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The First, Discrete Zn_4 Tetrahedron with a Selenium Atom in the Center: X-ray Structure and Solution Study of $[Zn_4(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6]$[†]

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The first discrete, selenium-centered tetranuclear zinc cluster $[Zn_4(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6]$ was isolated and characterized. The cluster consists of six edge-bridged dsep ligands with four zinc atoms in a slightly distorted tetrahedron and a μ_4-Se atom in the center. In addition, 12 μ_2-bridging selenium atoms form a Se_{12} icosahedron. From variable-temperature ^{31}P NMR studies, it was observed that the cluster $[Zn_4(Se)\{Se_2P(OPr)_2\}_6]$ is partly decomposed to $[Zn\{Se_2P(OPr)_2\}_2]$ and the monomeric species $[Zn\{Se_2P(OPr)_2\}_2]$ is further in equilibrium with its dimer $[Zn\{Se_2P(OPr)_2\}_2]_2$.

Chalcogenide-centered tetrahedral clusters are among the targets of current vigorous research activity in both biology and material science because of the novel μ_4-sulfide-bridged tetranuclear Cu_z cluster active site identified in nitrous oxide reductase[1] and supertetrahedral clusters aimed at the preparation of novel types of porous structures.[2] To our knowledge, there has been no report of a discrete selenium-centered tetranuclear zinc cluster, although discrete sulfur-centered tetranuclear zinc clusters, $[Zn_4(S)\{S_2P(OEt)_2\}_6]$ and $[Zn_4(S)\{S_2As(CH_3)_2\}_6]$, are known.[3] Moreover, tetranuclear Zn^{2+} clusters having a Zn_4O^{6+} core are well-known in the literature.[4]

Over the past several years, we have successfully utilized the *O*,*O*′-dialkyl diselenophosphato ligands as a selenium transfer reagent and characterized several selenide-centered clusters of copper and silver.[5] The geometries around the central selenium atom can be cubic, tricapped trigonal prismatic, and distorted cis-bicapped trapezoidal prismatic. Molecular orbital calculations by density functional theory at the B3LYP level indicate weak interactions between the central selenium atom and peripheral metal atoms.[6] To extend our research efforts in selenium-centered cluster synthesis, herein, we report the first selenide-centered, discrete Zn_4 tetrahedron, $[Zn_4(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6]$, and its stability in solution, which was also investigated by variable-temperature ^{31}P NMR techniques.

Treatment of $Zn(ClO_4)_2{\cdot}6H_2O$ and $(NH_4)[Se_2P(OPr)_2]$ in a molar ratio of 1:2 in deoxygenated H_2O at room temperature for 5 min affords an oily substance from which the compound $[Zn_4(Se)\{Se_2P(OPr)_2\}_6]$ (**1**) was formed in ~68% yield.[7] Elemental analyses of the compound are in good agreement with the molecular formulation of **1**. Positive FAB mass spectra of **1** reveal a peak at *m*/*z* 1874.0, which corresponds to the intact molecule with the loss of one dsep ligand, $(Zn_4SeL_5)^+$, and fragment peaks at *m*/*z* 1052.6 and 372.9, which belong to the dimeric $(Zn_2L_3{}^+)$ and monomeric (ZnL^+) species with the loss of one dsep ligand (vide infra),

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[†] Dedicated to Professor John P. Fackler, Jr., on the occasion of his 70th birthday.

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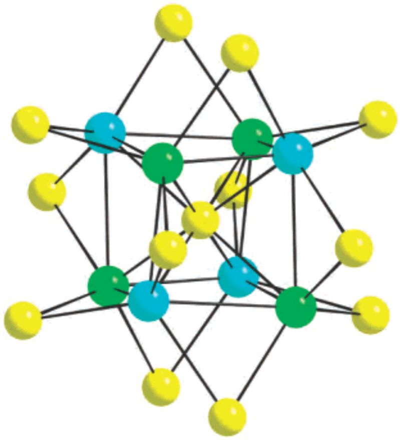

Figure 1. $Zn_4(\mu_4\text{-}Se)Se_{12}$ core of cluster **1**, of which eight Zn atom locations (50% occupancy for each Zn) are generated and have two interpenetrating Zn_4 tetrahedra (displayed in different colors) with a Se atom in the center.

respectively. ^1H NMR spectra exhibit chemical shifts at δ 0.98, 1.78, and 4.1 ppm for the propyl group of the dsep ligand in **1**.

Cluster **1** was structurally characterized by single-crystal X-ray diffraction and crystallizes in the trigonal space group $R\bar{3}$ with three molecules per unit cell.[8] The core unit of **1**, $Zn_4(\mu_4\text{-}Se)Se_{12}$, is displayed in Figure 1. A total of eight zinc atom locations are generated, each of them having 50% occupancy, as required by the symmetry so that two interpenetrating Zn_4 tetrahedra, depicted in different colors, with a Se atom in the center are produced. The structure can be described as a selenium-centered Zn_8 cube with each diselenophosphate ligand occupying a square face of the cube. In addition, 12 μ_2-bridging selenium atoms form a Se_{12} icosahedron.[9] Thus, the $\{Se_{13}\}$ framework, a selenium-centered selenium icosahedron, consists of a total of eight tetrahedral holes of which one-half are occupied by the zinc ions.

A perspective view of the cluster **1** is shown in Figure 2. The cluster consists of six edge-bridged dsep ligands and four zinc atoms in a tetrahedron with a selenium atom in the center. All of the zinc atoms are connected by bridging dsep ligands. Thus, the dsep ligands exhibit a bimetallic biconnective (μ_2, η^2) coordination pattern.[10] Each zinc atom is coordinated by three selenium atoms from three bridging dsep ligands and one central selenium atom. The Zn−μ_4-Se distances lie in the range 2.345(2)−2.495(3) Å, which is comparable to the 2.457−2.465 Å range in $[Zn_4(\mu_4\text{-}Se)(SnSe_4)_4]^{10-}$.[10] The average Zn···Zn distance is 3.888 Å, slightly shorter than the 4.027 Å value found in $[Zn_4(\mu_4\text{-}Se)(SnSe_4)_4]^{10-}$.[11] The Se···Se bite distance is 3.694 Å, comparable to Se···Se bite distances of 3.637−3.811 Å observed in Cu^I and Ag^I clusters.[5,12] The Zn−μ_2-Se distances lie between 2.460(2) and 2.640(2) Å, which are comparable to the Zn−Se distances of 2.462−2.481 Å in $[Me_4N]_2[Zn(SePh)_4]$.[13] The Se−Zn−Se angles are between 102.9(1)° and 115.5(1)°, which indicates that the geometry at the zinc center is distorted from normal tetrahedral. The geometry at the selenium center also deviates slightly from regular tetrahedral, and the Zn−μ_4-Se−Zn angles are 106.9(1)° and 112.0(1)°.

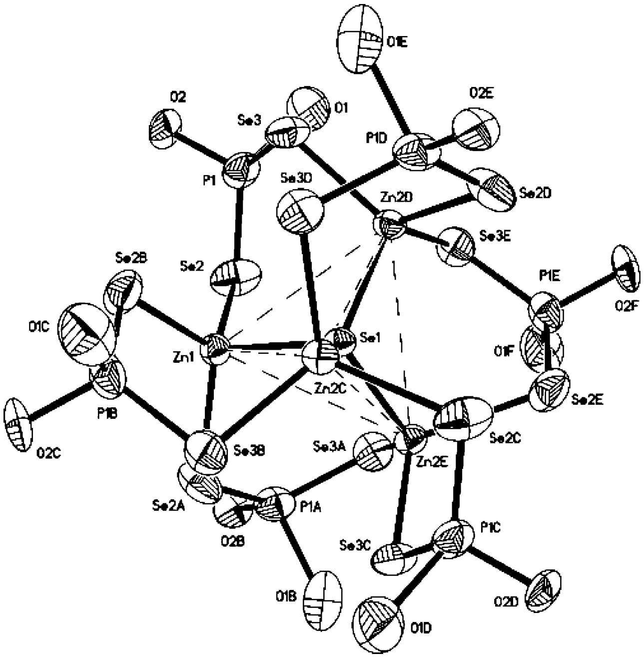

Figure 2. Thermal ellipsoid drawing (50% probability level) of $[Zn_4(Se)\{Se_2P(OPr)_2\}_6]$ (**1**) with atom-numbering scheme. The propyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): Se(1)−Zn(1) 2.495(3), Se(1)−Zn(2C) 2.345(2), Zn(1)−Se(2) 2.487(1), Zn(2C)−Se(3B) 2.460(2), Zn(2C)−Se(3D) 2.532(2), Zn(2C)−Se(2C) 2.640(2), Se(2)−P(1) 2.098(3), Se(3)−P(1) 2.129(4), Zn(1)−Se(1)−Zn(2C) 106.85(4), Zn(2C)−Se(1)−Zn(2D) 111.96(4), Se(2)−Zn(1)−Se(2B) 115.02(6), Se(1)−Zn(1)−Se(2) 103.10(8), Se(1)−Zn(2C)−Se(3B) 109.02(7), Se(1)−Zn(2C)−Se(2C) 102.85(7), Se(1)−Zn(2C)−Se(3D) 106.63(7), Se(3B)−Zn(2C)−Se(2C) 111.98(8), Se(3B)−Zn(2C)−Se(3D) 115.55(7), Se(2C)−Zn(2C)−Se(3D) 109.89(8), Se(2)−P(1)−Se(3) 121.84(13).

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(7) Synthesis of **1**: $Zn(ClO_4)_2 \cdot 6H_2O$ (2.4 mmol, 0.893 g) was dissolved in 40 mL of freshly distilled water in a 100-mL Schlenk flask. The aqueous solution was deoxygenated by freeze−pump−thaw cycles. This solution was then transferred by cannula to another 100-mL Schlenk flask containing diselenophosphate ligand $[\{NH_4Se_2P(OPr)_2\}$, 4.8 mmol, 1.560 g]. The solution mixture was stirred for 5 min at ambient temperature under nitrogen atmosphere. An oily white precipitate was formed during the reaction period. The resulting oily substance was further dissolved in diethyl ether (50 mL) and allowed to stand at room temperature for 1 day. Colorless crystals of **1** (0.89 g, 68%) suitable for single-crystal X-ray diffraction experiments were deposited. Anal. Calcd for $C_{36}H_{84}Zn_4O_{12}P_6Se_{13}$ (%): C, 19.79; H, 3.85. Found: C, 20.16; H, 4.02; FAB MS, m/z (m/z_{calcd}): 1874.0 (1875.9, $Zn_4SeL_5^+$), 1052.6 (1052.6, $Zn_2L_3^+$), 372.9 (372.8, ZnL^+). ^1H NMR (CD_2Cl_2) δ: 0.98 (t, 36H, $OCH_2CH_2CH_3$), 1.78 (m, 24H, $OCH_2CH_2CH_3$), 4.1 (m, 24H, $OCH_2CH_2CH_3$).

(8) Crystallographic data for **1**: $C_{36}H_{84}O_{12}P_6Se_{13}Zn_4$, crystal dimensions $0.46 \times 0.32 \times 0.26$ mm, trigonal, space group $R3$, $a = 22.977(2)$ Å, $c = 12.196(3)$ Å, $V = 5576.3(14)$ Å^3, $Z = 3$, ρ_{calcd} 1.950 g cm^{-3}, $2\theta_{max} = 50.08°$, Mo Kα radiation ($\lambda = 0.71073$ Å), ω scan, $T = 298$ K, $\mu = 7.811$ mm^{-1}, 9498 measured reflections, 2188 independent reflections ($R_{int} = 0.0403$), 1300 with $I > 2\sigma(I)$, Lorentzian and empirical absorption corrections were made, 186 parameters, 20 constraints, R values for reflections with $I > 2\sigma(I)$: R1 = 0.0598, wR2 = 0.1714. Maximum/minimum residual electron density 0.705/−0.635 e Å^3. All carbon and oxygen atoms of the propoxyl groups are disordered over two sites, and each in 50% occupancy is refined. H-atoms were not included.

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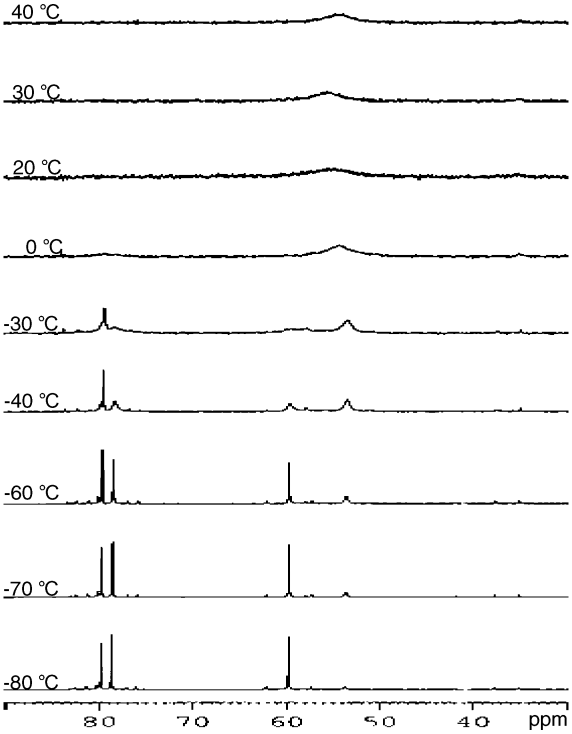
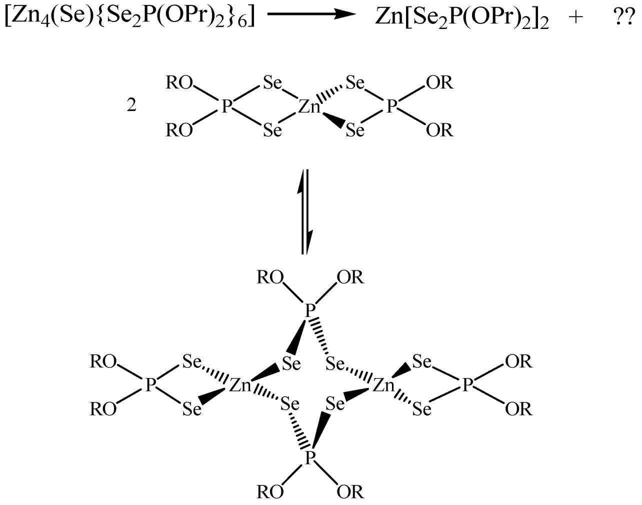


Figure 3. Variable-temperature ^{31}P NMR spectra of $[Zn_4(Se)\{Se_2P(OPr)_2\}_6]$ in CD_2Cl_2.

Scheme 1 Tetranuclear Zinc Cluster, $[Zn_4(Se)\{Se_2P(OPr)_2\}_6]$, Partially Decomposes to $[Zn\{Se_2P(OPr)_2\}_2]$, Which Is Further in Equilibrium with Its Dimer in CD_2Cl_2



$$[Zn_4(Se)\{Se_2P(OPr)_2\}_6] \longrightarrow Zn[Se_2P(OPr)_2]_2 \ + \ ??$$

Solution studies of the cluster **1** were performed by ^{31}P NMR spectroscopy at variable temperatures from 40 to −80 °C in CD_2Cl_2 (Figure 3). At the ambient NMR experimental temperature of 20 °C, compound **1** exhibits a broad peak at δ 55.2 ppm. Even at 40 °C, the peak remains broad. At −30 °C, a new peak appears at 80.1 ppm at the expense of the original broad peak, and this peak becomes sharp at −40 °C. At −40 °C, two other new peaks appeared at 78.8 and 60.0 ppm. Decreasing the temperature to −60 °C, these two new peaks at δ 78.8 and 60.0 ppm become sharp, and they are equal in intensity. Upon a further decrease in the temperature to −80 °C, the intensity of the peak at 80.1 ppm ($J_{SeP} = 667$ Hz) decreased slightly, whereas the other two peaks at δ 78.8 ppm ($J_{SeP} = 644$ Hz) and 60.0 ppm ($J_{SeP} = 589$ Hz) increased gradually. These observations suggest that the cluster $[Zn_4(Se)\{Se_2P(OPr)_2\}_6]$ partially decomposes into $[Zn\{Se_2P(OPr)_2\}_2]$ and some unidentified species in solution.[14] The compound $[Zn\{Se_2P(OPr)_2\}_2]$ is further in equilibrium with its dimer $[Zn\{Se_2P(OPr)_2\}_2]_2$, as demonstrated from its isopropyl derivatives.[15] Therefore, because of these two processes (Scheme 1), cluster **1** exhibits a broad peak at 55.2 ppm. The compound $[Zn\{Se_2P(OPr)_2\}_2]$ becomes a dimer at lower temperatures of approximately −80 °C and exhibits two sharp peaks at δ 78.8 and 60.0 ppm, which are the chemical shifts of bridging and chelating ligands, respectively, of the dimer. Thus, the resonance frequency at δ 80.1 ppm is the chemical shift of the tetranuclear cluster $[Zn_4(\mu_4\text{-}Se)\{Se_2P(OPr)_2\}_6]$.

The ^{77}Se{^{1}H} NMR spectrum of **1** in CD_2Cl_2 at −80 °C displays three doublets centered at δ 44.9 ($J_{SeP} = 668$ Hz), 58.8 ($J_{SeP} = 644$ Hz), and 193.9 ($J_{SeP} = 589$ Hz) ppm, as well as a singlet at −673.1 ppm. The doublet at 44.9 ppm is due to the presence of tetranuclear cluster in solution. Two doublets with equal intensity at 58.8 and 193.9 ppm are due to bridging and chelating ligands of the dimer. Thus, the resonance frequency for the quadruply bridging selenium atom in **1** is at −673.1 ppm.

Surprisingly, prolonged stirring of the above reaction in H_2O produces $[Zn_4(\mu_4\text{-}O)\{Se_2P(OPr)_2\}_6]$, and the details of plausible cluster transformation will be the subject of a future report.

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Supporting Information Available: X-ray crystallographic details for **1** in CIF format. The CCDC number for this CIF is 248021. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) It is known from the literature[14b] that "basic" zinc *O,O′*-dialkyldithiophosphates, $[Zn_4(O)\{S_2P(OR)_2\}_6]$, are in equilibrium with $[Zn\{S_2P(OR)_2\}]$ and ZnO in solution. Therefore, ZnSe might be one of the unidentified species. (b) Harrison, P. G.; Kikabhai, T. *J. Chem. Soc., Dalton Trans.* **1987**, 807.

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