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Heterobimetallic Aggregates of Copper(I) with Thiovanadate. Syntheses and Characterizations of $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)_n(PhS)_{4-n}]$ (n = 0, 1, 2)

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The chemistry of the mixed metal-sulfur complexes prepared from tetrathiometalates MS_4^{2-} (M = Mo, W) has been extensively explored.[1] It is well-known that the tetrathiometalates act as bidentate ligands to a wide variety of transition metals. Due to the large tendency of Cu^I to bind the sulfur atom, a series of complexes[2,3] have been obtained by the stepwise bidentate chelation of an MS_4 (M = Mo, W, Re) tetrahedron to one to six copper atoms. However, it is still a challenge to obtain the corresponding V/Cu/S complexes. Up to the present time, only two compounds, $VS_4Cu_3(PPh_3)_4$[4] and $VS_4Cu_6(PPh_3)_5Cl_3$,[5] incorporating three and six copper atoms, respectively, in a VS_4 unit were structurally characterized. We report here the syntheses and structural characterizations of several $[VS_4Cu_4]$ complexes with formula $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)_n(PhS)_{4-n}]$ ($OC_4H_8 = O(CH_2CH_2)_2$, dtc = dithiocarbamate, n = 0, 1, 2).

A mixture of $(NH_4)_3VS_4$, CuCl, OC_4H_8dtcNa, and PhSNa in molar ratio of 1:3:4:4 in DMF in the presence of Et_4NCl was stirred for 10–20 h under dinitrogen atmosphere at room temperature. Acetonitrile–acetone (v/v ratio 1:1) was added to the filtrate to cause deposition of a cubane-like cluster $(Et_4N)_2[V_2Cu_2S_4(OC_4H_8dtc)_2(PhS)_2]$, which had been briefly reported elsewhere.[6] After filtering out the cubane-like cluster and allowing the filtrate to stay at room temperature for several days, we obtained black hexagonal crystals of $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]$ (**2**, n = 2)[7] in 31% yield. A similar reaction system and procedures were used to obtain the complexes[7] $(Et_4N)_3[VS_4Cu_4(PhS)_4]$ (**0**, n = 0) and $(Et_4N)_3[VS_4Cu_4(OC_4H_8dtc)(PhS)_3]$ (**1**, n = 1) in 19% and 18% yield, respectively.

The structures of **1**, **2** and **0** are presented in Figure 1. They consist of a $[VS_4Cu_4(OC_4H_8dtc)_n(PhS)_{4-n}]^{3-}$ (n = 0, 1, 2) trianion and three Et_3N^+ cations. These complexes possess an essentially tetrahedral VS_4 unit (bond angles range from 107.8(3)° to 111.2(4)°), to which four copper atoms are bound with V–Cu distances ranging from 2.595(4) to 2.664(5) Å. The five metal atoms 4Cu + V are nearly planar with deviations of not more than 0.1 Å from the least squares plane. The Cu···V···Cu angles concerning the two mutually trans copper atoms are 177.1(1) and 174.7(1)° for **1**, 176.7(3)° for **2**, and 172.7(2) and 176.8(2)° for **0**. These features lead to an approximate D_{2d} symmetry for the VS_4Cu_4 core in each complex. However, the presence of ligand gives rise to the lowering of symmetry. The anion of **1** has no symmetry, and the anion of **0** has a crystallographically imposed C_s symmetry with a mirror plane including atoms S(2), V, and S(3), while the anion of **2** has two pairs of ligands, OC_4H_8dtc and PhS, bound to the four copper atoms in cis-form accompanying an approximate C_s symmetry which is not, however, crystallographically imposed. These complexes contain two types of copper atoms, one trigonally coordinated by two μ_3-S atoms and a terminal PhS group, the other pseudotetrahedrally coordinated by two μ_3-S atoms and a bidentate OC_4H_8dtc ligand. Shorter μ_3–S–Cu distances (2.182(8)-2.251(6) Å) are observed for the trigonal copper atoms than for the tetrahedral ones (2.270(7)-2.288(7) Å) as a consequence of variation of the coordination number. The $Cu–S_{ligand}$ distances including Cu-SPh (2.168(6)-2.204(6) Å) and $Cu–S_{dtc}$ (2.385(5)-2.487(5) Å) are comparable with those in certain Mo–Cu–S complexes, such as $[PhSCuS_2MoS_2]^{2-}$ (Cu-SPh,[8] 2.188(2) Å), and $[MoCu_3S_4(R_2dtc)_3]^{2-}$ ($Cu–S_{dtc}$,[9] 2.367(2)-2.446(2) Å), but the $Cu–S_{dtc}$ distances are obviously longer than those in $Cu^{II}(OC_4H_8dtc)_2$[10] (2.298(1)-2.304(1) Å). This comparison provides an estimation of the oxidation state of Cu(I). Also, X-ray photoelectron spectroscopy (XPS) gave a binding energy of 932.7 eV (Cu, $2P^{3/2}$) for complex **1**. It is a good fit to the electronic state of Cu(I) in Cu_2O. The measurement of bulk magnetic susceptibility showed that all these complexes were diamagnetic and offered a consistent result with the estimation of the metal oxidation states of V(V) + 4Cu(I).

^1H NMR and ^{13}C NMR spectra of complexes **0**–**2**, and of a homologue $(Et_4N)_3[VS_4Cu_4(Et_2dtc)(PhS)_3]$[11] (**1′**) ($n$ = 1) in DMSO-d_6 showed absorption peaks very near to those of free ligands with a reasonable intensity ratio, indicating the diamagneticity of all these complexes. ^{51}V NMR spectra have not been

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(7) Anal. Calcd for **1**, $VCu_4S_9ON_4C_{47}H_{83}$ (MW 1313.85): V, 3.88; Cu, 19.35; S, 21.96; N, 4.26; C, 42.96; H, 6.37. Found: V, 3.87; Cu, 19.09; S, 23.92; N, 4.03; C, 40.65; H, 6.09. Calcd for **2**, $VCu_4S_{10}O_2N_5C_{46}H_{86}$ (MW 1366.93): V, 3.73; Cu, 18.60; S, 23.45; N, 5.12; C, 40.42; H, 6.34. Found: V, 3.91; Cu, 18.30; S, 23.25; N, 5.17; C, 39.88; H, 6.29. Calcd for **0**, $VCu_4S_8N_3C_{48}H_{80}$ (MW 1260.81): V, 8.81; Cu, 10.99; S, 27.72; N, 4.85; C, 41.53; H, 6.10. Found: V, 8.87; Cu, 10.75; S, 27.96; N, 5.00; C, 38.18; H, 5.68. Diffraction data were collected at room temperature on an MSC/Rigaku diffractometer for **1** and **2** , and on an Enraf-Nonius CAD4 diffractometer for **0**. All calculations to solve and refine the structures of**1, 2** and **0** were performed on a VAX/785 computer using a SDP/VAX program by direct and difference Fourier methods. Crystal data for **1**: orthorhombic, space group $P2_12_12_1$ (No. 19), a = 16.917(5) Å, b = 25.996(3) Å, c = 14.937(9) Å, V = 6568.5 Å^3, Z = 4, R = 0.059, and R_w = 0.091 using 2793 reflections with $I > 3.0\sigma(I)$. Crystal data for **2**: orthorhombic, space group $Pna2_1$ (No. 33), a = 24.333(7) Å, b = 17.648(4) Å, c = 14.822(6) Å, V = 6364.8 Å^3, Z = 4, R = 0.058, and R_w = 0.060 using 2857 reflections with $I > 1.0\sigma(I)$. Crystal data for **0**: orthorhombic, space group $Pbnm$ (No. 62), a = 12.209(3) Å, b = 15.493(2) Å, c = 32.210(5) Å, V = 6092.6 Å^3, Z = 4, R = 0.060, and R_w = 0.065 using 1109 reflections with $I > 3.0\sigma(I)$.

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(10) 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), 2.304(1) Å.

(11) Crystals of **1′**were obtained from a similar reaction to that used to prepare **1**, in which Et_2dtcNa was used instead. X-ray parameters for **1′**: $VCu_4S_9N_4C_{47}H_{85}$, M_r 1299.91, triclinic, space group $P1$ (No. 1), a = 10.391(2) Å, b = 12.391(4) Å, c = 12.586(5) Å, α = 78.67(3), β = 82.48(2), γ = 81.59(2)°, V = 1563.1 Å^3, Z = 1, R = 0.039, and R_w = 0.042 using 4538 reflections ($I > 3.0\sigma(I)$).

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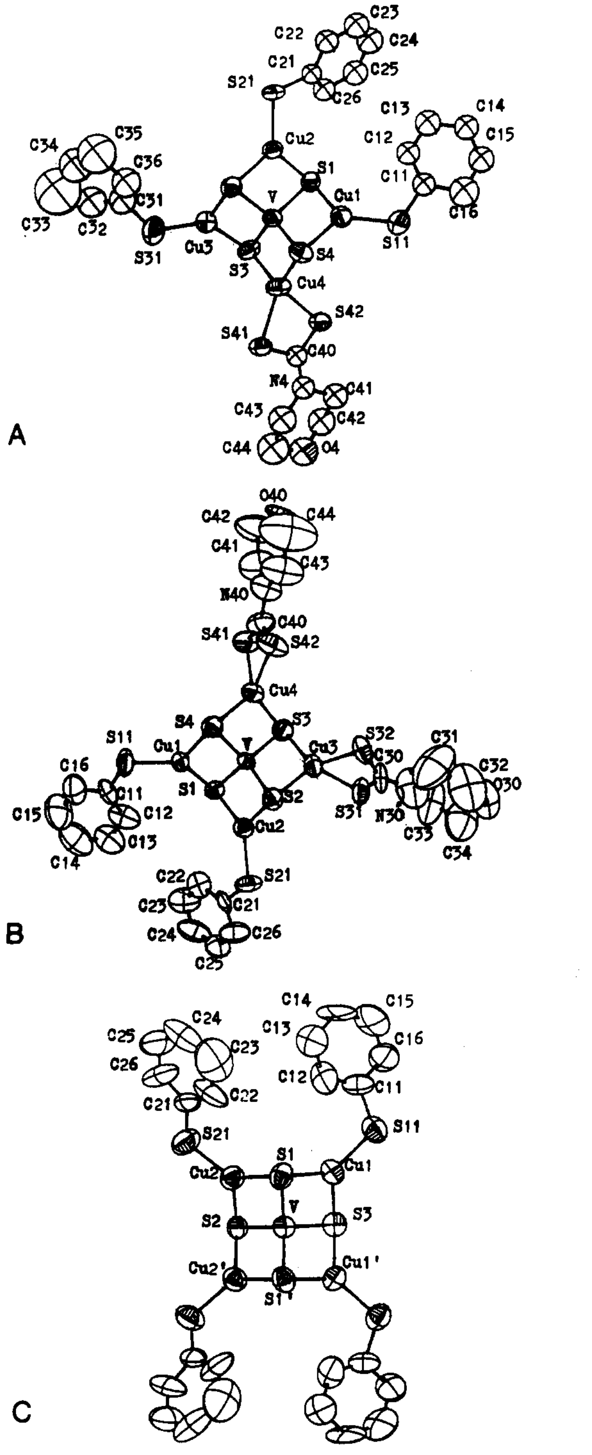

Figure 1. ORTEP diagrams showing 50% probability ellipsoids for (A) $[VS_4Cu_4(OC_4H_8dtc)(PhS)_3]^{3-}$, (B) $[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]^{3-}$, and (C) $[VS_4Cu_4(PhS)_4]^{3-}$.

reported for V–Cu–S clusters so far, although reports[12] on V–S(O) complexes have been seen recently. ^{51}V NMR spectra of complexes **1′**, **2**, and **0** in DMSO-d_6 are presented in Figure 2. Complex **0** has a single resonance at 670 ppm appearing downfield from that of $VOCl_3$, the standard adopted in ^{51}V NMR spectroscopy. Complex **1′** and **2** have rather complicated spectral features containing broad resonances near 663 and 670 ppm. Within the series of VS_4Cu_4 complexes, the variation of $\delta(^{51}V)$ is very small. This indicates that the electronic influences from the outermost ligands on the ^{51}V nucleus are small. A similar case for $[V_2(S_2CS)_4(\mu\text{-}S_2)_2]^{4-}$ [12b] has been noted.

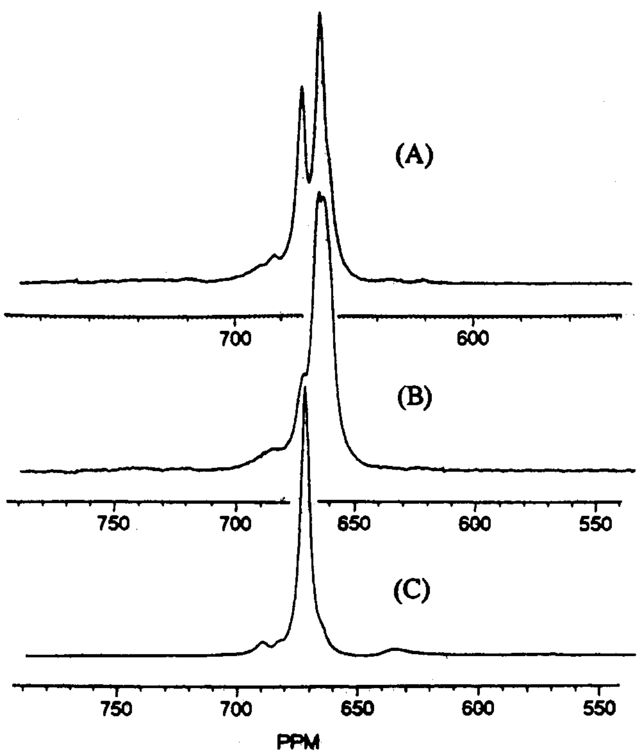

Figure 2. ^{51}V NMR spectra in DMSO solution of (A) $[VS_4Cu_4(Et_2dtc)(PhS)_3]^{3-}$, (B) $[VS_4Cu_4(OC_4H_8dtc)_2(PhS)_2]^{3-}$, and (C) $[VS_4Cu_4(PhS)_4]^{3-}$ at room temperature.

In order to interpret the ^{51}V NMR features of complexes **1′** and **2**, it would be proper to consider that several disproportion reactions caused by ligand exchange are present in solution. The following equations may express the possible disproportion processes

$$2[VS_4Cu_4(R_2dtc)(PhS)_3]^{3-} \rightleftharpoons [VS_4Cu_4(R_2dtc)_2(PhS)_2]^{3-} + [VS_4Cu_4(PhS)_4]^{3-} \quad (1)$$

$$2[VS_4Cu_4(R_2dtc)_2(PhS)_2]^{3-} \rightleftharpoons [VS_4Cu_4(R_2dtc)(PhS)_3]^{3-} + [VS_4Cu_4(R_2dtc)_3(PhS)]^{3-} \quad (2)$$

which lead to the coexistence of all complexes $[VS_4Cu_4(R_2dtc)_n(PhS)_{4-n}]^{3-}$ (n = 0–3) in solution and can reasonably explain the ^{51}V NMR spectra. In this event, complex **0** must be responsible for the resonance at 670 ppm. The effect of PhS/R_2dtc exchange on the spectra of **1′** and **2** is thus to give rise to the resonance at 670 ppm and to widen the resonances centered at 663 ppm, which could be considered to occur from complexes with n = 1–3. Moreover, all the above ^{51}V NMR spectra contain also several weak resonance peaks (682, 688, and 632 ppm) in the neighborhood of the main peaks. These may be caused by solvent/ligand substitution. These spectral results may suggest a synthetic route to complexes $[VS_4Cu_4(R_2dtc)_{3-4}(PhS)_{1-0}]^{3-}$ by a ligand substitution reaction of $[VS_4Cu_4(PhS)_4]^{3-}$ with R_2dtc^-. We are currently carrying out new experiments to address this concern.

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Supplementary Material Available: Tables of atomic coordiantes, anisotropic thermal parameters, crystallographic data, and bond lengths and angles for **1**, **2**, and **0** (25 pages). Ordering information is given on any current masthead page.

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