Syntheses and Structural Characterizations of Two New Cu−S Clusters of Dialkyl Dithiophosphates: A Sulfide-Centered Cu^{I}_{8} Cube, $\{Cu_8[S_2P(O^iPr)_2]_6(\mu_8\text{-}S)\}$, and a Distorted Octahedral $\{Cu_6[S_2P(OEt)_2]_6\cdot 2H_2O\}$ Cluster

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We report here the syntheses and structures of the first sulfur-centered Cu_8 cubic cluster, a cluster in which each edge of the cube is bridged by a sulfur atom of the dithiophosphate ligands, and the first example of an octahedral Cu_6 cluster formed with a dialkyl dithiophosphate ligand. The compound CuDDP (DDP = general dialkyl dithiophosphate) has been described[1a] to be an important antioxidant when added with ZnDDP in the compounding of lubricating oils. However, prior to this work only one structure type was known for Cu^I dialkyl dithiophosphates, namely, the tetranuclear $[Cu(S_2P(O^iPr)_2)]_4$ reported by Lawton.[1b]

Clusters or cage molecules with eight metal atoms in the geometry of a cube were virtually unknown until the synthesis and structural characterization of the $Cu_8(i\text{-MNT})_6^{4-}$ (i-MNT = $[S_2CC(CN)_2]^{2-}$) cluster anion.[2] Since then, several cubic transition-metal clusters have been characterized structurally by different groups.[3−7] Similar cubic frameworks are known in solid-state chemistry.[8] Tetrahedral, Cu_4, and octahedral, Cu_6, structures of Cu^I with sulfur ligands also are well established.[16−18]

Clusters and cages containing Cu^I with chalcogenide ligands have taken on renewed interest through their commercial[1a] use and their possible antioxidant properties in life systems[19] and their photophysics.[20] Cubic clusters encapsulating an additional metal atom recently were explored theoretically by Saillard *et al.*[21]

Treatment of $Cu(CH_3CN)_4PF_6$ (3.80 g, 10 mmol) with $(NH_4)[S_2P(O^iPr)_2]$ (2.54 g, 10 mmol) in the mixed solvent CH_2Cl_2/H_2O (30 mL/40 mL) for 1 day gave a light brown solution, from which at least[22] two products were isolated. Most of the material isolated (>60%) was the tetranuclear species $Cu_4[S_2P(O^iPr)_2]_4$, **1**. Compound **2**, $\{Cu_8[S_2P(O^iPr)_2]_6(S)\}$, was isolated as an air-stable, colorless crystalline material (<5%) and characterized by elemental analysis, NMR, and FAB MS (*m*/*e*, 1820). Both the molecular configuration and composition of **2** were established from X-ray crystallography. A third dialkyl dithiophosphate cluster, $\{Cu_6[S_2P(OEt)_2]_6\cdot 2H_2O\}$, **3**, was obtained[23] in high yield when $Cu(CH_3CN)_4PF_6$ (0.745 g, 2 mmol) in 60 mL of CH_2Cl_2/H_2O (1:1) was treated dropwise with NH_4OH(c) to adjust the pH to 9.5. Addition of $NH_4[S_2P(OEt)_2]$ (0.431 g, 2.12 mmol) produced a slightly cloudy aqueous phase and a greenish-yellow organic phase. After stirring overnight, separation and drying (over $MgSO_4$) of the organic phase followed by evaporation under nitrogen gave yields from 45 to 80% of **3**.

The structure[24] of **2** reveals a sulfur-centered Cu_8 cubic cage (Figure 1) with the six diisopropyl dithiophosphate ligands bridging across each cube face. The interstitial atom was established to be S^{2-} from the crystallography (uncharged molecule). The lattice contains a CH_2Cl_2 solvent molecule, which was confirmed by the ^{1}H-NMR spectroscopy.[22] Special care was taken to rule out Cl^- in the cube center since this structure is known in several clusters. One is the mixed-valence cluster, $[Cu^{I}_{8}Cu^{II}_{6}L_{12}Cl]^{5-}$; L is D-penicillamine.[25a] Another Cl^--centered compound related to **2** is $\{Cu_8[S_2P(OEt)_2]_6Cl\}Cl$, which was isolated[26] from the reaction of $CuCl_2\cdot 2H_2O$ with

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[8] Centered cubic solid-state structures are known in minerals $[(Fe, Co, or Ni)_9S_8]$[9a,b] and synthetic Co_9S_8 pentlandites[9c−e] and in the djerfisherites[10,11] $K_6LiFe_{24}S_{26}Cl$ or $Ba_6Co_{25}S_{27}$. The metallocarbohedrene clusters $Ti_8(C_2)_6$ and $V_8(C_2)_6$ also are proposed to contain a cubic M_8 core.[12] Electron-rich complexes which have an additional metal atom in the center of a metallic core of a cubic cage, $M_9(\mu_4\text{-E})_6$, are known for M = Ni or Pd with E = main group 14, 15, or 16 atoms.[13] A remarkable solid-state material $K_4Cu_8Te_{11}$ in which a potassium ion encapsulated in the center of a cubic Cu_8 core also has been reported.[14] Moreover, a complex with selenium ion in the center of a Cu_8 cube is known[15] in $[Cu_{20}Se_{13}(PEt_3)_{12}]$.

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[22] Compound **1** ($^{31}P\{^1H\}$, 96.7 ppm; LD-TOF-MS, *m*/*e*, 1169.3 ($(M+Cu)^+_{calcd}$ = 1169.5)) forms as the primary product. Compound **2**: ^{1}H NMR ($CDCl_3$, δ in ppm (mult; *J*, Hz)), 1.60 (d, 6.16; 72H, $CH(CH_3)_2$); 5.03 (m; 12H, $CH(CH_3)_2$); 5.48 (s; 2H, CH_2Cl_2); $^{31}P\{^1H\}$, 92 ppm. Anal. Calcd for $C_{36}H_{84}O_{12}P_6S_{13}Cu_8\cdot CH_2Cl_2$: C, 23.32; H, 4.51; S, 21.83. Found: C, 23.10; H, 4.22; S, 21.63. Mp: 195 °C dec. No ^{19}F signals were observed at 400 MHz for ^{19}F NMR which would be expected if the cluster were cationic and PF_6^- were in the lattice. The first crystals obtained were from the *n*-butyl derivative, which produced a LD-TOF-MS *m*/*e* ca. 2025 ($(M + K)^+_{calcd}$ = 2027). The FAB MS of a newly prepared batch of the isopropyl, ^{i}Pr, derivative shows a *m*/*e* of 1820 for the S-centered cluster and a strong peak at *m*/*e* 893 consistent with formation of $Cu_4[S_2P(O^iPr)_2]_3^+$.

[23] Compound **3**: ^{1}H NMR ($CDCl_3$, δ in ppm (mult; *J*, Hz)), 1.36 (t, 7.08; 36H, CH_2CH_3); 4.21 (m; 24H, CH_2CH_3); 1.67 (b; 4H, H_2O); $^{31}P\{^1H\}$, 99.6 ppm; mp 188 °C dec.

[24] Crystal data for complex **2**: monoclinic, space group $C2/c$, a = 23.92(2) Å, b = 12.956(3) Å, c = 24.413(5) Å, β = 91.41(4)°, V = 7563(6) Å^3, Z = 4, D_{calcd} = 1.673 Mg/m^3, μ = 2.805 mm^{-1}, GOF (on F^2) = 1.030, Mo Kα radiation, 4946 unique reflections. The structure was solved by the direct method and refined by using the SHELXL-93 crystallographic software package. The final $R_w(F^2)$ was 0.1205 with conventional $R(F)$ 0.0466 for 358 parameters.

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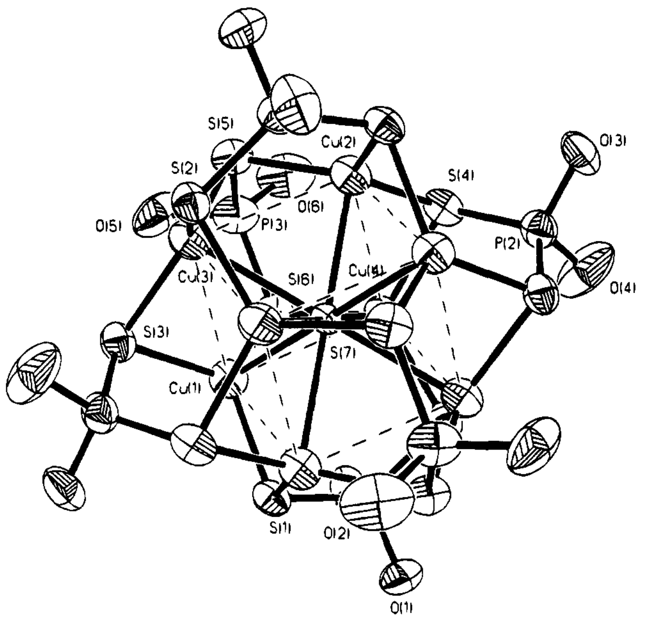

Figure 1. Thermal ellipsoid drawing (50% probability) of $\{Cu_8[S_2P(O^i\text{-}Pr)_2]_6(\mu_8\text{-}S)\}$, **2**. The isopropyl groups have been omitted for clarity. Selected bond distances (Å) and angles (deg): Cu(1)−S(3), 2.281(2); Cu(1)−S(6), 2.286(2); Cu(1)−S(1), 2.288(2); Cu(1)−S(7), 2.691(2); Cu(2)−S(7), 2.669(2); S(1)−P(1), 2.014(2); P(1)−O(1), 1.571(5); Cu(1)−Cu(3), 3.075(4); Cu(2)−Cu(3), 3.101(2); Cu(2)−Cu(4), 3.096(4); S(3)−Cu(1)−S(6) 120.79(7); S(3)−Cu(1)−S(1), 119.34(7); S(6)−Cu(1)−S(1), 118.05(8); S(3)−Cu(1)−S(7), 95.71(5); S(6)−Cu(1)−S(7), 93.86(8); S(1)−Cu(1)−S(7), 93.90(7); Cu(4)−Cu(2)−Cu(3), 91.1(1); Cu(4)−Cu(2)−Cu(1a), 89.9(4); Cu(3)−Cu(2)−Cu(1a), 90.9(4); Cu(3)−Cu(1)−Cu(2a), 90.3(2).

$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_2[\mu\text{-}SOP(OEt)_2][S_2P(OEt)_2]_3(O)_2$. It contains a distorted Cu_8 cube with one Cl^- encapsulated and the other linking Cu_8 cubes into linear polymer chains. The distorted cube is evident from the differences observed in the Cu−Cu edge distances, which range from 3.016(1) to 3.438(2) Å. Compound **2** crystallizes in the *C*2/*c* space group. The central S atom, S7, sits on the inversion center. The molecule has an idealized T_h point group symmetry like the $Cu_8(i\text{-}MNT)_6{}^{4-}$ cubane. The copper atoms are located at the corners of a nearly perfect cube. The average Cu−Cu distance along the edge of the cube is 3.105(6) Å. The Cu−Cu−Cu angle is close to 90° (average 90.6(3)°). The 12 μ_2-S atoms of the ligands are arranged in a nearly regular icosahedron. In addition to the trigonal coordination by three sulfur atoms, each copper atom is weakly bound to the central sulfur atom at a mean distance of 2.694(2) Å. *To our knowledge, compound 2 is the first molecular structure with a μ_8-S bridging ligand.* Previously, compounds containing μ_8-S have been observed in solid-state, antifluorite-type structures of M_2S, where M is Li, Na, K, and Rb.[27] The intraligand S−S "bite" distance in **2** is 3.527(3) Å.

Both symmetry arguments and molecular orbital calculations[28] on the $Cu^I{}_8S_{12}$ cluster suggest that the lowest energy empty atomic orbitals on each trigonally coordinated Cu^I atom combine to form low-lying a_{1g} and t_{1u} orbitals which become the LUMOs of this system. Thus it is not surprising that these MOs can be filled with Cl^-, Se^{2-}, or S^{2-} valence electrons in $Cu_8S_{12}X$-centered clusters. A Fenske−Hall MO calculation confirms[29] that the sulfur atom is primarily S^{2-}.

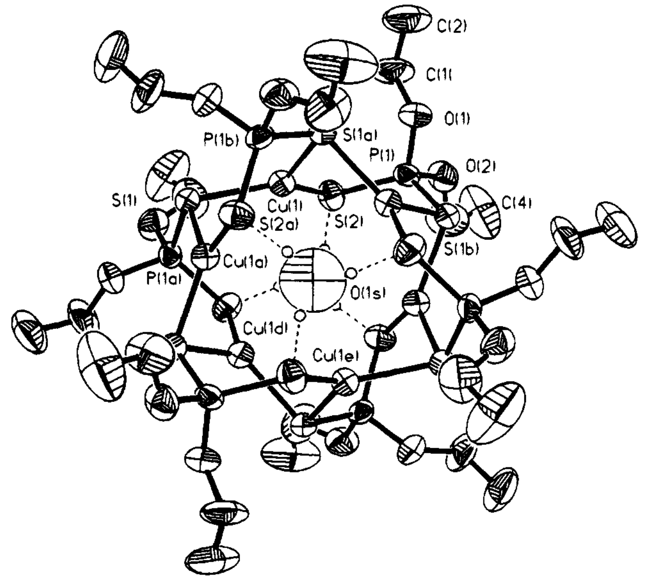

Figure 2. Thermal ellipsoid drawing (50% probability) of $\{Cu_6[S_2P(OEt)_2]_6\cdot 2H_2O\}$, **3**. Distances (Å) and angles (deg): Cu(1)−S(2), 2.234(2); Cu(1)−S(1), 2.249(2); Cu(1)−S(1a), 2.267(2); P(1)−O(2), 1.570(6); P(1)−O(1), 1.583(6); P(1)−S(2), 1.971(3); P(1)−S(1b), 2.035(3); O(1)−C(1), 1.43(1); S(2)−Cu(1)−S(1), 124.0(1); S(1)−Cu(1)−S(1a), 116.5(1); S(2)−P(1)−S(1b), 118.3(1); O(2)−P(1)−O(1), 101.4(4).

Compound[30] **3** crystallizes in the $R\bar{3}$ space group, producing a trigonal antiprism of the six Cu^I atoms in the distorted octahedral array shown in Figure 2 with Cu−Cu distances of 3.13 and 4.31 Å. The water molecules appear to be H-bonded in a disordered fashion to the nonbridging S atoms and sit on the 3-fold crystallographic axis. Thermal gravimetric analysis indicates that the water molecules are strongly held to the cage.

Compound **1** luminesces green under UV light and shows an interesting "luminescence thermochroism".[31] Compound **3** does not luminesce under UV excitation at room temperature. Data for single crystals of **2** are not available to date. We are currently studying this intriguing photophysics, developing a rational synthesis of **2** and classifying the various possible isomers of **3**.

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Supporting Information Available: ¹H NMR spectrum of **2** and listing of crystallographic data, complete bond distances and bond angles, atomic coordinates, and anisotropic displacement parametersfor **2** and **3** (18 pages); observed and calculated structure factors for **2** and **3** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(29) Fenske−Hall calculations performed on the $\{Cu_8[S_2P(OH)_2]_6S\}$ suggest that the HOMO is almost entirely associated with the valence p orbitals on sulfur.

(30) Crystal data for complex **3**: trigonal, space group $R\bar{3}$, a = 20.935(3) Å, c = 11.385(2) Å, V = 4321(1) Å^3, Z = 3, D_{calcd} = 1.762 Mg/m^3, μ = 2.825 mm^{-1}, GOF(F^2) = 1.126, Mo Kα radiation, 963 unique reflections. The structure was solved by the direct method and refined by using the SHELXL-93 crystallographic software package. The final $R_w(F^2)$ was 0.1345 with a conventional $R_1(F^2)$ of 0.0503 for 94 parameters for 805 data with $I > 2\sigma(I)$. Anal. Calcd for $Cu_6C_{24}H_{64}O_{13},P_6S_{12}$: C, 18.9; H, 4.2; S, 25.2. Found: C, 19.3; H, 3.9; S, 25.0.

(31) **1**: $\lambda^{em}{}_{max}$ = 547 nm (excited at 350 nm) at 295 K. $\lambda^{em}{}_{max}$ = 573 nm, 647 nm (excited at 350 nm) at 77 K.