were performed on a VAX computer using the SDP package.[15] The initial structure was solved by direct methods for each complex. The major atoms were located from an *E*-map. Subsequent difference Fourier calculations revealed the positions of remaining non-hydrogen atoms. All non-hydrogen atoms in these complexes were refined anisotropically by full-matric least-squares methods except as otherwise noted. For complex **I**, the V, Cu, and S atoms were refined anisotropically and the other non-hydrogen atoms were refined isotropically. Complex **II** contains two carbon atoms C(22) and C(24) belonging to the OC_4H_8-dtc group, which were found to be disordered over two positions with equal occupancies and were refined isotropically. The positions of the

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(14) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

(15) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978.

Table 3. Selected Positional Parameters and Their Estimated Standard Deviations for $[\mathrm{Et_4N}]_3[\mathrm{VS_4(CuSPh)_3(CuS_2CNEt_2)}]$

atom	*x*	*y*	*z*	*B*,[a] Å^2
V	0.9759(0)	0.1837(0)	0.8435(0)	3.21(2)
Cu(1)	0.9995(1)	0.01172(9)	1.00357(9)	4.37(2)
Cu(2)	0.8371(1)	0.28474(9)	0.98994(9)	4.38(2)
Cu(3)	0.9298(1)	0.36177(9)	0.69841(9)	4.54(2)
Cu(4)	1.1375(1)	0.07323(9)	0.71297(9)	4.18(2)
S(1)	1.0349(2)	0.1875(2)	1.0044(2)	4.13(5)
S(2)	0.7882(2)	0.2837(2)	0.8221(2)	4.55(5)
S(3)	1.1235(2)	0.2553(2)	0.7155(2)	4.39(5)
S(4)	0.9709(2)	0.0114(2)	0.8272(2)	4.21(5)
S(11)	1.1022(3)	−0.1441(2)	1.1074(2)	4.86(5)
S(12)	0.8251(2)	−0.0609(2)	1.1484(2)	5.07(6)
S(21)	0.7315(3)	0.3613(3)	1.1217(2)	7.04(8)
S(31)	0.9023(3)	0.5191(3)	0.5857(3)	6.97(7)
S(41)	1.2810(3)	−0.0322(2)	0.6237(2)	6.20(7)
N(10)	0.941(1)	−0.2393(7)	1.2722(7)	6.4(2)
C(10)	0.9573(9)	−0.1552(7)	1.1864(8)	4.8(2)
C(11)	0.818(1)	−0.251(1)	1.3363(9)	6.4(3)
C(12)	0.732(2)	−0.326(1)	1.298(1)	12.9(5)
C(13)	1.059(1)	−0.324(1)	1.294(1)	8.0(4)
C(14)	1.125(1)	−0.292(1)	1.381(1)	10.9(5)
C(21)	0.610(1)	0.4691(9)	1.0714(9)	6.3(3)
C(22)	0.596(1)	0.5081(9)	0.9644(9)	6.7(3)
C(23)	0.505(1)	0.604(1)	0.932(1)	9.2(4)
C(24)	0.429(2)	0.651(1)	1.001(1)	12.1(4)
C(25)	0.437(1)	0.618(1)	1.115(1)	12.5(4)
C(26)	0.538(1)	0.525(1)	1.149(1)	8.5(4)
C(31)	0.743(1)	0.5785(9)	0.6077(9)	8.0(3)
C(32)	0.639(1)	0.518(1)	0.599(1)	9.2(4)
C(33)	0.507(2)	0.565(1)	0.594(1)	12.3(5)
C(34)	0.488(2)	0.675(1)	0.612(1)	11.3(5)
C(35)	0.570(2)	0.733(1)	0.6262(9)	10.9(5)
C(36)	0.708(2)	0.675(1)	0.620(1)	10.2(5)
C(41)	1.3699(8)	0.050(1)	0.5105(7)	5.8(3)
C(42)	1.455(1)	−0.011(1)	0.4396(8)	8.7(3)
C(43)	1.522(1)	0.042(2)	0.347(1)	11.5(5)
C(44)	1.509(1)	0.163(1)	0.3306(9)	9.4(4)
C(45)	1.428(1)	0.227(1)	0.402(1)	9.4(4)
C(46)	1.3592(9)	0.166(1)	0.4917(8)	6.8(3)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

hydrogen atoms were calculated and included in the structure factor calculations but were not refined. The standard deviations of an observation with unit weight are 2.13, 0.93, 1.60, 0.85, and 1.48 for complexes **I**, **I′**, **II**, **III**, and **IV**, respectively. The maximum and minimum peak values in the final difference Fourier map are +0.76 and −0.43 e/Å^3 for **I**, +0.54 and −0.50 e/Å^3 for **I′**, +0.65 and −0.43 e/Å^3 for **II**, +0.39 and −0.45 e/Å^3 for **III**, and +0.54 and −0.48 e/Å^3 for **IV**, respectively.

Other Physical Measurements. Infrared spectra were recorded on an FTS-40 spectrophotometer. Electronic spectra were obtained in DMSO solution on a Shimazu UV-300 spectrophotometer. Electrochemical measurements were performed in the cyclic voltammetric mode on a DHZ-1 electrochemical multipurpose instrument and an X-Y recorder with SCE reference electrode, Pt plate working electrode, and Pt auxiliary electrode. The supporting electrolyte was $\mathrm{Bu_4NClO_4}$. ^{1}H, ^{13}C, and ^{51}V NMR spectra were recorded on a Bruker-AM 500 spectrometer with $\mathrm{Me_4Si}$ and $\mathrm{VOCl_3}$ as standards, respectively.

Results and Discussion

Synthesis. From a reaction mixture comprising $\mathrm{(NH_4)_3VS_4}$, CuCl, $\mathrm{R_2dtcNa}$, PhSNa, and $\mathrm{Et_4NCl}$ in DMF solution, we have isolated two kinds of complexes, $[\mathrm{V_2Cu_2S_4(R_2dtc)_2(PhS)_2}]^{2-}$ cubane-like clusters (**II** and **V**) and $[\mathrm{VS_4Cu_4(R_2dtc)}_n\mathrm{(PhS)}_{4-n}]^{3-}$ complexes (**I**, **I′**, **III**, and **IV**). It is suggested that the $\mathrm{VS_4Cu_4}$ complexes are formed by a coordination reaction and can be expressed by eq 1.

Table 4. Selected Positional Parameters and Their Estimated Standard Deviations for $\mathrm{(Et_4N)_2[V_2Cu_2S_4(SPh)_2(S_2CNC_4H_8O)_2]}$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Cu	0.58683(9)	0.1563(1)	0.7720(1)	4.62(4)
V	0.4915(1)	0.2721(2)	0.6701(1)	3.52(5)
S(1)	0.5898(2)	0.3070(3)	0.7698(2)	4.02(9)
S(2)	0.5093(2)	0.1297(3)	0.8482(2)	3.90(9)
S(11)	0.6897(2)	0.0868(3)	0.8080(2)	4.4(1)
S(21)	0.4059(2)	0.3348(3)	0.5543(2)	4.7(1)
S(22)	0.5528(2)	0.3281(3)	0.5820(2)	4.9(1)
O	0.4341(6)	0.405(1)	0.2883(6)	12.1(5)
N(20)	0.4605(6)	0.383(1)	0.4428(7)	6.7(4)
C(11)	0.6794(7)	−0.026(1)	0.8156(8)	4.3(4)
C(12)	0.6141(8)	−0.066(1)	0.8001(8)	5.0(4)
C(13)	0.6076(9)	−0.161(1)	0.804(1)	7.5(6)
C(14)	0.670(1)	−0.210(1)	0.828(1)	10.6(8)
C(15)	0.733(1)	−0.168(2)	0.844(1)	11.0(8)
C(16)	0.7375(9)	−0.079(1)	0.838(1)	8.0(6)
C(20)	0.4717(7)	0.354(1)	0.5154(8)	4.6(4)
C(21)	0.5192(8)	0.394(1)	0.4124(8)	8.3(5)
C(22)	0.502(1)	0.354(2)	0.346(2)	5.4(7)*
C(22′)	0.505(2)	0.443(3)	0.349(2)	8(1)*
C(23)	0.3909(9)	0.397(2)	0.390(1)	12.1(7)
C(24)	0.381(2)	0.436(2)	0.324(2)	5.6(8)*
C(24′)	0.379(1)	0.365(2)	0.323(2)	5.0(7)*

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

$$\mathrm{VS_4}^{3-} + 4\mathrm{CuCl} + n\mathrm{R_2dtc}^- + (4-n)\mathrm{PhS}^- \rightarrow [\mathrm{VS_4Cu_4(R_2dtc)}_n(\mathrm{PhS})_{4-n}]^{3-} + 4\mathrm{Cl}^- \tag{1}$$

In comparison with the synthetic system[3b-d,8c] using thiometalate synthon $\mathrm{OMS_3}^{2-}$ or $\mathrm{MS_4}^{2-}$ (M = Mo, W), although we can also expect V/Cu/S cubane-like structures similar to $[\mathrm{MCu_3S_3Cl}]$[3b-d] or $[\mathrm{M_2Cu_5S_6}]$[8c] (M = Mo, W), the failure of obtaining the structures in this reaction demonstrates that $\mathrm{VS_4}^{3-}$ ligand, just like $\mathrm{MoS_4}^{2-}$ or $\mathrm{WS_4}^{2-}$, is not a favorable synthon in the synthesis of a compound with the $[\mathrm{VCu_3S_4}]$ cubane skeleton. It was mentioned[3b-d] that the formation of the $[\mathrm{MCu_3S_3Cl}]$ structure was expected on using the synthon $\mathrm{OMS_3}^{2-}$ owing to the preferred formation of the Cu−S over the Cu−O bond. However, a new type of $\mathrm{V_2Cu_2S_4}$ cubane-like cluster is obtained in the present reaction system due to the reduction of $\mathrm{VS_4}^{3-}$. The $\mathrm{V_2Cu_2S_4}$ clusters have relatively less solubility in DMF or DMSO than the $\mathrm{VS_4Cu_4}$ complexes have, so that the former will be deposited first from the reaction solution when the mixed solvents $\mathrm{CH_3CN/(CH_3)_2CO}$ are added to. The molar ratio of $\mathrm{VS_4}^{3-}$/CuCl = 1/3 that we usually chose for syntheses is available for the formation of both kinds of complexes. The use of excess CuCl seems not to be always profitable for raising the yield of $[\mathrm{VS_4Cu_4(R_2dtc)}_n\mathrm{(PhS)}_{4-n}]^{3-}$ as yields of not more than 30% are generally observed in all reproducible preparations, while the yield of the $\mathrm{V_2Cu_2S_4}$ cluster is improved by adjusting the molar ratio of $\mathrm{VS_4}^{3-}$/CuCl to 1/1. It is also noticed that both $\mathrm{V_2Cu_2S_4}$ and $\mathrm{VS_4Cu_4}$ complexes contain mixed ligands, $\mathrm{R_2dtc}^-$ and PhS^-. A similar metal thiocubane, $[\mathrm{Fe_4S_4(Et_2dtc)_2(PhS)_2}]^{2-}$, had been obtained in a ligand substitution reaction of $[\mathrm{Fe_4S_4(Et_2dtc)_2Cl_2}]^{2-}$ with PhS^- by Coucouvanis and co-workers.[16] Interestingly, in the $\mathrm{V_2Cu_2S_4}$ clusters, $\mathrm{R_2dtc}^-$ and PhS^- ligands are ligated selectively to vanadium and copper, respectively, even though $\mathrm{R_2dtc}$ group

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[16] Kanatzidis, M. G.; Ryan, M.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A. *Inorg. Chem.* **1983**, *22*, 179.

Table 5. Selected Positional Parameters and Their Estimated Standard Deviations for $[Et_4N]_3[VS_4(CuSPh)_2(CuS_2CNC_4H_8O)_2]$

atom	*x*	*y*	*z*	*B*,[a] Å^2
V	0.4513(1)	0.7605(1)	0.6445(0)	3.83(6)
Cu(1)	0.37673(8)	0.8412(1)	0.7246(2)	4.91(5)
Cu(2)	0.51362(8)	0.7832(1)	0.7854(2)	4.85(5)
Cu(3)	0.53590(9)	0.6931(1)	0.5663(2)	6.46(6)
Cu(4)	0.3911(1)	0.7301(1)	0.4989(2)	6.71(6)
S(1)	0.4262(2)	0.7473(2)	0.7877(3)	4.54(9)
S(2)	0.5356(2)	0.8052(3)	0.6430(4)	5.5(1)
S(3)	0.4478(2)	0.6512(3)	0.5760(4)	6.5(1)
S(4)	0.3938(2)	0.8403(3)	0.5801(4)	5.9(1)
S(11)	0.3184(2)	0.9231(3)	0.7804(5)	7.8(2)
S(21)	0.5748(2)	0.7951(3)	0.8942(4)	7.0(1)
S(31)	0.6073(2)	0.5996(3)	0.5891(4)	7.0(1)
S(32)	0.5936(2)	0.6948(3)	0.4304(4)	6.9(1)
S(41)	0.3131(2)	0.6562(4)	0.4463(4)	7.4(2)
S(42)	0.3848(3)	0.7529(4)	0.3403(4)	8.9(2)
O(30)	0.7743(8)	0.548(1)	0.396(1)	15.2(7)
O(40)	0.256(2)	0.628(2)	0.110(2)	14(1)
C(11)	0.3136(8)	0.914(1)	0.895(1)	6.0(5)
C(12)	0.3499(9)	0.8787(9)	0.946(1)	8.1(6)
C(13)	0.346(1)	0.877(1)	1.035(2)	10.3(8)
C(14)	0.303(1)	0.915(2)	1.081(2)	15(1)
C(15)	0.263(1)	0.950(2)	1.026(2)	14(1)
C(16)	0.2703(9)	0.951(1)	0.934(2)	9.8(7)
C(21)	0.5501(7)	0.7738(9)	1.007(1)	5.5(4)
C(22)	0.4958(8)	0.7694(9)	1.029(1)	6.4(5)
C(23)	0.4826(9)	0.750(1)	1.117(2)	9.7(7)
C(24)	0.5228(9)	0.735(1)	1.181(1)	9.3(6)
C(25)	0.5752(9)	0.741(1)	1.158(1)	8.0(6)
C(26)	0.5915(9)	0.758(1)	1.070(2)	8.3(6)
N(30)	0.679(1)	0.612(1)	0.471(1)	14.4(8)
C(30)	0.6298(7)	0.632(1)	0.498(1)	6.7(5)
C(31)	0.691(1)	0.621(2)	0.378(3)	21(2)
C(32)	0.752(2)	0.618(2)	0.362(2)	18(1)
C(33)	0.705(1)	0.546(2)	0.509(2)	17(1)
C(34)	0.763(1)	0.543(2)	0.492(2)	16(1)
N(40)	0.3024(6)	0.6770(9)	0.274(1)	8.3(4)
C(40)	0.3313(8)	0.695(1)	0.351(2)	8.2(6)
C(41)	0.253(1)	0.625(2)	0.270(2)	13.0(9)
C(42)	0.222(1)	0.627(2)	0.186(2)	18(1)
C(43)	0.322(1)	0.708(2)	0.188(2)	15(1)
C(44)	0.292(2)	0.689(2)	0.105(3)	25(2)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta 1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 6. Selected Positional Parameters and Their Estimated Standard Deviations for $(Et_4N)_3[VS_4(CuSPh)_4]$

atom	*x*	*y*	*z*	*B*,[a] Å^2
V	0.5872(5)	0.0557(4)	0.7500(0)	4.9(1)
Cu(1)	0.7316(2)	0.0512(2)	0.6903(1)	5.93(7)
Cu(2)	0.4366(2)	0.0542(2)	0.6931(1)	6.27(7)
S(1)	0.5839(5)	0.1366(4)	0.6931(2)	6.2(2)
S(2)	0.4442(6)	−0.0281(5)	0.7500(0)	5.3(2)
S(3)	0.7363(8)	−0.0224(5)	0.7500(0)	5.6(2)
S(11)	0.8588(6)	0.0280(5)	0.6443(2)	7.4(2)
S(21)	0.2991(6)	0.0394(5)	0.6511(2)	8.8(2)
C(11)	0.813(2)	0.050(1)	0.5941(7)	6.4(7)
C(12)	0.714(2)	0.074(2)	0.5859(9)	9.4(8)
C(13)	0.682(2)	0.094(2)	0.5453(9)	9.3(9)
C(14)	0.754(3)	0.074(2)	0.5146(7)	11(1)
C(15)	0.856(2)	0.051(2)	0.5234(9)	12(1)
C(16)	0.890(2)	0.036(2)	0.5646(8)	10.2(9)
C(21)	0.312(2)	0.101(2)	0.6088(7)	6.7(7)
C(22)	0.386(2)	0.164(2)	0.6009(9)	10.5(9)
C(23)	0.401(3)	0.225(2)	0.567(1)	16(1)
C(24)	0.313(3)	0.204(2)	0.540(1)	14(1)
C(25)	0.232(3)	0.148(2)	0.5439(9)	13(1)
C(26)	0.234(3)	0.096(2)	0.5778(8)	13(1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 7. Selected Bond Distances and Angles for II

	Bond Distances in Å		
Cu−Cu′	3.338(3)	Cu−S(11)	2.224(4)
Cu−V	2.791(3)	V−S(1)	2.263(4)
Cu−V′	2.772(3)	V−S(1′)	2.303(4)
V−V′	2.787(4)	V−S(2)	2.156(4)
Cu−S(1)	2.258(4)	V−S(21)	2.425(4)
Cu−S(2)	2.431(4)	V−S(22)	2.459(4)
Cu−S(2′)	2.426(4)		
	Bond Angles in deg		
S(1)−Cu−S(2)	101.4(1)	S(2)−V−S(21)	106.4(2)
S(1)−Cu−S(2′)	99.6(1)	S(2)−V−S(22)	102.6(2)
S(1)−Cu−S(11)	116.5(1)	S(21)−V−S(22)	71.4(1)
S(2)−Cu−S(2′)	90.1(1)	Cu−S(1)−V	76.2(1)
S(2)−Cu−S(11)	118.2(1)	Cu−S(1)−V′	74.9(1)
S(2′)−Cu−S(11)	125.8(1)	V−S(1)−V′	75.2(1)
S(1)−V−S(1′)	98.7(1)	Cu−S(2)−Cu′	86.8(1)
S(1)−V−S(2)	108.1(1)	Cu−S(2)−V	74.1(1)
S(1)−V−S(21)	142.2(1)	Cu′−S(2)−V	74.7(1)
S(1)−V−S(22)	86.4(1)	Cu−S(11)−C(11)	111.1(5)
S(1′)−V−S(2)	109.1(1)	V−S(21)−C(20)	89.1(5)
S(1′)−V−S(21)	84.2(1)	V−S(22)−C(20)	87.7(5)
S(1′)−V−S(22)	144.4(1)		

has a high tendency to chelate to the copper atom. This selective coordination can be attributed to the required coordination number (not more than four) of copper. In contrast with this situation, copper atoms in the VS_4Cu_4 complexes bind to either benzenethiolate or R_2dtc ligand to give three or four coordinate geometry. Therefore, a series of $[VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-}$ complexes with $n = 0$, 1, and 2 have been obtained from the assembly system. However, the attempt to prepare the complexes with $n = 3$ and 4 has not yet been successful even by using an excess of R_2dtcNa. As both ligand and reducing agent, benzenethiolate coordinates to copper atom and could be involved in the reduction of V(V) to V(IV), which has been found in the V/S/PhS complex,[17] promoting the formation of the $V_2Cu_2S_4$ cluster. Besides, in the coordination reaction to give VS_4Cu_4 complexes, the presence of thiolate in the reaction system is proved to be necessary, since its absence or presence in less than a 1/1 molar ratio of PhS^-/R_2dtc^- has led to the oxidation of Cu(I) and later the formation of $Cu(R_2dtc)_2$ as the only separable product. We propose that $[Cu^I(SPh)]$ and $[(R_2dtc)Cu^I]$ are the reactive intermediates which occur in the reaction process and are coordinated gradually by the VS_4 unit to form the final product $[VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-}$ (Figure 1). Because dialkyldithiocarbamate can stabilize the high oxidation state of the metal atom in $M(R_2dtc)_n$,[18] the intermediate $[(R_2dtc)Cu]$ will be easily oxidized to give $(R_2dtc)_2Cu$. The other reactive intermediate [Cu(SPh)] may be protected from the rapid oxidation by using excess PhSNa to produce $[Cu(SPh)_3]^{2-}$ which was obtained by Coucouvanis[19] and Garner.[20] In this case, the action of the thiolate can be envisioned to restrain the formation of the unstable intermediate $[(R_2dtc)Cu]$ when increasing the molar ratio of PhS^-/R_2dtc^-. It should also be pointed out that, in addition to complex **V**, we have separated a little amount of $[V_3S_7(Me_2dtc)_3]^-$,[11b] a triangular V_3 cluster with yield of ≈3%. Manifold products being obtained and having no high yield indicate that the

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(17) Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E. B.; Huffman, J. C.; Rehder, L.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204.

(18) Kanatzidis, M. G.; Baenziger, N. C.; Coucouvanis, D.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1984**, *106*, 4500.

(19) Coucouvanis, D.; Murphy, C. N.; Kanodia, S. K. *Inorg. Chem.* **1980**, *19*, 2993.

(20) Garner, C. D.; Nicholson, J. R.; Clegg, W. *Inorg. Chem.* **1984**, 23, 2148.

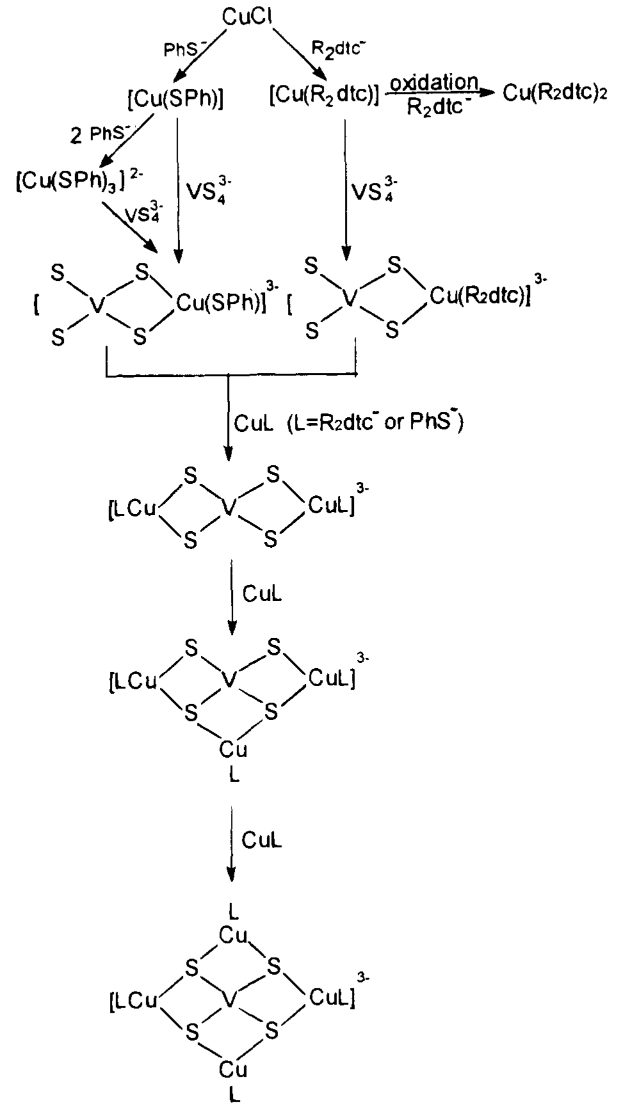

Figure 1. Supposed scheme of the formation process for the VS_4Cu_4 complexes.

reaction system would be more complex beyond expectation and that such reactions are expected to be under statistical control.

Structure. VS_4Cu_4 Complexes I, I′, III and IV. In these structures, the Et_4N^+ cations in the asymmetric units are well separated from the respective anion. The structures of the anions **I**, **I′**, **III** and **IV**, are presented in parts A, B, D, and E of Figure 2. All the anions contain a common essentially tetrahedral VS_4 unit with S−V−S bond angles ranging from 107.8(3) to 111.2(4)°. Five metal atoms 4Cu + V are nearly coplanar with deviations of not more than 0.1 Å from the least squares plane. The two mutually trans copper atoms together with central V atom form a nearly linear array with Cu···V···Cu angles ranging from 172.7(2) to 177.1(1)°. These features make the VS_4Cu_4 core an approximate D_{2d} symmetry for each complex. However, the presence of ligands causes the lowering of symmetry. The anion of **IV** with a PhS^- ligand ligated to each copper atom has a crystallographically imposed C_s symmetry, while the anion of **III** has two pairs of ligands, $OC_4H_8dtc^-$ and PhS^-, bound to the four copper atoms in a cis-form, accompanying an approximate C_s symmetry which is not, however, crystallographically imposed. Both two anions of **I** and **I′** have no symmetry due to unsymmetrical arrangement of the ligands. These complexes except of **IV** contain two types of copper atoms, one trigonally and the other pseudotetrahedrally coordinated. In Table 8 are collected the main structural features of the VS_4Cu_4 cores in these complexes. Shorter Cu−S distances (2.180(3)−2.251(6) Å) are observed for the trigonal copper atoms than those for the tetrahedral ones (2.264(3)−2.288(7) Å) as a consequence of variation of metal coordination number. It is evident that chemically equivalent V−S , Cu−S, and V−Cu distances in each VS_4Cu_4 complexes lie respectively within narrow ranges and are comparable with those in the other two V/Cu/S complexes shown in Table 8. This indicates that either vanadium or copper atoms in each VS_4Cu_4 complex are electronically similar. A comparison (Table 9) of $Cu-S_{ligand}$ distances between the VS_4Cu_4 complexes and certain complexes containing the Cu atom in a comparable coordination environment is used to estimate the Cu oxidation state. The Cu−SPh distances (2.166(3)−2.204(6) Å) in the VS_4Cu_4 complexes are near to those in $[(PhSCu)MoS_4]^{2-}$ (2.188(2) Å)[4c] and $[(PhSCu)_2MoS_4]^{2-}$ (2.171(2) Å).[4c] The $Cu-S_{dtc}$ distances in the VS_4Cu_4 complexes are comparable with those in $[(R_2dtcCu)_3MoS_4]^{2-}$[7] ($R_2 = Et_2$, C_5H_{10}; 2.367(2)−2.446(2) Å) but are obviously longer than those in $Cu^{II}(OC_4H_8dtc)_2$[21] (2.298(1)−2.304(1) Å). This comparison provides an estimate of the formal oxidation state of Cu(I), even though somewhat shorter Cu−SPh distances than those in $[Cu^I(SPh)_3]^{2-}$[20] (2.235(4)−2.274(4) Å) were observed for the VS_4Cu_4 complexes, which could be attributed to the transfer of charge from Cu(I) to V(V), similar to delocalization from Cu(I) to Mo(VI), suggested for $[(PhSCu)MoS_4]^{2-}$ and $[(PhSCu)_2MoS_4]^{2-}$ by Garner,[4c] causing the shortening of Cu−SPh in Mo/Cu/S or V/Cu/S complexes. Also, X-ray photoelectron spectroscopy (XPS) gave a binding energy of 932.7ev (Cu $2P^{3/2}$) for complex **I**, which was a good fit to the electronic state of Cu(I) in Cu_2O. All these VS_4Cu_4 complexes are diamagnetic according to the measurements of bulk magnetic susceptibility and NMR spectra (vide infra), offering a consistent result with the estimation of the metal oxidation states of V(V) + 4Cu(I).

$(Et_4N)_2[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]$ (II). Complex **II** contains well discrete $[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]^{2-}$ dianion and two Et_4N^+ cations. The structure of **II** dianion is presented in Figure 2C and the selected bond distances and angles in Table 7. Each asymmetrical independent unit includes a half molecule. The dianion is located on a crystallographic 2-fold axis. Each five-coordinate V atom is chelated by a $OC_4H_8dtc^-$ group and coordinated by three μ_3-S atoms in a distorted square pyramidal site. The vanadium atom lies out of the equatorial plane toward the apical S(2) atom with the S(2)−V−S angles ranging from 102.6(2) to 109.1(1)°. Each four-coordinate Cu atom is coordinated in a seriously distorted tetrahedron by three μ_3-S atoms and a terminal PhS^- group with S−Cu−S angles ranging from 85.2(2) to 130.4(2)°. The $V_2Cu_2S_4$ cuboidal core is condensed along the C_2 axis. Metal−S bonds to the parallel C_2 axis are obviously shorter than those perpendicular to the axis. This feature is also observed in the other $V_2Cu_2S_4$ cubane cluster **V**.[12c] The estimation for the oxidation state of V(IV) stemmed from the fact that V−V′ distances (**II**, 2.787(4) Å; **V**, 2.803(5) Å) are comparable with those of certain V(IV) complexes which are believed to contain a V−V single bond, such as $V_2(S_2)_2(Et_2dtc)_4$ (2.884(4) Å),[11a] $V_2(S_2)_2(MeCS_2)_4$ (2.800(2) Å),[22] and $[V_2(S_2)_2(CS_3)_4]^{4-}$ (2.841(6), 2.872(6) Å),[17] and from the fact that $V-S_{dtc}$ bond distances (**II**, 2.459(4)−

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(21) Crystal data for $Cu(OC_4H_8dtc)_2$: monoclinic, space group $P2_1/n$ (No.14), $a = 4.274(2)$ Å, $b = 20.713(8)$ Å, $c = 8.402(3)$ Å, β=99.71(0)°, $V = 733.2$ Å^3, $Z = 2$, $R = 0.042$, $R_w = 0.041$. using 1129 reflections with $I > 3.0\sigma(I)$; $Cu-S_{dtc}$ = 2.298(1), 2.298(1), 2.304(1), and 2.304(1) Å.

(22) Duraj, S. A.; Andras, M. T.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 1232.

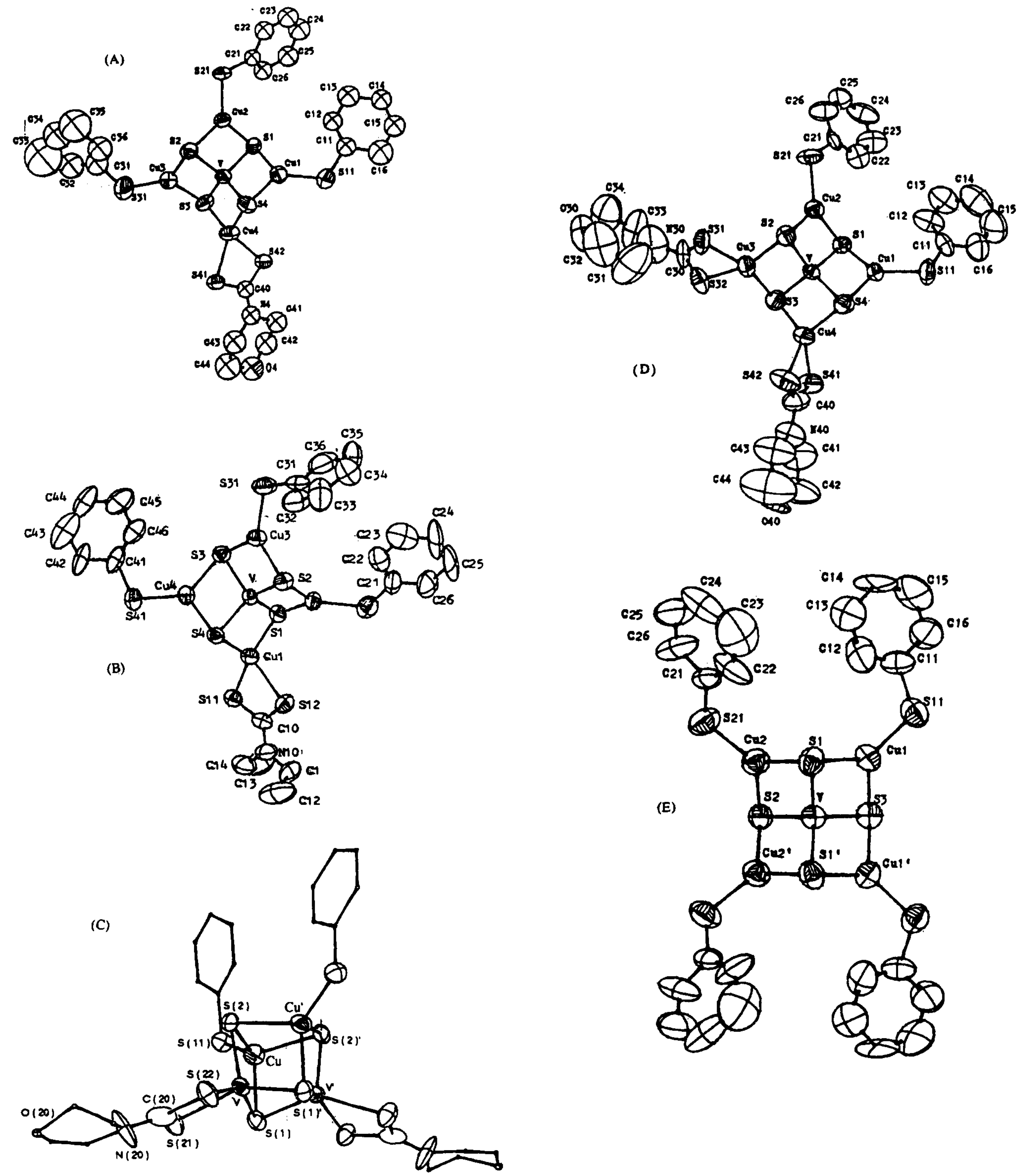

Figure 2. ORTEP diagrams showing 50% probability ellipsoids for (A) $[VS_4Cu_4(OC_4H_8dtc)(PhS)_3]^{3-}$, (B) $[VS_4Cu_4(Et_2dtc)(PhS)_3]^{3-}$, (C) $[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]^{2-}$, (D) $[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]^{3-}$, and (E) $[VS_4Cu_4(PhS)_4]^{3-}$.

2.603(6) Å; **V**, 2.434(5)−2.443(5) Å) are near to (or somewhat longer than) those of $VO(Et_2dtc)_2$[23] (2.387(2)−2.410(2) Å). The measurement of bulk magnetic susceptibility of **II** offers a diamagnetic result and supports that d^1-d^1 electrons are spin-paired leading to a V−V single bond. Meanwhile, the oxidation state of Cu(I) was deduced from a comparison which showed shorter Cu−SPh bonds (**II**, 2.224(4) Å; **V**, 2.229(5) Å) than those observed in $[Cu(SPh)_3]^{2-}$ (2.235(4)−2.274(4) Å) and a transfer of charge from Cu to V similar to that observed in the VS_4Cu_4 complexes.

As a electron-deficient 58e cuboidal core, three types of intermetallic distances are observed including a V−V bond, four V−Cu bonds ranging from 2.772(3) to 2.791(3) Å, and Cu···Cu separations (**II**, 3.338(3) Å, **V**, 3.351(5) Å). These features indicates a "butterfly" geometry of metal atoms with two copper atoms in the "wing" positions. Interestingly, the butterfly arrays of four metal atoms are also observed in other 58e $M_2M'_2S_4$ cubane-like clusters (Table 10). All the $M_2Cu_2S_4$ (M = Mo,

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[23] Henrick, K.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 26.

Table 8. Summary of Bond Distances (Å) in VS_4Cu_{3-6} Cores for V−Cu−S Complexes Containing a VS_4 Tetrahedral Unit

		V−S	Cu^a−S	Cu^b−S	V−Cu	ref
I	mean[c]	2.199(8)	2.236(5)	2.272(4)	2.618(13)	this work
	range	2.186(5)−2.218(6)	2.216(5)−2.250(5)	2.269(5)−2.276(6)	2.599(3)−2.654(4)	
I′	mean[c]	2.197(10)	2.230(11)	2.271(8)	2.613(10)	this work
	range	2.171(3)−2.220(3)	2.180(3)−2.251(4)	2.264(3)−2.279(3)	2.593(2)−2.636(2)	
III	mean[c]	2.201(8)	2.216(14)	2.278(4)	2.629(16)	this work
	range	2.182(7)−2.221(7)	2.182(3)−2.251(6)	2.270(7)−2.288(7)	2.595(4)−2.664(5)	
IV	mean[c]	2.203(10)	2.229(8)		2.604(8)	this work
	range	2.18(2)−2.220(8)	2.205(7)−2.239(7)		2.596(6)−2.611(6)	
$VS_4Cu_3(PPh_3)_4$		2.213(7) (μ_3-S) 2.156(8) (μ_2-S)	2.197(6)−2.233(7)	2.336(6)	2.615(2)−2.760(8)	3f
$VS_4Cu_6(PPh_3)_5Cl_3$	mean	2.214 (μ_4-S)		2.238(3)−2.344(3)	2.596(3)−2.680(2)	4e
	range	2.208(3)−2.222(2)				

[a] The coordination number of copper atom is 3. [b] The coordination number of copper atom is 4. [c] Number in parentheses represents the standard devistion from the mean, $\sigma = [\sum_{i=1}^{N} (x_i - \bar{x})^2/N(N-1)]^{1/2}$.

Table 9. Summary of $Cu-S_{ligand}$ Distances (Å) in Certain V/Cu/S, Mo/Cu/S, and Cu/S Complexes

		$Cu-S_{dtc}$	Cu−SPh	ref
I	mean[a]	2.436(51)	2.180(6)	this work
	range	2.385(5)−2.487(5)	2.168(6)−2.190(7)	
I′	mean[a]	2.4(1)	2.176(5)	this work
	range	2.312(4)−2.526(3)	2.166(3)−2.182(4)	
III	mean[a]	2.424(14)	2.197(8)	this work
	range	2.390(8)−2.455(7)	2.189(6)−2.204(6)	
IV	mean[a]		2.171(4)	this work
	range		2.168(8)−2.175(8)	
$(Et_4N)_2[Cu(SPh)_3]$	mean[a]		2.250(5)	20
	range		2.239(2)−2.258(2)	
$(Ph_4P)_2[Cu(SPh)_3]$	mean[a]		2.295(35)	19
	range		2.274(4)−2.235(4)	
$Cu(OC_4H_8dtc)_2$	mean[a]	2.301(3)		21
	range	2.298(1)−2.304(1)		
$(Pr_4N)_2[(PhSCu)MoS_4]$			2.188(2)	4c
$(Pr_4N)_2[(PhSCu)_2MoS_4]$			2.171(2)	4c
$(Et_4N)_2[(R_2dtcCu)_3MoS_4]$				
$R_2 = Et_2$	mean[a]	2.406(23)		7c
	range	2.328(7)−2.479(6)		
$R_2 = C_5H_{10}$	mean[a]	2.413(48)		7a
	range	2.288(3)−2.560(3)		

[a] Number in parentheses represents the standard devistion from the mean, $\sigma = [\sum_{i=1}^{N} (x_i - \bar{x})^2/N(N-1)]^{1/2}$.

Table 10. Intermetallic Distances (Å) in 58e $M_2M'_2S_4$ Cubane-like Clusters

	the longest M••M	M−M′ bond	M′−M′ bond	ref
$[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]^{2-}$	Cu••Cu 3.338(3)	2.772(3)−2.791(3)	V−V 2.784(4)	this work
$[V_2Cu_2S_4(Me_2dtc)_2(PhS)_2]^{2-}$	Cu••Cu 3.351(5)	2.762(3)−2.791(3)	V−V 2.803(5)	12c
$[V_2Ag_2S_4(OC_4H_8dtc)_2(PhS)_2]^{2-}$	Ag••Ag 3.898(3)	3.014(4)−3.038(4)	V−V 2.793(7)	12a
$[Mo_2Cu_2S_4(edt)_2(PPh_3)_2]$	Cu••Cu 3.095(2)	2.782(2)−2.831(1)	Mo−Mo 2.858(1)	5a
$[W_2Cu_2S_4(edt)_2(PPh_3)_2]$	Cu••Cu (no bond)	2.799(2)−2.845(2)	W−W 2.851(1)	5b
$[V_2Fe_2S_4(MeCp)_2(NO)_2]$	V•••V 2.95	2.59	Fe−Fe 2.75	10a
$[Fe_4S_4(Et_2dtc)_2(Ph_5)_2]^{2-}$	Fe••Fe 3.053(3)	2.779(2)−2.780(2)	Fe−Fe 2.733(3)	16

W, V) and $V_2Ag_2S_4$ cubanes contain the longest intermetallic separations of Cu••Cu and Ag••Ag, respectively, since copper and silver atoms have saturated d^{10} electronic shells.

Spectral Features and Solution Behavior. Infrared Spectra. In the 400−500 cm^{-1} region where $\nu(M\text{-}S_b)$ frequencies are expected,[24] either the VS_4Cu_4 or $V_2Cu_2S_4$ complexes exhibit a strong absorption at 465 cm^{-1} for the former and at 480 cm^{-1} for the latter. An absorption in the region of 350−360 cm^{-1} for complexes **II** and **V** is assigned to $V\text{-}S_{dtc}$ vibration.[25]

Electronic Spectra. The absorption at ca. 350 nm for both types of complexes occurs from S_{ligand}—Cu LMCT in accordance with a similar assignment in $[(PhSCu)_{1-2}MoS_4]^{2-}$.[4c] The VS_4Cu_4 complexes have absorptions at 410−450 nm and 520−550 nm assigned to the charge transfer transition of the MS_4 moiety.[3a] Other V/Cu/S complexes[3f,4e] containing the VS_4 moiety have also absorptions near to these energies.

NMR Spectra. The ^1H and ^{13}C chemical shifts for the ligands R_2dtc^- and PhS^- of the compounds we reported here in DMSO-d_6 solution at room temperature are listed in the experimental section. All the ^1H and ^{13}C NMR spectra determined exhibit the absorption peaks very near to those of free ligands R_2dtc^- and PhS^-, indicating the diamagneticity of these compounds. It is difficult to understand whether the compounds undergo a ligand substitution or solvation by using the ^1H and ^{13}C NMR spectra. Fortunately, ^{51}V NMR spectra afford some useful informations. Figure 3 shows the ^{51}V NMR spectra of the VS_4Cu_4 complexes **I′**, **III**, and **IV** in DMSO of which complexes with mixed ligands exhibit rather complicated spectral features. In comparison with the ^{51}V chemical shifts (Table 11) of other relative V−S complexes, the VS_4Cu_4

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(24) Müller, A.; Jaegermann, W.; Hellmann, W. *J. Mol. Struc.* **1983**, *100*, 559.

(25) Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. A* **1969**, 1152.

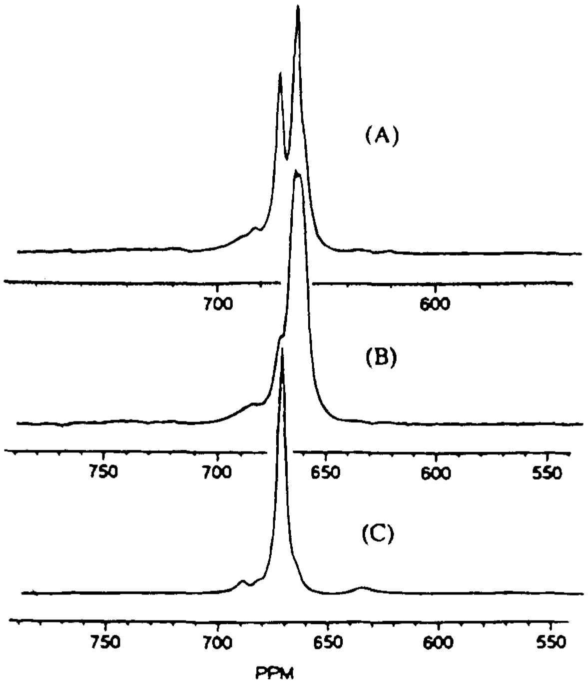

Figure 3. ^{51}V NMR spectra in DMSO-d_6 solution at 297 K for (A) $(Et_4N)_3[VS_4Cu_4(Et_2dtc)(PhS)_3]$, (B) $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]$, and (C) $(Et_4N)_3[VS_4Cu_4(PhS)_4]$.

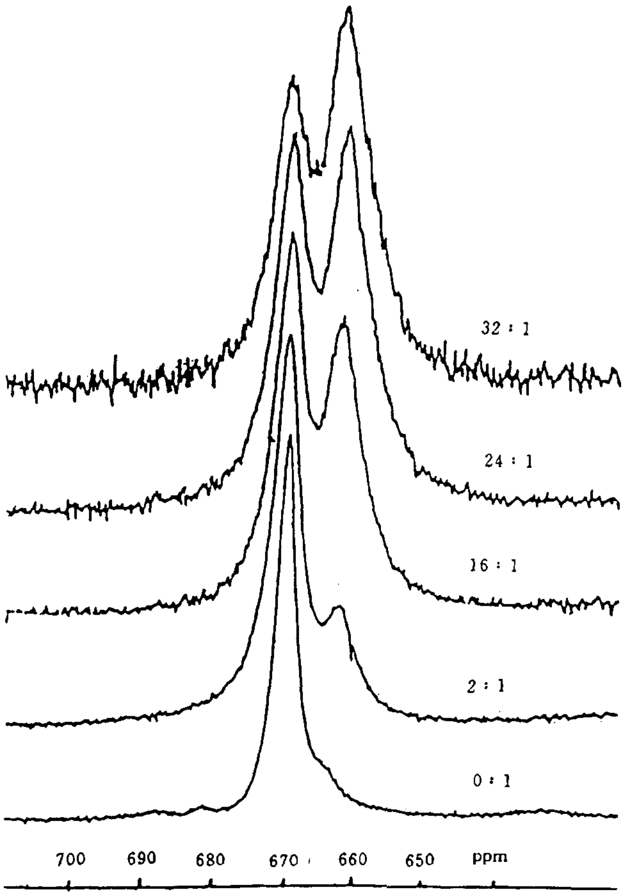

Figure 4. Variation of ^{51}V NMR spectra of $(Et_4N)_3[VS_4Cu_4(PhS)_4]$ in DMSO solution with the addition of OC_4H_8dtcNa.

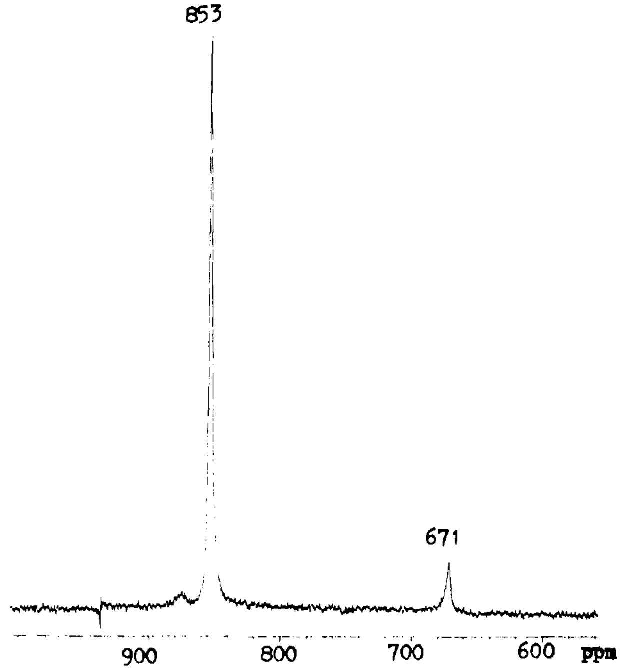

Figure 5. ^{51}V NMR spectrum in DMSO solution initially containing $(Et_4N)_3[VS_4Cu_4(PhS)_4]$ and PPh_3 in a mole ratio of 1:100 at 297 K, showing formation of the VS_4Cu_3 complex.

Table 11. ^{51}V NMR Shifts for the VS_4Cu_4 Complexes and for Selected V/S Complexes

complex	solvent	$\delta(^{51}V)$	ref
I′	DMSO	663, 670	this work
III	DMSO	663(sh), 670	this work
IV	DMSO	670	this work
$[VS_2(S_2)SPh]^{2-}$	DMSO/CD_3CN	970	17
$[VS_4]^{3-}$	DMSO	1388	26
$[V_2(S_2)_2(Et_2dtc)_4]$	$CDCl_3$	103	17

complexes have a vanadium nucleus to be less effectively deshielded than that in VS_4^{3-} [26] by ca. 720 ppm. Meanwhile, it is noticed that, within the series of VS_4Cu_4 complexes, the variation of $\delta(^{51}V)$ is very small by ca. 7 ppm, indicating very small electronic influences from the outermost ligands on the ^{51}V nucleus.

In order to interpret the ^{51}V NMR features of the VS_4Cu_4 complexes containing mixed ligands, we have previously suggested several disproportion reactions[12b] in solution.

$$2[VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-} \rightleftarrows [VS_4Cu_4(R_2dtc)_{n+1}(PhS)_{3-n}]^{3-} + [VS_4Cu_4(R_2dtc)_{n-1}(PhS)_{5-n}]^{3-} \quad (n = 1-3) \qquad (2)$$

These disproportions are caused by ligand exchange and lead to the coexistence of the series of VS_4Cu_4 complexes (n = 0–3 or 4). In this event, the resonance at 670 ppm must be assigned to complex **IV**, while the broad resonance peak centered at 663 ppm is considered to be the contribution of the complexes containing the R_2dtc^- ligand (n = 1–4) which gives rise to higher shielding than PhS^- does, though the difference is very small, only 7 ppm. The effect of PhS^-/R_2dtc^- exchange on the spectra of **I′** and **III** is thus to cause the resonance at 670 ppm and to widen the resonances centered at 663 ppm. In order to establish the disproportion, a ligand substitution reaction has been used. Sodium dialkylthiocarbamate (OC_4H_8dtcNa) was added to the DMSO solution of complex **IV**, causing the substitution of the coordinated PhS^- ligand. The ^{51}V NMR spectra are presented in Figure 4. When mole ratio of R_2dtc^-/**IV** is increased from 2:1 to 32:1, the original resonance peak at 670 ppm gradually lowers accompanied by a gradually risen peak occurring at 663 ppm. It means that complex **IV** is

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(26) Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 3875.

undergoing nucleophilic substitution to form dithiocarbamate complexes.

$$[VS_4Cu_4(PhS)_4]^{3-} + nR_2dtc^- \rightarrow [VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-} + nPhS^- \quad (3)$$

Figure 5 also exhibits the difficulty of "complete" substitution of complex **IV** and explains why we have not yet obtained the VS_4Cu_4 complexes with $n = 3$ or 4 by using an excess of R_2dtc^- in the assembly system. Another substitution reaction of complex **IV** was studied by using a large excess of PPh_3 in DMSO. A strong ^{51}V resonance occurs at 853 ppm (Figure 5), which may arise from a change of $[VS_4(CuL)_4]^{3-}$ to VS_4Cu_3 skeleton bound to PPh_3 ligands. A possible product $[VS_4Cu_3(PPh_3)_4]$ has been reported.[3f] Here each CuL unit is supposed to contribute to the mean decrease of ^{51}V chemical shift versus that of VS_4^{3-} by ca. 180 ppm. The fact that the metal chemical shifts decrease regularly as additional CuL units are bound to the MS_4 moiety has previously been seen in $[MoS_4(CuL)_n]^{m-}$ complexes[27] (L = Cl, Br, I, CN, SPh, and R_2dtc, $m = 2$, or L = PPh_3).

Cyclic Voltammetry. None of all the complexes exhibits any reversible feature. For the VS_4Cu_4 complexes, anodic scans in DMF revealed an irreversible process at +0.65−+0.70 V. Under similar conditions compound **II** gave an irreversible wave at +0.85 V. No corresponding reduction peak was observed on the return scan for all these compounds. However, the oxidation peak would be assigned to the oxidation process of the PhS^- group, because the addition of PhSNa to the solution of **IV** causes a rise in the oxidation peak at 0.70 V. This implies a dissociable property of the coordinated ligand PhS^- in the solution and is consistent with the result of NMR spectra of these complexes.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, crystallographic data, and bond lengths and angles for compounds I, I′, II, III, and IV (45 pages). Ordering information is given on any current masthead page.

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