

Zinc Chalcogenolate Complexes as Capping Agents in the Synthesis of Ternary II–II'–VI Nanoclusters: Structure and Photophysical Properties of $[(N,N'-tmeda)_5Zn_5Cd_{11}Se_{13}(SePh)_6(thf)_2]$

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Clusters and colloids of II–VI semiconductors represent an area of ever-increasing research interest, due to the unique optical and electronic properties demonstrated by these quantum-confined particles (quantum dots or QDs).¹ Nanometer-sized clusters whose structures can be determined crystallographically are of interest because they allow an investigation of the development of materials properties from the molecular-size regime.² Banin and co-workers reported on the photophysical properties of a series of crystallographically characterized CdSe clusters, and demonstrated that the quantum confinement effects observed for colloidal CdSe particles could be extended into this molecular-size range.³ The chemistry of ternary II–II'–VI nanoclusters remains undeveloped, primarily due to the lack of a general synthetic pathway for their formation. Bulk II–II'–VI semiconductors, such as $Zn_xCd_{1-x}Se$, find use in a wide array of applications in devices such as light-emitting diodes, lasers, and photodetectors.⁴ The development of molecular nanometer-sized analogues of these systems is attractive for the understanding of structure–property relationships pertaining to the optical properties of these and related colloidal nanoparticles.⁵ Surface passivation of II–VI QDs is often achieved via the growth of one II–VI material onto the surface of a quantum dot seed of another. In these so-called core/shell particles,⁶ the emission properties and photostability can be significantly enhanced with respect to the cores themselves. Herein, we describe a powerful approach to ternary II–II'–VI clusters with synthesis of the zinc(II)–selenolate complex $[(N,N'-tmeda)Zn(SeSiMe_3)_2]$ (**1**) and its use in the synthesis of the nanocluster $[(N,N'-tmeda)_5Zn_5Cd_{11}Se_{13}(SePh)_6(thf)_2]$ (**2**).

Complex **1** was synthesized in high yield via the addition of 2 equiv of $Se(SiMe_3)_2$ to a solution of $(N,N'-tmeda)Zn(OAc)_2$ in THF at 0 °C. Single crystals were obtained from a 3:1 pentane:THF mixture upon cooling to –78 °C. M–ESiMe₃ complexes are rare,⁷ yet they are powerful synthons for the formation of M–E–M' complexes,⁸ due to the preformed M–E bonds, and the existence of reactive pendant trimethylsilyl groups. The molecular structure (Figure 1⁹) confirms the presence of terminally coordinated $SeSiMe_3$ groups [Zn–Se = 2.3785(6), 2.3881(6) Å]. The coordination geometry of the zinc center is distorted from the expected tetrahedral by a compression of the $\angle N1–Zn–N2$ [85.12(13)°] and a large $Se1–Zn1–Se2$ angle [129.21(3)°]. These are consistent with those found for the related complex $[(N,N'-tmeda)Zn(SePh)_2]$.¹⁰ The chelating TMEDA ligand in **1** permits the “ $ZnSe_2$ ” units to act as surface metallachalcogenolate ligands when reacted with metal salts.

When **1** is reacted with 2 equiv of $(PnPr_3)_2Cd(OAc)_2$ in the presence of 2 equiv of $PhSeSiMe_3$ at –78 °C, followed by slow warming to room temperature, a pale yellow solution is obtained.

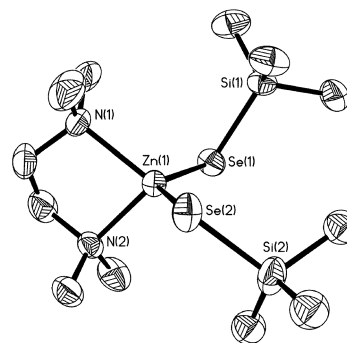


Figure 1. Molecular structure of $[(N,N'-tmeda)Zn(SeSiMe_3)_2]$ (**1**). Hydrogen atoms are omitted, and thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances [Å] and angles [deg]: Zn–N = 2.148(4)–2.154(3), Se–Si = 2.2545(16)–2.4546(12); N1–Zn1–N2 = 85.12(13), N–Zn–Se = 103.39(9)–111.40(9), Si–Se–Zn = 101.05(4)–105.02(4).

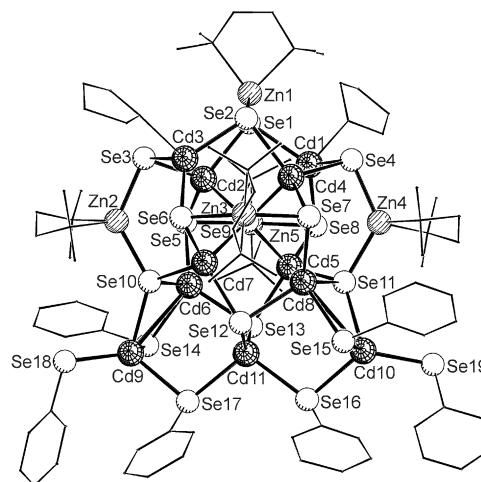
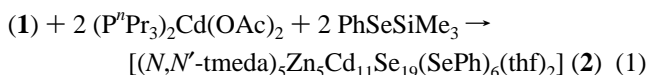


Figure 2. Molecular structure of $[(N,N'-tmeda)_5Zn_5Cd_{11}Se_{13}(SePh)_6(thf)_2]$ (**2**). For clarity, the carbon atoms of the phenyl groups and TMEDA and THF ligands are represented as lines.

Pale yellow crystals of $[(N,N'-tmeda)_5Zn_5Cd_{11}Se_{13}(SePh)_6(thf)_2]$ (**2**) grow in good yield from a THF/Et₂O mixture at –25 °C [eq 1].



The molecular structure of **2** (Figure 2) was revealed by X-ray crystallographic analysis.⁹ It consists of a CdSe cluster core in which 11 Cd atoms are bridged by 13 selenide ions. Ten of the Se^{2-} are provided by five $(N,N'-tmeda)ZnSe_2$ units, which reside at the

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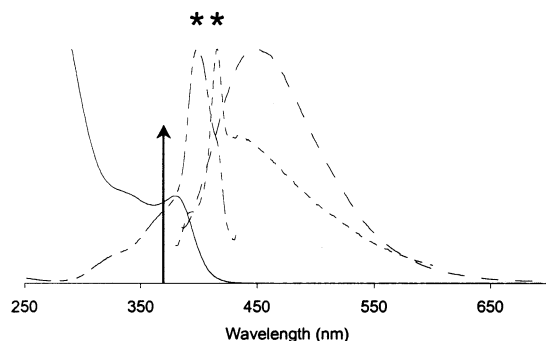


Figure 3. Summary of the room-temperature spectroscopic data for **2**. Solution (DMF) absorption (—), photoluminescence excitation (PLE) (-----), photoluminescence (PL) (-·-·-) spectra; solid-state PL (····) spectrum. The arrow indicates the excitation energy for the PL spectra. Raman bands of the DMF solvent in the PL and PLE spectra are designated by (*). The data are normalized for the sake of clarity.

surface of the cluster, acting as capping groups to stabilize the CdSe core. Thus, **2** can be viewed as a molecular limit of a CdSe/ZnSe core/shell nanoparticle. The cluster is further protected by four μ -bridging and two terminal phenylselenolate ligands. Three of the Se^{2-} ligands (Se9, Se10, and Se11) are each coordinated to four metal centers, while all others act as μ_3 -bridges. All metal ions adopt pseudotetrahedral coordination, with the largest deviations from ideal geometry occurring for Se–Zn–Se linkages [125.65–(15)–136.86(14)°]. Each Zn atom is coordinated to two Se^{2-} ions, as well as the two N atoms of the chelating TMEDA ligand. Cd atoms are bonded to four Se^{2-} or SePh (Cd2, Cd4–Cd11) or three Se^{2-} (Cd1 and Cd3) with the tetrahedral geometry of the latter completed by coordination to a THF ligand. The ZnCdSe core of this cluster measures 0.9 nm \times 0.9 nm \times 1.0 nm, with the arrangement of core atoms very similar to that of the binary ZnTe cluster reported by Pfister and Fenske.¹¹ The solution absorption profile of **2** features an onset of absorption at \sim 430 nm, with a maximum at 379 nm that we have tentatively assigned to “excitonic” absorption ($E_g = 3.27$ eV). The cluster exhibits “band-edge” luminescence at room-temperature both in solution and in the solid-state, with emission maximum ($\lambda_{\text{sol}} = 432$ nm) occurring near the onset of absorption. The solid-state emission is shifted to lower energy with respect to the solution maximum ($\lambda_{\text{ss}} = 450$ nm). The band-edge photoluminescence observed is in contrast to that from binary CdSe nanoclusters which demonstrate deep-trapped emission and are luminescent only at low temperature.³ Emission quenching was attributed to a multiphonon relaxation mode of phenylselenolate ligands. The enhanced emission properties of **2** may be a consequence of inorganic passivation of the cluster core by the ZnSe₂ units or due to the fact that only part of the cluster core is covered by surface SePh ligands (see Figure 3).

Utilization of a (trimethylsilyl)telluroate analogue of **1** in eq 1 leads to the formation of the isostructural telluride/telluroate cluster derivative of **2**, [(N,N'-tmeda)₅Zn₅Cd₁₁Te₁₃(TePh)₆(thf)] (**3**). Cluster **3** has been structurally characterized,⁹ and the photophysical properties have been investigated. Solid **3** exhibits an absorption maximum at 375 nm (cf. λ_{ss} (**2**) = 348 nm), and emission at 490 nm in the solid state.

The use of the silylated zinc(II) chalcogenolate complexes reported here offers an efficient route for the controlled introduction

of surface ZnE₂ groups in ternary nanocluster and colloidal synthesis. We are currently investigating the synthesis of other amine-ligated precursor complexes to access a wide range of ternary II–II'–VI nanoclusters.

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Supporting Information Available: Experimental procedures, spectroscopic and characterization data for **1–3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) X-ray structure analysis: Enraf-Nonius Kappa CCD diffractometer (Mo K α radiation) (**1**) or Bruker APEX diffractometer (Mo K α radiation) (**2** and **3**). Crystal data for C₁₂H₃₄N₂ZnSe₂Si₂ **1**: colorless needle, $M_r = 485.88$, monoclinic, space group $P2_1/n$, $a = 8.4454(17)$ Å, $b = 14.340(3)$ Å, $c = 18.769(4)$ Å, $\beta = 90.11(3)^\circ$, $V = 2273.1(8)$ Å³, at 200 K, $Z = 4$, $\rho_{\text{calcd}} = 1.420$ g cm⁻³, $\mu = 4.381$ mm⁻¹, $2\theta_{\text{max}} = 55.08^\circ$, 14907 reflections collected (5229 independent, $R_{\text{int}} = 0.090$). Final $R = 0.0447$ ($wR_2 = 0.0808$) and GoF = 1.003. For C₇₄H₁₂₆N₁₀O₂Zn₅Cd₁₁Se₁₉(OC₄H₉)₂ **2**: weakly diffracting pale yellow prism, $M_r = 4467.65$, orthorhombic, space group $Pbca$, $a = 17.3933(14)$ Å, $b = 36.592(3)$ Å, $c = 46.151(4)$ Å, $V = 29373(4)$ Å³, at 150 K, $Z = 8$, $\rho_{\text{calcd}} = 2.021$ g cm⁻³, $\mu = 7.103$ mm⁻¹, $2\theta_{\text{max}} = 45.98^\circ$, 131518 reflections collected, (20404 independent, $R_{\text{int}} = 0.1765$). Final $R = 0.0927$ ($wR_2 = 0.2018$) and GoF = 1.176. For C₇₀H₁₁₈N₁₀OZn₅Cd₁₁Te₁₃(OC₄H₉)(C₆H₁₄)_{0.5} **3**: yellow plate, $M_r = 5218.58$, triclinic, space group $P1$, $a = 18.2135(11)$ Å, $b = 19.0174(11)$ Å, $c = 22.9457(13)$ Å, $\alpha = 67.153(1)^\circ$, $\beta = 67.873(1)^\circ$, $\gamma = 62.286(1)^\circ$, $V = 6293.9(6)$ Å³, at 150 K, $Z = 2$, $\rho_{\text{calcd}} = 2.754$ g cm⁻³, $\mu = 7.104$ mm⁻¹, $2\theta_{\text{max}} = 50.06^\circ$, 35513 reflections collected (22085 independent, $R_{\text{int}} = 0.0578$). Final $R = 0.0685$ ($wR_2 = 0.1199$) and GoF = 1.130. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-191272 (**1**), -191273 (**2**), and -191274 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Telephone: (+44) 1223-336-408; Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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