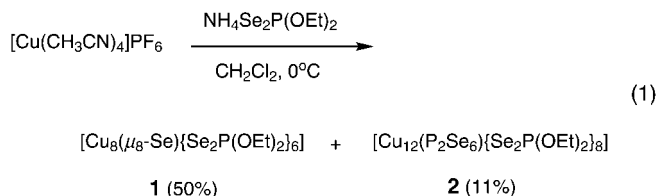


[Cu₁₂(P₂Se₆){Se₂P(OR)₂}]₈: Discrete Copper Clusters Containing an Ethane-Like Hexaselenodiphosphate(IV)**

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

Most of the structures containing hexaselenodiphosphate(IV), P₂Se₆^{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 M₂P₂Se₆ (M = Pb,^[1a] Hg^[1b]) and Ti₄P₂Se₆^[1c] from Brockner et al., M₄(P₂Se₆)₃ (M = Sb, Bi)^[2], and Ag₄P₂Se₆.^[3] The quaternary phases are α,β-KMP₂Se₆ (M = Sb, Bi),^[4a, b] A₂MP₂Se₆ (A = K, Rb, Cs; M = Mn, Fe,^[4c] Pd, Zn, Cd, Hg^[4d]), A₂M₂P₂Se₆ (A = K, Cs; M = Cu, Ag),^[4c] A₂AuP₂Se₆ (A = K, Rb),^[4e] A₂Au₂-P₂Se₆ (A = K, Rb),^[4f] and Cs₈M₄(P₂Se₆)₃ (Sb, Bi)^[4g] from Kanatzidis and co-workers; KReP₂Se₆ (Re = Y, La, Ce, Pr, Gd)^[5] from Dorhout et al.; and CuMP₂Se₆ (M = Cr, In).^[6] A rare quinary selenophosphate, Rb₄Sn₂Ag₄(P₂Se₆)₃, was recently reported by Kanatzidis and Chondroudis.^[7]

The P₂Se₆^{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 P₂Se₆^{4−} ions into compounds that are soluble in organic solvents; however, PX₄^{3−} (X = S, Se) ions may be isolated from aqueous solution as hydrates.^[8] As a result, very few discrete molecular complexes possessing selenophosphates (PSe₄^{3−}) are known.^[9] They are all ionic species. Here we report the serendipitous isolation of [Cu₁₂(P₂Se₆){Se₂P(OEt)₂}]₈ (**2**) during the preparation of the selenide-centered Cu₈ cube **1** [Eq. (1)].^[10] This is the first



example of a discrete, neutral molecule containing an ethane-like P₂Se₆^{4−} bridging group. The coexistence of P⁴⁺ and P⁵⁺ centers in one complex is also rare and until now has only been observed in low dimensional compounds with mixed chalcophosphate anions such as K₄In₂(PSe₃)₂(P₂Se₆),

Rb₃Sn(PSe₃)(P₂Se₆),^[11a] K₂MP₂S₇ (M = V, Cr),^[11b] and A₂(RE)P₂Se₇ (A = Rb, Cs; RE = Ce, Gd).^[11c]

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 P₂Se₆^{4−} ion (Figure 1).^[12] The latter is located in the center

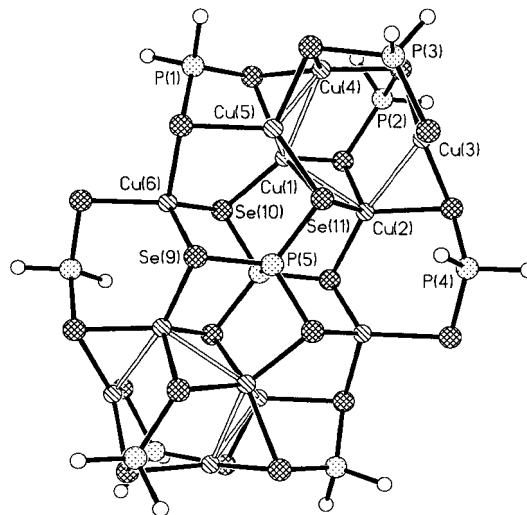
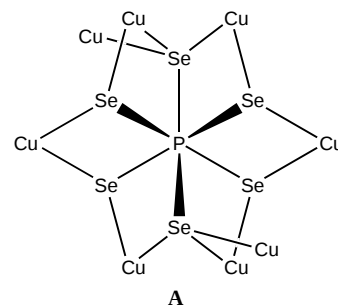


Figure 1. Structure of **2** · 4CH₂Cl₂. Hatched, cross-hatched, dotted, and white spheres represent Cu, Se, P, and O atoms, respectively; the ethyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–Cu(2) 2.726(2), Cu(1)–Cu(5) 2.774(2), Cu(1)–Cu(4) 2.824(2), Cu(2)–Cu(3) 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).

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 “PSe₃” moiety of the P₂Se₆^{4−} ligand consists of one μ₃-Se atom and two μ₂-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 P₂Se₆^{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 μ₃-Se atom (2.234(3) Å) is significantly longer than the P(5)–Se(9) and P(5)–Se(10) bonds at the μ₂-Se atom (2.185(3) and 2.177(3) Å, respectively). While the μ₃-Se–Cu bond lengths are in the range of 2.338(2)–2.657(2) Å, the μ₂-Se–Cu bonds within P₂Se₆^{4−} are close to 2.440(2) Å.

Overall the hexaselenodiphosphate ligand adopts the unprecedented μ₈:η³:η²:η²:η²:η² 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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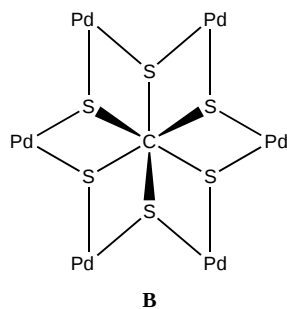
[**] R = Et, *i*Pr. This research was supported by the National Science Council of Taiwan (NSC 89-2113-M-033-017).

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 hexathioorthoxalate 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 $\mu_6:\eta^2:\eta^2:\eta^2:\eta^2:\eta^2$ coordination mode **B**. Although the $C_2S_6^{6-}$ anion is isostructural

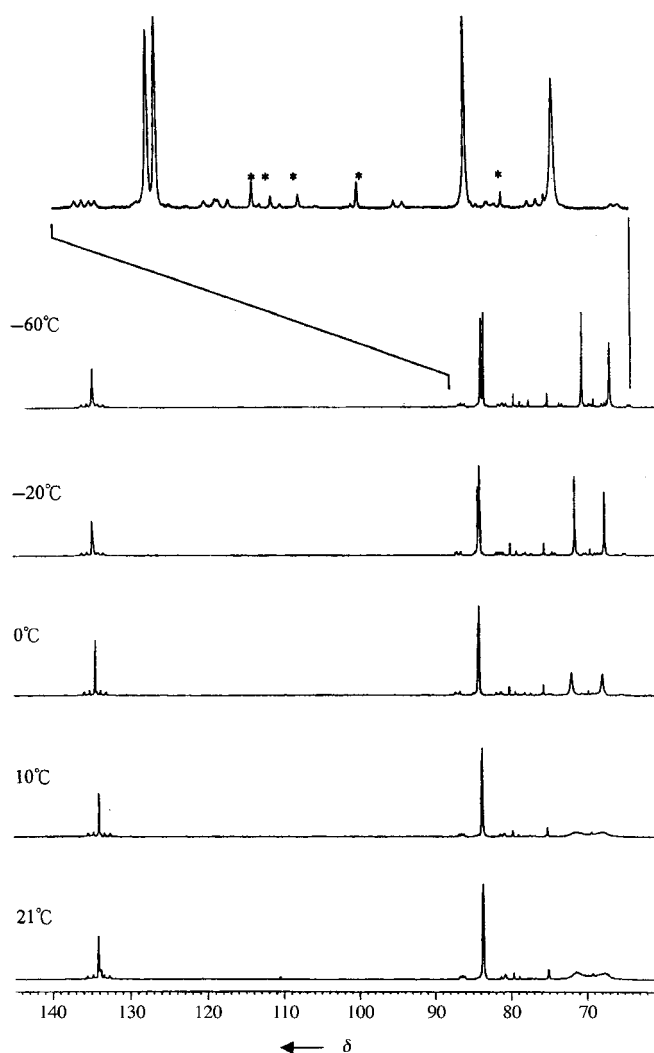


Figure 2. Variable-temperature ^{31}P NMR spectra of cluster **2**. The asterisks indicate impurities.

and isoelectronic to $P_2Se_6^{4-}$, the coordination patterns demonstrated by these two anions are dramatically different.

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 $0^\circ C$ 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 $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ (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 $\text{C}_{24}\text{H}_{60}\text{Cu}_8\text{O}_{12}\text{P}_6\text{Se}_{13}$: C 12.75, H 2.67; found: C 12.77, H 2.42; $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ = 78.5 ($^1J(\text{Se,P})$ = 674 Hz); ^1H NMR (CDCl_3 , 25 °C): δ = 1.34 (t, $^3J(\text{H,H})$ = 7 Hz, 36H; CH_3), 4.13 (m, 24H; CH_2); positive-ion FAB-MS (nitrobenzyl alcohol): m/z : 2261.4 [M^+].

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

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- [12] Crystal data for **2** · $4\text{CH}_2\text{Cl}_2$ (R = Et; $\text{C}_{36}\text{H}_{88}\text{Cl}_8\text{Cu}_{12}\text{O}_{16}\text{P}_{10}\text{Se}_{22}$): T = 293 K, triclinic, space group $P\bar{1}$, a = 13.1963(7), b = 14.2952(8), c = 15.1684(8) Å, α = 63.016(1), β = 82.315(1), γ = 86.789(1)°, V = 2527.0(2) Å³, Z = 1, ρ_{calcd} = 2.543 g cm^{–3}, μ = 10.807 mm^{–1}, $2\theta_{\text{max}}$ = 50.10°, $R1$ = 0.0672 and $wR2$ = 0.1799 for 12 163 data (8440 independent), 469 parameters, max./min. residual electron density 1.557/–1.317 e Å^{–3}. Crystal data for **3** · $2\text{H}_2\text{O}$ (R = *i*Pr; $\text{C}_{48}\text{H}_{116}\text{Cu}_{12}\text{O}_{18}\text{P}_{10}\text{Se}_{22}$): T = 298 K, triclinic, space group $P\bar{1}$, a = 14.5231(8), b = 14.5733(8), c = 14.5958(8) Å, α = 84.055(1), β = 71.493(1), γ = 78.208(1)°, V = 2865.1(3) Å³, Z = 1, ρ_{calcd} = 2.197 g cm^{–3}, μ = 9.350 mm^{–1}, $2\theta_{\text{max}}$ = 50.06°, $R1$ = 0.0522 and $wR2$ = 0.1274 for 14 084 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 MoK_α radiation (λ = 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 CB2 1EZ, 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 $\text{Ce}^{4+}/\text{H}_2\text{O}_2$ or $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, using rapid-mixing flow techniques in the cavity of the ESR

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