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Cluster Compounds

Imine-Stabilized Zinc Trimethylsilylchalcogenolates: Powerful Reagents for the Synthesis of II-II′-VI Nanocluster Materials**

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A new class of metal–chalcogen complexes is being pursued in which the presence of reactive silyl functional groups offers an entry into high nuclearity ternary cluster and (nanometer sized) nanocluster materials. Both $[E(SiMe_3)]^-$ (E = S, Se, Te)[1,2] and $[S(SiMe_2S)_2]^{2-}$[3,4] groups can be used, provided their coordination to metal centers can be stabilized by additional ancillary ligands. Metal–chalcogenolate reagents for the controlled incorporation of the heavier congeners selenium and tellurium are particularly difficult to prepare owing to the inherent reactivity of these chalcogen elements. These are desirable targets however because of the demonstrated composition-dependant photophysical properties of metal–chalcogenide semiconductor nanomaterials. This property is highlighted by the recent synthesis of a series highly luminescent $Zn_xCd_{1-x}Se$ nanocrystals whose optical properties can be tuned across the visible spectrum by changing the Zn:Cd ratio.[5] The development of reagents for controlled access to mixed-metal ternary clusters and nanoclusters is of importance in elucidating the effects of composition on the structure and photophysical properties of MM′Se and MM′Te materials. Herein, we describe the synthesis and initial reactivity studies of the complexes $[(3,5\text{-}Me_2C_5H_3N)_2Zn(ESiMe_3)_2]$ (E = Se (**1**), Te (**2**)), where the labile 3,5-lutidine ligands of **1** and **2** afford the opportunity to access ternary II-II′-VI nanoclusters in which the metal ions are intimately mixed by the controlled delivery of $\{ZnE_2\}$.

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Supporting information for this article (synthesis, spectroscopic, and characterization data for **1**–**4** and figures detailing the Zn/Cd site disorder in **3** and **4**) is available on the WWW under http://www.angewandte.org or from the author.

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Complexes **1** and **2** were synthesized in high yield by the addition of two equivalents of $E(SiMe_3)_2$ to a solution of $Zn(OAc)_2$ solublized by 3,5-lutidine in CH_2Cl_2 at −78 °C. Single crystals of **2** suitable for X-ray crystallography were obtained by addition of cold pentane to the point of incipient precipitation, followed by storage at −78 °C. Figure 1 shows the molecular structure of **2**.[6] The key structural feature is the presence of terminally coordinated, highly reactive $TeSiMe_3$ groups. The zinc center has a distorted tetrahedral geometry with a large Te1-Zn1-Te2 angle (129.21(3)°) compensated by a compression of the N1-Zn-N2 angle (85.12(13)°), as observed in related zinc tellurolate complexes with N-donor ligands.[7,8] Complex **2** is infinitely stable in the solid state if maintained at low temperatures (−80 °C) and is thus a convenient, storable precursor. Consistent with the demonstrated reactivity of reagents such as $E(SiMe_3)_2$ and $RESiMe_3$ (E = S, Se, Te) in binary cluster synthesis,[9] M-$ESiMe_3$ complexes are powerful precursors for the formation of M-E-M′ nanoclusters[1,2] owing to their preformed M−E bonds and the reactive pendant trimethylsilyl groups. Thus the reaction of **2** with $(P\mathit{n}Pr_3)_2Cd(OAc)_2$ in the presence of $PhTeSiMe_3$ at −78 °C, followed by slow warming to room temperature yields single crystals of the ternary nanocluster $[Zn_{2.6}Cd_{7.4}Te_4(TePh)_{12}(P\mathit{n}Pr_3)_4]$ (**3**) in 60 % yield [Eq. (1)].

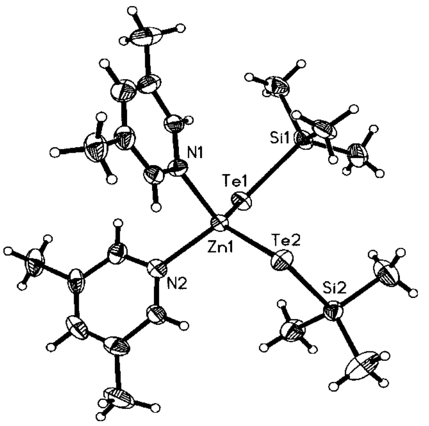

Figure 1. The molecular structure of **2**. Thermal ellipsoids are set at 50 % probability. Selected interatomic distances [Å] and angles [°]: Zn-Te 2.580(2), 2.582(1), Te-Si 2.485(3), 2.486(3), Zn-N 2.094(7), 2.100(7); N1-Zn1-N2 96.2(3), N-Zn-Te 104.7(2)-107.8(2), Si-Te-Zn 97.45(7)-101.92(7).

$$0.35\,\mathbf{2} + (P\mathit{n}Pr_3)_2Cd(OAc)_2 + 1.3\,PhTeSiMe_3 \rightarrow \mathbf{3} \qquad (1)$$

The structure of **3** (Figure 2) was confirmed by X-ray crystallographic analysis.[6] The nanocluster **3** is crystallographically isomorphous to the binary ZnTe analogue $[Zn_{10}Te_4(TePh)_{12}(P\mathit{n}Pr_3)_4]$.[10] The overall arrangement of metal and tellurium ions generates a tetrahedral framework consisting of four fused $\{M_4Te_6\}$ adamantane units, similar to the building blocks that constitute the cubic (sphalerite) phases of the bulk materials ZnTe and CdTe. The four apices of the tetrahedron are terminated by phosphane ligands. This $\{M_{10}\}$ architecture is prevalent among II-VI clusters and makes this compound a candidate with which to examine the effect of metal-ion composition on optical properties.[11] The average metal composition of the clusters in the crystal was determined by energy dispersive X-ray spectroscopy (EDX) and atomic absorption spectroscopy (AAS) of single crystals of **3**. A measured 2.6:7.4 Zn:Cd ratio (see Supporting Information) is remarkably consistent with the Zn:Cd reaction stoichiometry, which illustrates that the precursor complex **2** is an efficient delivery agent of $\{ZnTe_2\}$ in cluster synthesis. The inability to fully resolve zinc and cadmium from crystallographic data is indicative of intimate mixing of the metal ions within the clusters. A satisfactory model however was achieved with site occupancy of $Zn_{0.5}Cd_{0.5}$ given to the metal ion sites bonded to the apical $P\mathit{n}Pr_3$ ligands. As this accounts for only 77 % of the zinc present in the clusters, the remaining zinc ions would be distributed among the rest of the metal sites in the structure. This mixing is unlike the positions of the zinc centers in the II-II′-VI nanoclusters $[(tmeda)_5Zn_5Cd_{11}E_{13}(EPh)_6]$ (E = Se, Te; tmeda = *N*,*N*,*N′*,*N′*-tetramethyl-1,2-ethanediamine) in which the chelating tmeda ligands constrain Zn^{II} to the surface the nanocluster.[1]

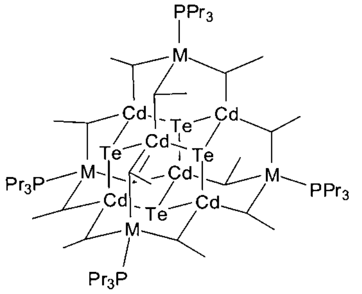

Figure 2. Line diagram of the fused adamantane structure of **3**. Sites labeled "M" indicate the highest concentration of Zn (50 % site occupancy) in the cluster, as discussed in the text. For clarity, labels for the TePh ligands are omitted.

There are relatively few reports involving the general preparation of ternary II-II′-VI nanoparticles[5,12] In these mixed-metal compounds, manipulation of the band-gap energy can be achieved by changing both particle size and composition (i.e. the ratio of M to M′). Thus, the development of controlled approaches to ternary nanoparticles is an attractive pursuit and nanocluster materials whose structures can be determined crystallographically allow an investigation of the development of materials properties with increasing molecular size.[13] The solution absorption spectrum for cluster **3** features a sharp maximum at 321 nm. A marked blue shift in the absorption profile relative to the cluster $[Cd_{10}Te_4(TePh)_{12}(P\mathit{n}Pr_3)_4]$ ($\lambda_{max} = 328$ nm)[14] suggests the optical properties of these nanocluster materials can be manipulated by controlling the metal ion composition. Compound **3** is luminescent only at low temperature, with the emission maximum significantly shifted to lower energy relative to the excitation onset. Consistent with the optical properties of related CdSe clusters, the "trapped" emission is assigned to forbidden transitions involving the surface phenyltellurolate ligands.[13,14] Photoluminescence excitation (PLE) spectra confirm the emitting species as **3** (see Supporting Information).

Ternary Zn/CdSe nanoclusters can be prepared from the selenolate analogue **1**. Reaction of **1** with $(PnPr_3)_2Cd(OAc)_2$ and $PhSeSiMe_3$ in a 2:8:12 ratio at low temperature leads to the formation of the ternary cluster $[Zn_{1.8}Cd_{8.2}Se_4(SePh)_{12}(PnPr_3)_4]$ (**4**). Cluster **4** has also been structurally characterized.[6] The first absorption maximum (310 nm) of this ZnCdSe cluster is blue shifted relative to that of the all cadmium derivative $[Cd_{10}Se_4(SePh)_{12}(PnPr_3)_4]$[13] ($\lambda_{max} = 320$ nm), whereas the observed emission maximum for **4** (525 nm) is virtually identical to that observed for $[Cd_{10}Se_4(SePh)_{12}(PnPr_3)_4]$ ($\lambda_{em} = 527$ nm) (see Supporting Information). This result is consistent with the emission being from "trapped" aryl–selenolate surface states, which are relatively insensitive to the size and, as demonstrated in this case, composition of the metal–selenide core.[13,14]

The use of the silylated zinc(II) chalcogenolate complexes reported herein offers a general route for the controlled introduction of zinc into ternary nanoclusters and nanoparticles. This approach affords the opportunity to modulate the optical properties of nanoclusters and related materials by controlling the metal-ion composition. We are currently developing their utility in a variety of ternary cluster and nanoparticle syntheses.

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[1] a) M. W. DeGroot, N. J. Taylor, J. F. Corrigan, *J. Am. Chem. Soc.* **2003**, *125*, 864; a) M. W. DeGroot, N. J. Taylor, J. F. Corrigan, *J. Mater. Chem.* **2004**, *14*, 654.

[2] a) D. T. T. Tran, N. J. Taylor, J. F. Corrigan, *Angew. Chem.* **2000**, *112*, 965; *Angew. Chem. Int. Ed.* **2000**, *39*, 935; b) D. T. T. Tran, L. M. C. Beltran, C. M. Kowalchuk, N. R. Trefiak, N. J. Taylor, J. F. Corrigan, *Inorg. Chem.* **2002**, *41*, 5693.

[3] T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *Angew. Chem.* **2003**, *115*, 481; *Angew. Chem. Int. Ed.* **2003**, *42*, 465.

[4] T. Komuro, T. Matsuo, H. Kawaguchi, K. Tatsumi, *Chem. Commun.* **2002**, 988.

[5] X. Zhong, M. Han, Z. Dong, T. J. White, W. Knoll, *J. Am. Chem. Soc.* **2003**, *125*, 8589.

[6] Crystal data for $C_{20}H_{36}N_2ZnTe_2Si_2$ (**2**): colorless block, $M_r = 681.26$, triclinic, space group $P\bar{1}$, $a = 9.3005(19)$, $b = 10.215(2)$, $c = 16.614(3)$ Å, $\alpha = 94.94(3)$, $\beta = 91.20(3)$, $\gamma = 115.66(3)°$, $V = 1414.5(5)$ Å^3, at 200 K, $Z = 2$, $\rho_{calcd} = 1.602$ g cm^{-3}, $\mu = 2.982$ mm^{-1}, $2\theta_{max} = 55.02°$, 9223 reflections collected (6464 independent, $R_{int} = 0.045$). Final $R = 0.0659$ ($wR_2 = 0.1604$) and GoF = 1.054. For $C_{108}H_{144}P_4Zn_{2.6}Cd_{7.4}Te_{16}$ (**3**): colorless prism, $M_r = 4637.65$, tetragonal, space group $I4_1/a$, $a = 25.9100(2)$, $c = 21.6000(2)$ Å, $V = 14500.7(2)$ Å^3, at 200 K, $Z = 4$, $\rho_{calcd} = 2.124$ g cm^{-3}, $\mu = 4.709$ mm^{-1}, $2\theta_{max} = 54.94°$, 16307 reflections, (8298 independent, $R_{int} = 0.0348$). Final $R = 0.0309$ ($wR_2 = 0.0779$) and GoF = 1.067. For $C_{108}H_{144}P_4Zn_{1.2}Cd_{8.8}Se_{16}$ (**4**): colorless prism, $M_r = 3897.04$, tetragonal, space group $I4_1/a$, $a = 25.3442(5)$, $c = 20.2084(6)$ Å, $V = 12980.4(5)$ Å^3, at 200 K, $Z = 4$, $\rho_{calcd} = 1.994$ g cm^{-3}, $\mu = 6.205$ mm^{-1}, $2\theta_{max} = 55.1°$, 14327 reflections (7449 independent, $R_{int} = 0.0821$). Final $R = 0.0510$ ($wR_2 = 0.1037$) and GoF = 1.006. CCDC-235976–CCDC-235978 (**2**–**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[7] P. J. Bonasia, J. Arnold, *Inorg. Chem.* **1992**, *31*, 2508.

[8] Y.-K. Jun, C.-S. Choi, J. Cheon, *Chem. Commun.* **2001**, 101.

[9] S. Dehnen, A. Eichhöfer, D. Fenske, *Eur. J. Inorg. Chem.* **2002**, *2*, 279.

[10] A. Eichhöfer, D. Fenske, H. Pfistner, M. Wunder, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1909.

[11] a) M. W DeGroot, J. F. Corrigan in *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*, *Vol. 7* (Eds.: M. Fujita, A. Powell, C. Creutz), Pergamon, Oxford, **2004**, p. 57; b) I. Dance, K. Fisher, *Prog. Inorg. Chem.* **1994**, *41*, 637.

[12] a) Y. Tian, T. Newton, N. A. Kotov, D. M. Guldi, J. H. Fendler, *J. Phys. Chem.* **1996**, *100*, 8927; b) M. T. Harrison, S. V. Kershaw, M. G. Burt, A. Eychmüller, H. Weller, A. L. Rogach, *Mater. Sci. Eng. B* **2000**, *69*, 355; c) B. A. Korgel, H. G. Monbouquette, *Langmuir* **2000**, *16*, 3588; d) D. V. Petrov, B. S. Santos, G. A. L. Pereira, C. D. M. Donegá, *J. Phys. Chem. B* **2002**, *106*, 5325; e) W. Wang, I. Germanenko, M. S. El-Shall, *Chem. Mater.* **2002**, *14*, 3028.

[13] V. N. Soloviev, A. Eichhöfer, D. Fenske, U. Banin, *J. Am. Chem. Soc.* **2001**, *123*, 2354.

[14] A. Eichhöfer, A. Aharoni, U. Banin, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2415.