$[Cu_{12}(P_2Se_6)\{Se_2P(OR)_2\}_8]$: Discrete Copper Clusters Containing an Ethane-Like Hexaselenodiphosphate(IV)**

C. W. Liu,* Hsiu-Chih Chen, Ju-Chung Wang, and Tai-Chiun Keng

Most of the structures containing hexaselenodiphosphate(IV), $P_2Se_6^{4-}$, are ternary and quaternary solid-state materials. In addition to the high-temperature reactions of the metals with P and Se, these compounds are usually synthesized by the application of the polychalcophosphate flux method. Notable examples of ternary phases are $M_2P_2Se_6$ (M = Pb,[1a] Hg[1b]) and $Tl_4P_2Se_6$[1c] from Brockner et al., $M_4(P_2Se_6)_3$ (M = Sb, Bi)[2], and $Ag_4P_2Se_6$.[3] The quaternary phases are α,β-KMP_2Se_6 (M = Sb, Bi),[4a, b] $A_2MP_2Se_6$ (A = K, Rb, Cs; M = Mn, Fe,[4c] Pd, Zn, Cd, Hg[4d]), $A_2M_2P_2Se_6$ (A = K, Cs; M = Cu, Ag),[4c] $A_2AuP_2Se_6$ (A = K, Rb),[4e] $A_2Au_2P_2Se_6$ (A = K, Rb),[4f] and $Cs_8M_4(P_2Se_6)_3$ (Sb, Bi)[4g] from Kanatzidis and co-workers; $KReP_2Se_6$ (Re = Y, La, Ce, Pr, Gd)[5] from Dorhout et al.; and $CuMP_2Se_6$ (M = Cr, In).[6] A rare quinary selenophosphate, $Rb_4Sn_2Ag_4(P_2Se_6)_3$, was recently reported by Kanatzidis and Chondroudis.[7]

The $P_2Se_6^{4-}$ moiety has never been observed in discrete molecular structures isolated by the conventional "wet" chemistry method. This may be due to the difficulties arising from the transfer of discrete $P_2Se_6^{4-}$ ions into compounds that are soluble in organic solvents; however, PX_4^{3-} (X = S, Se) ions may be isolated from aqueous solution as hydrates.[8] As a result, very few discrete molecular complexes possessing selenophosphates (PSe_4^{3-}) are known.[9] They are all ionic species. Here we report the serendipitous isolation of $[Cu_{12}(P_2Se_6)\{Se_2P(OEt)_2\}_8]$ (**2**) during the preparation of the selenide-centered Cu_8 cube **1** [Eq. (1)].[10] This is the first example of a discrete, neutral molecule containing an ethane-like $P_2Se_6^{4-}$ bridging group. The coexistence of P^{4+} and P^{5+} centers in one complex is also rare and until now has only been observed in low dimensional compounds with mixed chalcophosphate anions such as $K_4In_2(PSe_5)_2(P_2Se_6)$, $Rb_3Sn(PSe_5)(P_2Se_6)$,[11a] $K_2MP_2S_7$ (M = V, Cr),[11b] and $A_2(RE)P_2Se_7$ (A = Rb, Cs; RE = Ce, Gd).[11c]

$$[Cu(CH_3CN)_4]PF_6 \xrightarrow[CH_2Cl_2,\ 0^{\circ}C]{NH_4Se_2P(OEt)_2} \underset{\mathbf{1}\ (50\%)}{[Cu_8(\mu_8\text{-}Se)\{Se_2P(OEt)_2\}_6]} + \underset{\mathbf{2}\ (11\%)}{[Cu_{12}(P_2Se_6)\{Se_2P(OEt)_2\}_8]} \qquad (1)$$

The single-crystal X-ray diffraction analysis of **2** establishes the presence of a dodecanuclear copper cluster that is stabilized by eight diselenophosphate (dsep) ligands and a $P_2Se_6^{4-}$ ion (Figure 1).[12] The latter is located in the center of the cluster and has an ethane-like geometry in a staggered conformation; the Se-P(5)-Se angle averages 113.1(1)°. With a center of symmetry at the midpoint of the P–P bond, each "PSe_3" moiety of the $P_2Se_6^{4-}$ ligand consists of one μ_3-Se atom and two μ_2-Se atoms that bridge seven Cu atoms. The P–P bond length of 2.241(5) Å corresponds to the value expected for a P–P single bond and has been observed in several compounds that contain $P_2Se_6^{4-}$ ions.[1–7] The variation of the bonding modes can be seen in the different P–Se and Cu–Se bond lengths. The P(5)–Se(11) bond at the μ_3-Se atom (2.234(3) Å) is significantly longer than the P(5)–Se(9) and P(5)–Se(10) bonds at the μ_2-Se atom (2.185(3) and 2.177(3) Å, respectively). While the μ_3-Se–Cu bond lengths are in the range of 2.338(2)–2.657(2) Å, the μ_2-Se–Cu bonds within $P_2Se_6^{4-}$ are close to 2.440(2) Å.

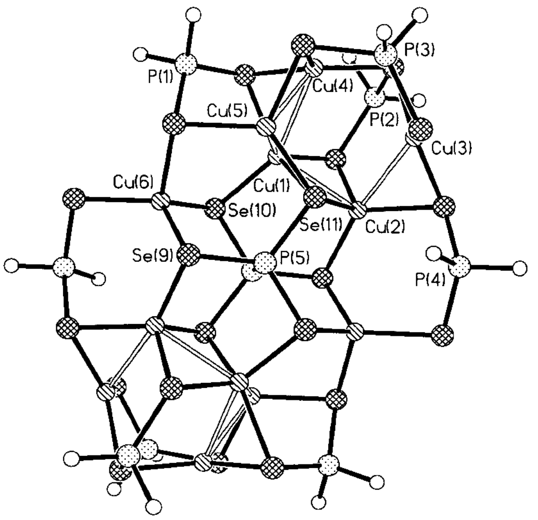
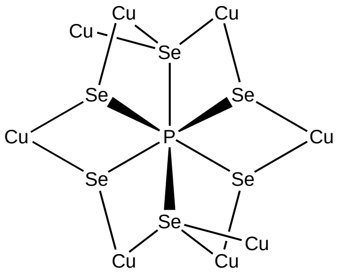


Figure 1. Structure of $\mathbf{2}\cdot 4CH_2Cl_2$. Hatched, cross-hatched, dotted, and white spheres represent Cu, Se, P, and O atoms, respectively; the ethyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–Cu(2) 2.726(2), Cu(1)–Cu(5) 2.774(2), Cu(1)–Cu(4) 2.824(2), Cu(2)–Cu(3) 2.917(2), Cu(4)–Cu(5) 2.610(2), Se(11)–Cu(5) 2.338(2), Se(11)–Cu(2) 2.519(2), Se(11)–Cu(1) 2.657(2), Se(9)–Cu(6) 2.438(2), Se(9)–Cu(2a) 2.445(2), Se(10)–Cu(6) 2.431(2), Se(10)–Cu(1) 2.449(2), P(5)–Se(11) 2.234(3), P(5)–Se(9) 2.185(3), P(5)–Se(10a) 2.177(3), P(5)–P(5a) 2.241(5), P–O 1.564(9)–1.596(9); Se(9)-P(5)-Se(11) 114.8(1), Se(9)-P(5)-Se(10a) 114.2(1), Se(11)-P(5)-Se(10a) 110.3(1).

Overall the hexaselenodiphosphate ligand adopts the unprecedented μ_8:η^3:η^2:η^2:η^3:η^2:η^2 coordination mode **A**. The four outer copper atoms are additionally connected to the eight inner copper atoms by eight dsep ligands. Thus three kinds of coordination



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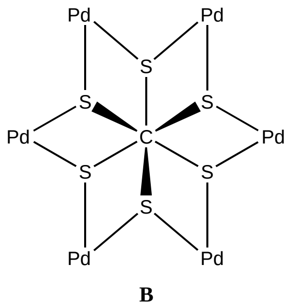
environments are observed around the copper atoms. While Cu(3) and Cu(4) and their symmetric counterparts Cu(3a) and Cu(4a) are trigonally coordinated by three selenium atoms from three dsep ligands, Cu(5) and Cu(5a) are coordinated by two Se atoms from two dsep ligands, with a selenium atom of the $P_2Se_6^{4-}$ moiety occupying the third coordination site. On the other hand, Cu(1), Cu(2), and Cu(6) are each tetrahedrally coordinated by two selenium atoms from $P_2Se_6^{4-}$ and two selenium atoms from two dsep ligands. The dsep ligands also exhibit two distinct bridging modes. Four of them (P(3), P(3a), P(4), P(4a)) are trimetallic triconnective (μ_2, μ_1), and the rest (P(1), P(1a), P(2), P(2a)) show tetrametallic tetraconnective (μ_2, μ_2) coordination patterns.[13]

Several "short" Cu–Cu distances for metal centers connected by dsep ligands are noteworthy: While the bond lengths of Cu(1)–Cu(2), Cu(1)–Cu(5), and Cu(5)–Cu(4) (2.726(2), 2.774(2), and 2.610(2) Å, respectively) are shorter than the sum of the van der Waals radii for copper (2.80 Å),[14] those of Cu(1)–Cu(4) and Cu(2)–Cu(3) (2.824(2) and 2.917(2) Å) are slightly longer. The short Cu–Cu separations may be rationalized by either the strong $d^{10}-d^{10}$ interactions between the metal centers[15] or the ligand-imposed cluster geometry.[16]

The ^{31}P NMR spectrum of **2** exhibits intriguing fluxional behavior in solution. A singlet at $\delta = 134.0$ flanked by two sets of satellites with coupling constants of 173 and 347.8 Hz ($^1J_{P-Se}$) can be reasonably assigned to the P^{4+} center of the $P_2Se_6^{4-}$ moiety; these coupling constants are comparable with those observed in $P_2Se_8^{2-}$,[9b] $[Fe_2(CO)_4(PSe_5)_2]^{2-}$,[9b] and $[SeW(PSe_4)(PSe_2)]^{2-}$.[9a] The satellite with smaller coupling can be assigned to μ_3-Se (Se(11)), as it displays a slightly longer P–Se bond length (see above). The cluster core, $Cu_8(P_2Se_6)$, remains intact in solution, as reflected by the variable temperature ^{31}P NMR study (Figure 2). On the other hand, the peripheral eight dsep ligands are fluxional in solution. This indicates labile Cu–Se bonding.[17] The four chemical shifts for P^{5+} in the range of $\delta = 65-84$ cannot be resolved until $-60\,^\circ C$ in $CDCl_3$. Each resonance is flanked by two sets of satellites, which indicates slightly different selenium environments in the dsep ligand.

The coordination of $P_2Se_6^{4-}$ observed in **2** is unprecedented and has not even been identified in mixed ligands containing Group 15/16 elements.[18] Several years ago Kanatzidis and Kim isolated and structurally characterized two hexanuclear palladium clusters containing a hexathioorthooxalate ligand, $C_2S_6^{6-}$, in its center.[19] The $C_2S_6^{6-}$ ligand, which presumably originated from the methanolothermal reaction of Na_2S_4 and a liberated methyl group of the starting cation $[(CH_3)N(CH_2CH_2)_3N(CH_3)]^{2+}$, also has an ethane-like geometry in a staggered conformation. Each sulfur atom in the cluster bridges two palladium(II) atoms in the $\mu_6{:}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2{:}\eta^2$ coordination mode **B**. Although the $C_2S_6^{6-}$ anion is isostructural and isoelectronic to $P_2Se_6^{4-}$, the coordination patterns demonstrated by these two anions are dramatically different.



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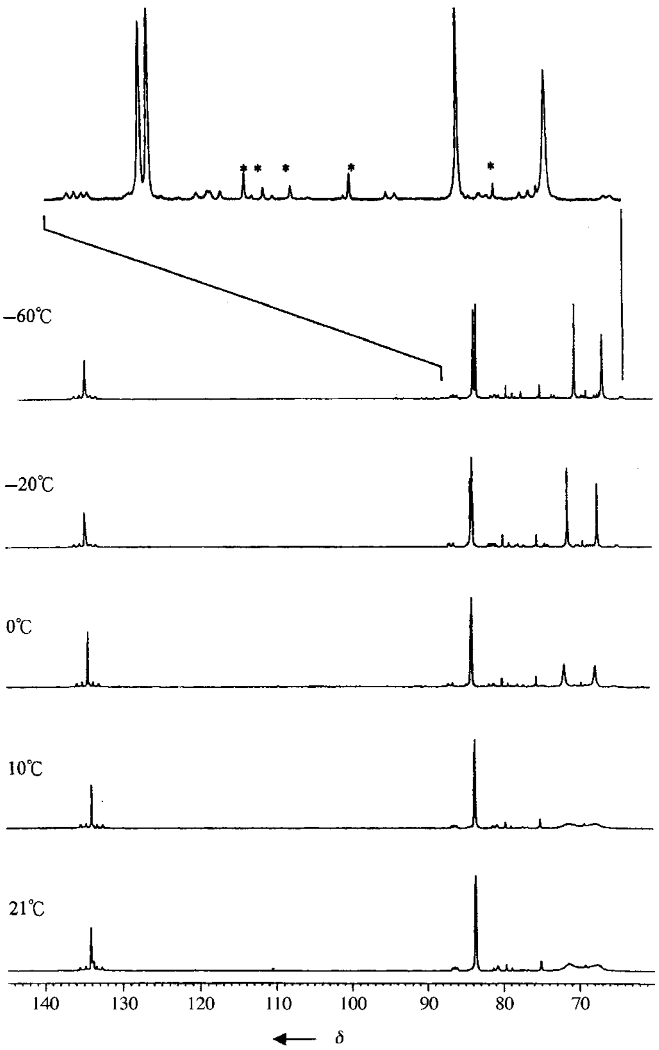

Figure 2. Variable-temperature ^{31}P NMR spectra of cluster **2**. The asterisks indicate impurities.

In conclusion, the first molecular cluster containing the hexaselenodiphosphato ligand has been isolated as the novel dodecanuclear copper species **2**, in which tetravalent and pentavalent phosphorus atoms coexist. The isopropyl derivative **3** has also been structurally characterized.[12] Although it is still not known how the $P_2Se_6^{4-}$ anion in these clusters is formed, it evidently originates from $Se_2P(OR)_2^-$ during the reaction. Recently Fenske et al. used $SP(SSiMe_3)_3$ as a precursor to $P_2S_6^{4-}$ ligands.[20] Work toward the development of a rational synthesis of **2** is currently underway.

Experimental Section

All operations were carried out under N_2 atmosphere with standard Schlenk techniques.

1 and **2**: $NH_4Se_2P(OEt)_2$ (600 mg, 2.02 mmol) in CH_2Cl_2 (30 mL) at 0 °C was stirred for 30 min and then $[Cu(CH_3CN)_4]PF_6$ (250 mg, 0.60 mmol) was added; a yellow solution was obtained after 24 h of stirring. The solvent was evaporated under vacuum, and the residue was washed with copious amounts of diethyl ether. Column chromatography of the residue on silica gel with CH_2Cl_2/*n*-hexane (1/5) as eluent yielded a yellow band of **1** (85.6 mg, 50 %) and an orange band of **2** (20 mg, 11 %).

1: Elemental analysis calcd for $C_{24}H_{60}Cu_8O_{12}P_6Se_{13}$: C 12.75, H 2.67; found: C 12.77, H 2.42; $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 78.5$ (^1J(Se,P) = 674 Hz); ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.34$ (t, ^3J(H,H) = 7 Hz, 36 H; CH_3), 4.13 (m, 24 H; CH_3); positive-ion FAB-MS (nitrobenzyl alcohol): *m*/*z*: 2261.4 [M^+].

2: Elemental analysis calcd for $C_{32}H_{80}Cu_{12}O_{16}P_{10}Se_{22}$: C 10.89, H 2.28; found: C 10.99, H 2.35; $^{31}P\{^1H\}$ NMR ($CDCl_3$, −60 °C): $\delta = 134.0$ (^1J(P,Se) = 173.0, 347.8 Hz), 65.7 (^1J(Se,P) = 573, 660 Hz), 69.6 (^1J(Se,P) = 660, 729 Hz), 82.8 (^1J(Se,P) = 608, 677 Hz), 83.2 (^1J(Se,P) = 624, 712 Hz); ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.33$ (t, ^3J(H, H) = 7 Hz; CH_3), 1.40 (t, ^3J(H, H) = 7 Hz; CH_3), 4.09 (m; CH_2), 4.20 (m; CH_2).

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[12] Crystal data for **2** · 4 CH_2Cl_2 (R = Et; $C_{36}H_{88}Cl_8Cu_{12}O_{16}P_{10}Se_{22}$): $T = 293$ K, triclinic, space group $P\bar{1}$, $a = 13.1963(7)$, $b = 14.2952(8)$, $c = 15.1684(8)$ Å, $\alpha = 63.016(1)$, $\beta = 82.315(1)$, $\gamma = 86.789(1)°$, $V = 2527.0(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.543$ g cm^{-3}, $\mu = 10.807$ mm^{-1}, $2\theta_{max} = 50.10°$, $R1 = 0.0672$ and $wR2 = 0.1799$ for 12163 data (8440 independent), 469 parameters, max./min. residual electron density 1.557/−1.317 e Å^{-3}. Crystal data for **3** · 2 H_2O (R = *i*Pr; $C_{48}H_{116}Cu_{12}O_{18}P_{10}Se_{22}$): $T = 298$ K, triclinic, space group $P\bar{1}$, $a = 14.5231(8)$, $b = 14.5733(8)$, $c = 14.5958(8)$ Å, $\alpha = 84.055(1)$, $\beta = 71.493(1)$, $\gamma = 78.208(1)°$, $V = 2865.1(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.197$ g cm^{-3}, $\mu = 9.350$ mm^{-1}, $2\theta_{max} = 50.06°$, $R1 = 0.0522$ and $wR2 = 0.1274$ for 14084 data (9588 independent), 446 parameters and 8 restraints, max./min. residual electron density 1.197/−0.875 e Å^{-3}. Single crystals were obtained directly from the reaction products. Data were collected on a Siemens SMRT diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and were corrected for Lorentzian, polarization, and Ψ-scan absorption effects. The structures were solved by direct methods and refined against all data using SHELXTL-Plus 5.03. Nine out of 36 carbon atoms were disordered in the crystal of **3** (R = *i*Pr). The bond distances were constrained for disordered atoms and atoms connected to them during the structural refinement (C−C 1.550, O−C 1.450 Å). All but the disordered atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157620 (**2**, R = Et), and CCDC-157621 (**3**, R = *i*Pr). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Superoxovanadium(V) Complex Linking the Peroxide and Dioxygen Chemistry of Vanadium[**]

Harald Kelm and Hans-Jörg Krüger[*]

Dedicated to Professor Ernst G. Jäger
on the occasion of his 65th birthday

Within the one-electron redox chemistry of dioxygen species, the superoxide anion links the chemistry of molecular oxygen and peroxide. While peroxovanadium complexes are well established, superoxovanadium complexes are quite rare and have only been observed transiently by ESR spectroscopic methods as short-lived species in the reaction of vanadyl(IV) ions with hydrogen peroxide or in the reaction of metavanadate with mixtures of Ce^{4+}/H_2O_2 or Fe^{2+}/H_2O_2, using rapid-mixing flow techniques in the cavity of the ESR

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