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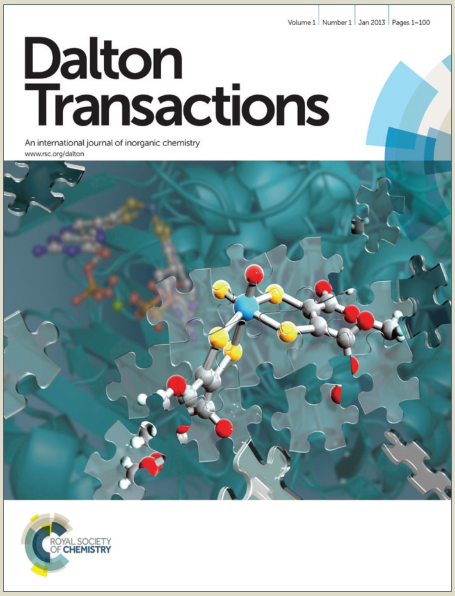

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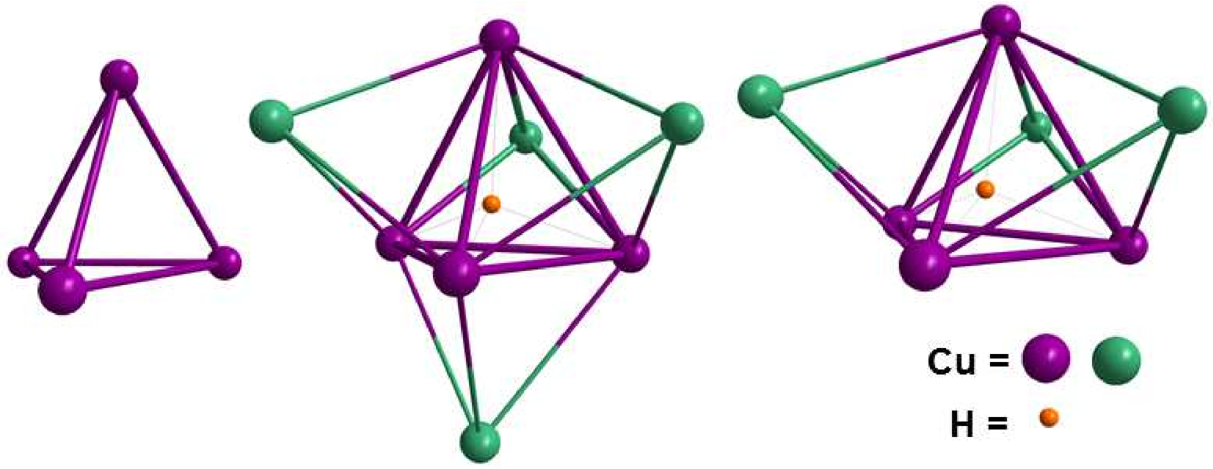
The first Cu(I) compounds supported by dialkyl diselenocarbamates were reported to exhibit tetrahedral, hydride-centered tetracapped tetrahedral and hydride-centered tricapped tetrahedral core structures. In addition, a tetracapped tetrahedral Cu_8 compound was studied to demonstrate the potentials of these compounds as single-source precursors for copper selenide nanocomposites via a solvothermal route.



Copper(I) Diselenocarbamate Clusters: Synthesis, Structures and Single-Source Precursors for Cu and Se Composite Materials

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Abstract: A neutral tetrahedral $[Cu_4(Se_2CN^nPr_2)_4]$ (**1**), monocationic hydride-centered tetracapped tetrahedral $[Cu_8(H)\{Se_2CNR_2\}_6]^+$ (R = ^{n}Pr, $\mathbf{2_H}$; Et, $\mathbf{3_H}$) and neutral hydride-centered tricapped tetrahedral $[Cu_7(H)\{Se_2CNR_2\}_6]$ (R = ^{n}Pr, $\mathbf{4_H}$; Et, $\mathbf{5_H}$) clusters were formed. They are the first Cu(I) complexes supported by dialkyl diselenocarbamates. The as-synthesized complexes $\mathbf{2_H}$ and $\mathbf{3_H}$, formed from a reaction mixture of Cu(I) salts, diselenocarbamates, and $[BH_4]^-$ in an 8:6:1 ratio, can be further reduced into $\mathbf{4_H}$ and $\mathbf{5_H}$, respectively, in the presence of one equiv. of $[BH_4]^-$. Replacement of $[BH_4]^-$ with $[BD_4]^-$ afforded deuteride analogues $[Cu_8(D)\{Se_2CNR_2\}_6]^+$ (R = ^{n}Pr, $\mathbf{2_D}$; Et, $\mathbf{3_D}$) and $[Cu_7(D)\{Se_2CNR_2\}_6]$ (R = ^{n}Pr, $\mathbf{4_D}$; Et, $\mathbf{5_D}$), which confirm the presence of hydride in the corresponding ($\mathbf{2_H}$, $\mathbf{3_H}$, $\mathbf{4_H}$ and $\mathbf{5_H}$) compounds. These complexes were fully characterized by elemental analysis, ESI-MS, and ^{1}H,

^{2}H, ^{77}Se NMR spectroscopy and their molecular structures were unequivocally established by single crystal X-ray crystallographic analyses (**1**, $\mathbf{2_H}$ – $\mathbf{5_H}$). The hydride-encapsulated copper framework of ($\mathbf{2_H}$, $\mathbf{3_H}$) and ($\mathbf{4_H}$, $\mathbf{5_H}$) reveals a tetracapped tetrahedral cage of Cu_8 and a tricapped tetrahedral cage of Cu_7, respectively, which are enclosed within a Se_{12} icosahedron constituted by six dialkyl diselenocarbamate ligands. Compounds $\mathbf{2_H}$ and $\mathbf{3_H}$ display an orange emission in both solid and solution state under UV irradiation at 77 K. In addition, thermolysis behaviors of $\mathbf{2_H}$ were studied to demonstrate the potentials of these compounds as single-source precursors for copper selenide nanocomposites, which were analyzed by XRD, EDX, and SEM techniques.

Introduction

A variety of organoselenium compounds as well as transition metal complexes stabilized by selenium donor ligands have received increasing attention in recent years.[1,2] The organoselenium compounds are widely applicable in biological and pharmacological activity due to their potential antioxidant, antitumor, and antiviral properties.[3] On the other hand, the selenium-containing transition metal complexes are also excellent precursors for the fabrication of metal selenide nanomaterials.[4,2a,] Among them, the various copper selenide composites are promising functional materials with potential applications in solar cells, optical filters, nanoswitches, thermoelectric and photoelectric transformers, and superconductors.[5] Copper selenide materials accompanied by doping of alternative metals (In, Ga, *etc*.) can enhance the stability and efficiency in their applications.[6] Copper selenides have been fabricated by several methods such as hydro- or solvo-thermal,[7] sonochemical,[8] photochemical,[9] chemical vapor deposition (CVD),[10] template-directed synthesis,[11] and others.[12] A few reports on the synthesis of copper selenide materials using single molecule precursors are known.[13] For example, by taking advantage of the labile P-Se bond, diselenophosphates-stabilized tetrahedral copper cluster $[Cu_4\{Se_2P(O^iPr)_2\}_4]$ was employed as a single source precursor for the fabrication of $Cu_{2-x}Se$ nanowires with lengths of several micrometers and diameters of 30–50 nm via CVD process.[10] Along this line a group of metal complexes including alkali and d-block elements passivated by a number of selenium containing ligands, namely, diselenophosphates (dsep), diselenophosphonates (dsepo), diselenophosphinates (dsepi), and triselenophosphonates (tsepo) have been established so that they could be useful sources on the metal selenide nanomaterial synthesis.[2a]

Discrete group 11 metals (Cu^I, Ag^I, and Au^I) with diselenophosph(in)ates ligands[14-18] are primarily studied by the Liu and O'Brien groups.[19] Anion-centered multinuclear Cu^I and Ag^I clusters of this kind are particularly interesting due to their intrinsic characteristics, a reminiscent of guest-host supramolecules. Thus, among the selenium-containing [(dsep), (dsepo), (dsepi), (tsepo)] ligands, *Cu(I) complexes with diselenocarbamates (dsec) are, surprisingly, unknown*. Indeed an investigation of such copper(I) clusters stabilized by diselenocarbamates is of immediate interest in order to explore their structural characteristics and herein we report the first examples of $[Cu_4(Se_2CN^nPr_2)_4]$ followed by their hydride-encapsulated products, $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_4\{Se_2CNR_2\}_6](PF_6)$ (R = ^{n}Pr, $\mathbf{2_H}$; Et, $\mathbf{3_H}$) and $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{Se_2CNR_2\}_6]$ (R = ^{n}Pr, $\mathbf{4_H}$; Et, $\mathbf{5_H}$). Thermolysis behaviors of $\mathbf{2_H}$ as a single molecule precursor were demonstrated and revealed the formation of both stoichiometric CuSe and non-stoichiometric $Cu_{2-x}Se$ (in fractional amount), which were characterized by XRD, EDX, and SEM techniques.

Experimental Section

Materials and Instruments. All chemicals were purchased from commercial sources and used as received. Solvents were purified following standard protocols. All reactions were carried out under N_2 atmosphere by using standard Schlenk techniques. The preparation of $[Cu(CH_3CN)_4]PF_6$ [20] and the $(R_2NH_2)(Se_2CNR_2)$ (R = ^{n}Pr, Et) ligands have been reported previously.[21] Melting points were measured by using a Fargo MP-2D melting point apparatus. The elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on Bruker Advance DPX300 FT-NMR spectrometer that operates at 300.13 MHz while recording ^1H, 121.49 MHz for ^{31}P, 57.2 MHz for ^{77}Se, and 46.1 MHz for ^2H. The $^{31}P\{^1H\}$ and ^{77}Se NMR spectra were referenced externally against 85% H_3PO_4 (δ = 0 ppm) and PhSeSePh (δ = 463 ppm), respectively. The chemical shift (δ) and coupling constant (J) are reported in parts per million and hertz. The NMR spectra were recorded at ambient temperature. ESI-mass spectra were recorded on a Fison Quattro Bio-Q (Fisons Instruments, VG Biotech, UK). UV−visible absorption spectra were measured on a Perkin-Elmer Lambda 750 spectrophotometer using quartz cells with path length of 1 cm recording in the 250−750 nm region. Emission spectra were recorded on a Cary Eclipse B10 fluorescence spectrophotometer.

Safety note

Selenium and its derivatives are toxic! These materials should be handled with caution.

Synthesis of Compounds 1, (2_H / 2_D) – (5_H / 5_D).

[Cu$_4$(Se$_2$CN^{n}Pr$_2$)$_4$], (1). [Cu(CH$_3$CN)$_4$]PF$_6$ (0.200 g, 0.54 mmol), and (^{n}Pr$_2$NH$_2$)(Se$_2$CN^{n}Pr$_2$) (0.200 g, 0.54 mmol) in 30 mL of THF solvent were added to a flame dried two-necked round bottom flask (100 mL) and the resulting reaction mixture was stirred for 30 minutes at room temperature under nitrogen atmosphere. After stirring the reaction for a further 20 minutes, a yellow precipitate formed and the purple colored solvent was decanted. The yielded yellow precipitate was washed with acetone (5 × 3 mL) and dried under vacuum to obtain complex [Cu$_4$(Se$_2$CN^{n}Pr$_2$)$_4$] **1_H** (0.086 g, 57%) as a yellow powder. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.92 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$CH$_2$*CH$_3$*), 1.88 (m, 2H, CH$_2$*CH$_2$*CH$_3$), 3.94 (t, $^3J_{HH}$ = 9 Hz, 2H, C*H$_2$*CH$_2$CH$_3$).

[Cu$_4$(μ_4-H)(μ_3-Cu)$_4${Se$_2$CN^{n}Pr$_2$}$_6$]PF$_6$, (2_H). In a Flame-dried, round bottom flask (100 mL), [Cu(CH$_3$CN)$_4$]PF$_6$ (0.200 g, 0.54 mmol), and (^{n}Pr$_2$NH$_2$)(Se$_2$CN^{n}Pr$_2$) (0.150 g, 0.40 mmol) were suspended in THF (30 mL) solvent and stirred for 5 minutes at room temperature. After addition of [LiBH$_4$·thf] (2M, 0.034 mL, 0.068 mmol), the resulting reaction mixture was further stirred for 1 h under nitrogen atmosphere and yielded an orange-yellow colored solution. The reaction mixture was evaporated to obtain a brown-yellow solid. The solid residue was dissolved in 30 mL of dichloromethane (CH$_2$Cl$_2$) and washed with deionized water (3 × 20 mL). The organic layer of CH$_2$Cl$_2$ was separated, filtered and dried by vacuum. Finally, the solid residue was washed with acetone [(CH$_3$)$_2$CO] to remove impurities and obtained a bright yellow solid of [Cu$_4$(μ_4-H)(μ_3-Cu)$_4${Se$_2$CN^{n}Pr$_2$}$_6$](PF$_6$). Yield: 0.086 g (57%) Mp: 184 °C (dec). Anal. Calcd for Cu$_8$H$_{85}$C$_{42}$N$_6$PF$_6$Se$_{12}$·[(CH$_3$)$_2$CO]: C, 23.91; H, 4.06; N, 3.56 %. Found: C, 23.65; H, 3.77; N, 3.31

%. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.03 (bs, 1H, μ_4-H), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 36H, $CH_2CH_2CH_3$), 1.89 (m, 24H, $CH_2\mathit{CH_2}CH_3$), 4.07 (t, $^3J_{HH}$ = 8.2 Hz, 24H, $\mathit{CH_2}CH_2CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −143.0 (septet, $^1J_{PF}$ = 713.1 Hz, PF_6). ^{77}Se NMR ($CHCl_3$, δ, ppm): 374.9(s, 12Se). ESI-MS (m/z)(cal.): 2130.6 (2130.1) for $[Cu_8(H)\{Se_2CN^nPr_2\}_6]^+$. UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 292 (43000), 367 (23000).

$[Cu_4(\mu_4\text{-}D)(\mu_3\text{-}Cu)_4\{Se_2CN^nPr_2\}_6]PF_6$, ($2_D$). **$2_D$** was also prepared as described for **2_H** by using $NaBD_4$ instead of $LiBH_4$. Yield: 0.085 g (56%) Mp: 186 °C (dec). Anal. Calcd for $Cu_8H_{84}DC_{42}N_6PF_6Se_{12}\cdot(CH_3)_2CO$: C, 24.69; H, 4.24; N, 3.84%. Found: C, 24.35; H, 4.21; N, 3.86 %. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.97 (t, $^3J_{HH}$ = 7.5 Hz, 36H, $CH_2CH_2\mathit{CH_3}$), 1.89 (m, 24H, $CH_2\mathit{CH_2}CH_3$), 4.07 (t, $^3J_{HH}$ = 8.1 Hz, 24H, $\mathit{CH_2}CH_2CH_3$). ^{2}H NMR (CH_2Cl_2, δ, ppm): 3.03 (bs, 1D, μ_4-D) $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ, ppm): −143.0 (septet, $^1J_{PF}$ = 719.5 Hz, PF_6). ^{77}Se NMR ($CHCl_3$, δ, ppm): 376.9 (s, 12Se) ESI-MS (m/z)(cal.) 2130.8 (2131.1) for $[Cu_8(D)\{Se_2CN^nPr_2\}_6]^+$. UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 290(44000), 365(23000).

$[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_4\{Se_2CNEt_2\}_6]PF_6$, ($3_H$). In a Flame-dried, round bottom flask (100 mL), $[Cu(CH_3CN)_4]PF_6$ (0.200 g, 0.540 mmol), and $(Et_2NH_2)(Se_2CNEt_2)$ (0.130 g, 0.400 mmol) were suspended in THF (30 mL) solvent and stirred for 5 minutes at room temperature. After addition of $[LiBH_4\cdot thf]$ (2M, 0.034 mL, 0.068 mmol), the resulting reaction mixture was further stirred for 30 minutes under nitrogen atmosphere which yielded an orange-yellow colored turbid solution. The reaction mixture was evaporated under vacuum to obtain a red-brown solid. The solid residue was dissolved in 30 mL of CH_2Cl_2 and washed with deionized water (3 × 20 mL). The organic layer of CH_2Cl_2 was separated, filtered and dried via applying vacuum. Finally, solid residue was washed with

$CHCl_3$ (10 mL), and obtained precipitate was dissolved in acetone (15 mL) and passed through a packed column of Al_2O_3. Finally, after dried of the solvent yielded a yellow powder form of $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_4\{Se_2CNEt_2\}_6]PF_6$. Yield: 0.08 g (56%) Mp: 162°C (dec). Anal. Calcd for $Cu_8H_{61}C_{30}N_6PF_6Se_{12}$: C, 17.10; H, 2.92; N, 3.99 %. Found: C, 17.52; H, 2.86 ; N, 4.42 %. ^1H NMR ($CDCl_3$, δ, ppm): 1.36 (t, $^3J_{HH} = 7.2$ Hz, 36H, $CH_2\mathit{CH_3}$), 4.15 (t, $^3J_{HH} = 7.1$ Hz, 24H, $\mathit{CH_2}CH_3$), 3.01 (bs, 1H, μ_4-H). ^{77}Se NMR ($CHCl_3$, δ, ppm): 364.8 (s, 12Se). ESI-MS (m/z) (cal.) 1961.3(1961.9) for $[Cu_8(H)\{Se_2CNEt_2\}_6]^+$. UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 290(49000), 362(24000).

$[Cu_4(\mu_4\text{-D})(\mu_3\text{-Cu})_4\{Se_2CNEt_2\}_6]PF_6$, (**$3_D$**). **$3_D$** was also prepared as described for **3_H** by using $NaBD_4$ instead of $LiBH_4$. Yield: 0.07 g (50%). Mp: 168°C (dec). Anal. $Cu_8H_{60}DC_{30}N_6PF_6Se_{12}\cdot(CH_3)_2CO$ Calcd: C, 18.30; H, 3.16; N, 3.88 %. Found: C, 18.06; H, 3.12; N, 4.11 %. ^1H NMR ($CDCl_3$, δ, ppm): 1.41 (t, $^3J_{HH} = 7.2$ Hz, 36H, $CH_2\mathit{CH_3}$), 4.28 (t, $^3J_{HH} = 7.1$ Hz, 24H, $\mathit{CH_2}CH_3$) .^2H NMR (CH_2Cl_2, δ, ppm): 3.07 (bs, 1D, μ_4-D). ^{77}Se NMR (CH_2Cl_2, δ, ppm): 365.2 (s,12Se). ESI-MS (m/z) (cal.) 1963.0 (1962.7) for $[Cu_8(H)\{Se_2CNEt_2\}_6]^+$. UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 289 (47000), 362 (23000).

Note: Alternatively, compounds **2_H** and **3_H** have also been synthesized in lower yield via aforementioned process by using $(R_2CNSe_2)_2Zn$ {0.063 g, 0.200 mmol (R = Et); 0.075 g, 0.200 mmol (R = ^{n}Pr)}[26] instead of $(Et_2NH_2)(Se_2CNEt_2)$.

$[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{Se_2CN^nPr_2\}_6]$, ($4_H$). To a dichloromethane solution (30 mL) of $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_4\{Se_2CN^nPr_2\}_6]PF_6$ (0.500 g, 0.220 mmol) was added $LiBH_4\cdot$thf (2M, 0.100 mL, 0.200 mmol). The solution color changed from yellow to red-brown after 2 h of stirring, after which the solution was washed with deionized water (2 × 20 mL) and CH_2Cl_2 was filtered using filter paper and further was passed through a packed column of Al_2O_3 to remove copper particles and then evaporated to dryness under vacuum. The solid product was washed with acetone (3 × 5 mL), and then the solid was dried under vacuum to obtain complex $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{Se_2CN^nPr_2\}_6]$, **$4_H$** as yellow powder. Yield: 0.232 g (51%) Mp: 170°C (dec.) Anal. Calcd for $Cu_7H_{85}C_{42}N_6Se_{12}$: C, 24.41; H, 4.15; N, 4.07%. Found: C, 24.42; H, 4.21; N, 4.31%. ^{1}H NMR ($CDCl_3$, δ, ppm): 3.32 (bs, 1H, μ_4-H), 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 36H, $CH_2CH_2CH_3$), 1.85 (m, 24H, $CH_2CH_2CH_3$), 3.99 (t, $^3J_{HH}$ = 7.7 Hz, 24H, $CH_2CH_2CH_3$). ^{77}Se NMR ($CHCl_3$, δ, ppm): 448.6(s, 12Se). ESI-MS (m/z) (cal.) 2129.8 (2130.1) for ($[Cu_7(H)\{Se_2CN^nPr_2\}_6] + Cu^+$) . UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 289(43000), 379(17000).

$[Cu_4(\mu_4\text{-D})(\mu_3\text{-Cu})_3\{Se_2CN^nPr_2\}_6]$, ($4_D$). 4_D was also prepared as-synthesis of **3_H** by using $NaBD_4$ instead of $LiBH_4$. Yield: 0.186 g (50%) Mp: 172°C (dec). Anal. Calcd for $Cu_7H_{84}DC_{42}N_6Se_{12}$: C, 24.40; H, 4.19; N, 4.06 %. Found: C, 24.56; H, 4.29; N, 4.01 %. ^{1}H NMR ($CDCl_3$, δ, ppm): ^{2}H NMR (CH_2Cl_2, δ, ppm): 3.34 (bs, 1D, μ_4-D). ^{77}Se NMR (CH_2Cl_2, δ, ppm): 449.7 (s, 12Se). ESI-MS (m/z) (cal.) 2130.9(2131.1) for ($[Cu_7(D)\{Se_2CN^nPr_2\}_6] + Cu^+$). UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 291 (46000), 384 (18000).

$[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{Se_2CNEt_2\}_6]$, ($5_H$). To a THF solution (30 mL) of $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_4\{Se_2CN^nPr_2\}_6](PF_6)$ (0.500 g, 0.220 mmol) was added $LiBH_4$·thf (2M, 0.100 mL, 0.200 mmol). The solution color changed from yellow to red-brown within 5 h of stirring, after which the solution was washed with deionized water (2 × 20 mL) and CH_2Cl_2, the organic layer was filtered using filter paper and dried under vacuum to obtained a brown solid, which was further dissolved in CH_2Cl_2 and passed through a packed column of Al_2O_3 to remove copper particles and then solvent was evaporated to dryness under vacuum. The solid product was washed with acetone (3 × 5 mL), and then was dried under vacuum to obtain compound $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{Se_2CNEt_2\}_6]$, **$5_H$** as yellow powder. Yield: 0.30 g (60%). Mp: 160 °C (dec). Anal. Calcd for $Cu_7H_{61}C_{30}N_6Se_{12}$: C, 18.98; H, 3.24; N, 4.43 %. Found: C, 19.57; H, 3.25; N 4.44 %. ^1H NMR ($CDCl_3$, δ, ppm): 1.35 (t, $^3J_{HH}$ = 7.5 Hz, 36H, $CH_2\mathit{CH_3}$), 3.24 (bs, 1H, μ_4-H), 4.13 (q, $^3J_{HH}$ = 7.2 Hz, 24H, $\mathit{CH_2}CH_3$). ^{77}Se NMR ($CHCl_3$, δ, ppm): 443.8(s, 12Se). ESI-MS (m/z) (cal.) 1962.4(1961.7) for ($[Cu_7(H)\{Se_2CNEt_2\}_6]$ + Cu^+). UV-vis [λ_{max} in nm, (ε in M^{-1} cm^{-1})]: 291(49000), 358(22000).

$Cu_4(\mu_4\text{-D})(\mu_3\text{-Cu})_3\{Se_2CNEt_2\}_6]$, ($5_D$). 5_D was also prepared as described for **5_H** by using $NaBD_4$ instead of $LiBH_4$. Yield: 0.272 g (34 %). Mp: 165 °C (dec). Anal. Calcd for $C_{30}H_{60}DCu_7N_6Se_{12}\cdot(CH_3)_2CO$: C, 20.25; H, 3.50; N, 4.29 %. Found: C, 19.99; H, 3.58; N, 4.47%. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.33 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $CH_2\mathit{CH_3}$), 4.10 (q, $^3J_{HH}$ = 7.2 Hz, 2H, $\mathit{CH_2}CH_3$). ^2H NMR (46.1MHz, CH_2Cl_2, δ, ppm): 3.18 (bs, 1D, μ_4-D). ^{77}Se NMR (57.2 MHz, CH_2Cl_2, δ, ppm): 443.5 (s, 12 Se). $[Cu_7(D)\{Se_2CNEt_2\}_6]$. UV-vis [$\lambda_{max}$ in nm, (ε in M^{-1} cm^{-1})]: 287(47000), 358(22000).

Copper selenide. A powder of $[Cu_8(H)(Se_2CN^nPr_2)_6]PF_6$ (**2_H**) (0.070 g , 0.030 mmol) was autoclaved together with 1-dodecanethiol (3 mL) and was heated at 200 °C for 1 h. Black residue was filtered off, which was washed with methanol (10 x 2 mL) and then finally with $CHCl_3$ (10 x 2 mL) until getting clear solution. The black precipitate was re-dispersed in MeOH under sonication for 3 h, and then centrifuged to separate solution of MeOH and solid. The solid was dried under vacuum to obtain black particles of copper selenides (0.048 g, 77%).

X-ray Crystallography. Single crystals suitable for X-ray diffraction were grown by diffusing hexane into a $CHCl_3$ solution of the compounds. Crystals were mounted on the tip of glass fibers with epoxy resin. X-ray diffraction analyses of the crystals were performed with a Bruker APEX-II CCD diffractometer (Mo-*K*α radiation, $\lambda = 0.71073$ Å). Absorption corrections for the area detector were performed by using the SADABS program.[22] Structures were solved by direct methods and refined by least-squares methods on F^2 by using the SHELXL-2014/7 package[23] incorporated in SHELXTL/PC V6.14.[24] CCDC-1037451 (**1**), 1037452 (**2**$_\mathbf{H}$), 1037453 (**3**$_\mathbf{H}$), 1037454 (**4**$_\mathbf{H}$) and 1037455 (**5**$_\mathbf{H}$) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected X-ray crystallographic data for **1**, and $\mathbf{2_H}$-$\mathbf{5_H}$.

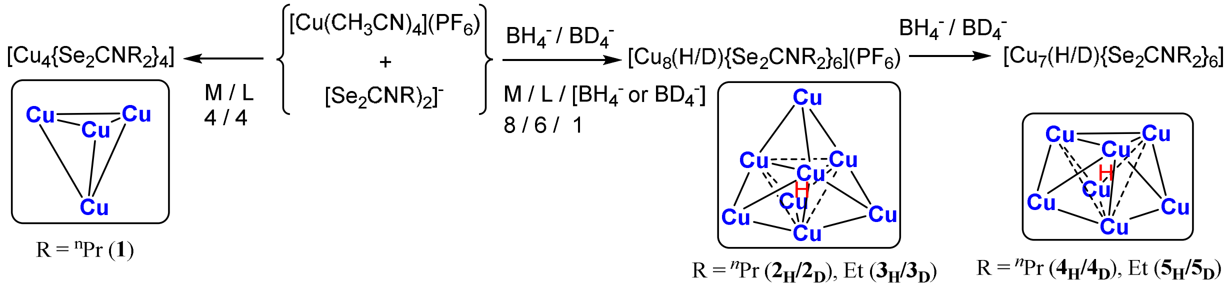
	$\mathbf{1}\cdot 2(CHCl_3)$	$\mathbf{2_H}$	$\mathbf{3_H}\cdot 2[(CH_3)_2CO]$	$\mathbf{4_H}$	$\mathbf{5_H}\cdot(CH_2Cl_2)$
Formula	$C_{30}H_{58}Cl_6Cu_4N_4Se_8$	$C_{42}H_{85}Cu_8F_6N_6PSe_{12}$	$C_{36}H_{73}Cu_8F_6N_6O_2PSe_{12}$	$C_{42}H_{85}Cu_7N_6Se_{12}$	$C_{31}H_{63}Cl_2Cu_7N_6Se_{12}$
F_w	1573.34	2274.96	2222.81	2066.45	1983.07
Space group	*P*can	*P*(-)31c	*P*4/n	*R*(-)3	*C*2/c
a(Å)	11.7089(5)	15.5076(11)	23.6157(11)	15.3215(5)	19.1629(6)
b(Å)	17.4277(7)	15.5076(11)	23.6157(11)	15.3215(5)	11.8176(4)
c(Å)	26.6735(12)	18.5340(15)	12.1113(6)	24.1704(9)	24.1013(7)
α(°)	90	90	90	90	90
β(°)	90	90	90	90	91.2070(8)
γ(°)	90	120	90	120	90
V($Å^3$)	5443.0(4)	3860.0(6)	6754.5(7)	4913.8(4)	5456.8(3)
Z	4	2	4	3	4
ρ_{calc} (Mg/m^3)	1.920	1.957	2.186	2.095	2.414
F(000)	3024	2176	4224	2970	3744
μ(mm^{-1})	7.211	7.882	9.009	8.928	10.809
θ_{max}(°)	25.00	24.98	26.40	26.33	26.42
Relections collected / unique	15181 / 4765 (R_{int} = 0.0684)	13863 / 2277 (R_{int} = 0.0902)	44703 / 6935 (R_{int} = 0.0422)	10891 / 2224 (R_{int} = 0.0225)	26936 / 5589 (R_{int} = 0.0384)
Goodness-of-fit	1.023	1.067	1.074	1.048	1.036
$R1^a$, $wR2^b$ [$I>2\sigma(I)$]	0.0621, 0.1666	0.0468, 0.1243	0.0338, 0.0786	0.0210, 0.0466	0.0325,0.0709
$R1^a$, $wR2^b$ (all data)	0.1028, 0.1912	0.0760, 0.1424	0.0471, 0.0833	0.0243, 0.0477	0.0421, 0.0743
Largest diff. peak and hole (e/$Å^3$)	0.760 and -1.043	0.905 and -0.504	0.601 and -0.566	1.178 and -1.371	2.305 and -1.534

$R1^a = \Sigma \mid \mid Fo \mid - \mid Fc \mid \mid / \Sigma \mid F_o \mid$. $wR2^b = \Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]$.

Results and Discussion:

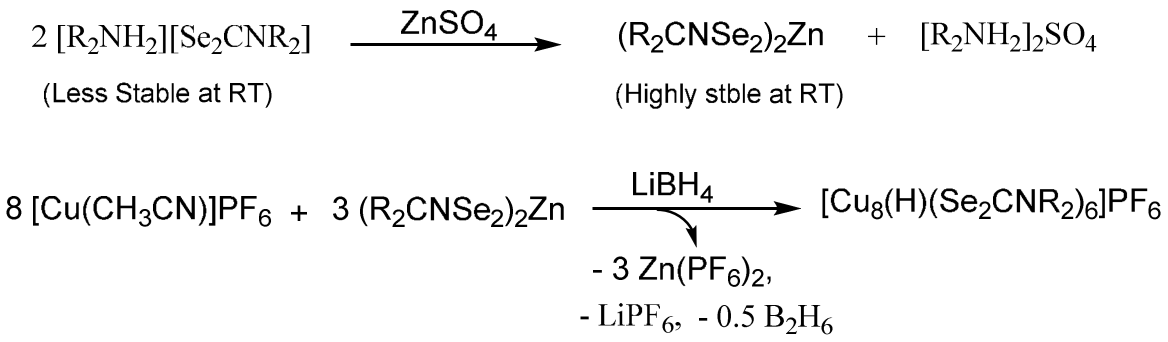
Synthesis

A tetrahedral copper(I) cluster $[Cu_4(Se_2CN^nPr_2)_4]$, **1** was formed from a reaction of Cu(I) salts with $(R_2NH_2)(Se_2CN^nPr_2)$ ligands in an equal molar ratio in THF (Scheme 1). Cluster **1** is very air-sensitive and prevented both satisfactory elemental analysis data and ^{77}Se NMR spectrum from being obtained. This result may be a reason why Cu(I) diselenocarbamates complexes have never been reported prior to this study. Instead, only structures of $Cu^{II}[Se_2CNR_2]_2$ (R= alkyl groups) are known.[25] The hydride-centered octanuclear $[Cu_8(H)\{Se_2CNR_2\}_6](PF_6)$ (R = ^{n}Pr, $\mathbf{2_H}$; Et, $\mathbf{3_H}$) clusters were isolated from a reaction mixture of Cu^+, $R_2NH_2(Se_2CNR_2)$ and $[BH_4]^-$ in an 8:6:1 molar ratio (Scheme 1). Unlike an empty $[Cu_8\{Se_2P(CH_2CH_2Ph)_2\}_6]^{2+}$ cubic complex, which can be easily isolated and subsequently converted into $[Cu_8(X)\{Se_2P(CH_2CH_2Ph)_2\}_6](PF_6)$ (X = H^-, Cl^-, Br^-) in the presence of anion sources,[18] the synthesis of analogous, empty cubic complex failed in the presence of diselenocarbamate ligands under similar circumstances. However, the formation of $[Cu_8(H)\{Se_2CNR_2\}_6](PF_6)$ ($\mathbf{2_H}$, $\mathbf{3_H}$) compounds do suggest that the transient species, empty Cu_8 cubic complexes, $[Cu_8(Se_2CNR_2)_6](PF_6)_2$, are plausible precursors for the subsequent hydride insertion reaction. Further reduction of these hydride-centered octanuclear complexes ($\mathbf{2_H}$, $\mathbf{3_H}$) with one equivalent $[BH_4]^-$ produced the hydride-centered hepatanuclear $[Cu_7(H)\{Se_2CNR_2\}_6]$ (R = ^{n}Pr, $\mathbf{4_H}$; Et, $\mathbf{5_H}$) complexes. The deuteride analogues $[Cu_8(D)\{Se_2CNR_2\}_6](PF_6)$ (R = ^{n}Pr, $\mathbf{2_D}$; Et, $\mathbf{3_D}$) and $[Cu_7(D)\{Se_2CNR_2\}_6]$ (R = ^{n}Pr, $\mathbf{4_D}$; Et, $\mathbf{5_D}$) were also synthesized by using $[BD_4]^-$ instead of $[BH_4]^-$ to confirm the presence of hydride (Scheme 1).



Scheme 1. Preparation of complexes **1**, ($\mathbf{2_H}$ / $\mathbf{2_D}$) – ($\mathbf{5_H}$ / $\mathbf{5_D}$).

Remarkably, both complexes $\mathbf{2_H}$ and $\mathbf{3_H}$ can also be synthesized by transmetallation through replacing $R_2NH_2(Se_2CNR_2)$ ligands with $[Zn(Se_2CNR_2)_2]$ (R = ^{n}Pr, Et) (Scheme 2).[26] In fact, we have initially and successfully synthesized $\mathbf{2_H}$ and $\mathbf{3_H}$ by using $[Zn(Se_2CNR_2)_2]$ as sources of diselenocarbamate ligands due to the following reasons; a) the synthesis of $[Se_2CNR_2]^-$ ligand is not trivial and easy to polymerize into another forms,[26] which can be terminated via immediate reaction with Zn^{2+} salt, and b) the $[Se_2CNR_2]^-$ ligand can be stored for a prolonged time at ambient temperature in the complex form with Zn^{2+} salts rather than with $[R_2NH_2]^+$ salts.[26]



Scheme 2. An alternate synthesis of $\mathbf{2_H}$ and $\mathbf{3_H}$ via replacing of diselenocarbamates with zinc diselenocarbamates.

Spectroscopic (NMR, Elementary and Mass) Studies

Structural characteristics of the as-synthesized complexes were confirmed by ^{1}H, ^{2}H, ^{31}P, and ^{77}Se NMR spectroscopy. The ^{1}H NMR spectrum of each compound reveals a single type of resonances for alkyl (propyl and ethyl) groups of diselenocarbamates to postulate the identical electronic environment around all ligands. The ^{1}H NMR spectra of compounds $\mathbf{2_H}$ and $\mathbf{3_H}$ besides the resonances of alkyl groups show a broad peak at δ 3.05 and 3.01 ppm, respectively, the chemical shift of an encapsulated hydride, which was further corroborated by ^{2}H NMR spectra of their analogous deuterium species ($\mathbf{2_D}$, and $\mathbf{3_D}$) at δ 3.03 and 3.07 ppm (Figure S1-S4). In a similar way, the presence of hydride in the reduced products $\mathbf{4_H}$ and $\mathbf{5_H}$ of $\mathbf{2_H}$ and $\mathbf{3_H}$, respectively, was also defined at δ 3.32 and 3.21 ppm (Figure S5-S8). Thus, the positions of hydride resonance in the reduced products display a slightly downfield shift, which is contrast to chemical shifts of sulfur analogues $[Cu_8(H)\{S_2CNR_2\}_6]^+$ (R = ^{n}Pr at 7.05 ppm, Et at 7.02 ppm), and $[Cu_7(H)\{S_2CNR_2\}_6]$ (R = ^{n}Pr at 6.55 ppm, Et at 6.49 ppm).[27] Additionally, these observed values are also noticeably fluctuated from those of diselenophosphate-ligated analogous, $[Cu_8(H)\{Se_2P(OR)_2\}_6]^+$ (-0.58 ppm),[15a] and diselenophosphinato copper hydride $[Cu_8(H)\{Se_2P(C_2H_4Ph)_2\}_6]^+$ (-1.93 ppm).[19] The ^{31}P NMR spectrum of compounds $\mathbf{2_H}$, $\mathbf{3_H}$ and their deuteride analogous ($\mathbf{2_D}$, $\mathbf{3_D}$) displays clearly the presence of $[PF_6]^-$ counter anion, while the absence of this counter anion in the reduced products ($\mathbf{4_H}$, $\mathbf{4_D}$ and $\mathbf{5_H}$, $\mathbf{5_D}$) reflected from the ^{31}P NMR spectrum confirms to be the neutral species. Further study of $\mathbf{2_H}$ - $\mathbf{5_H}$ with ^{77}Se NMR spectroscopy indicates the presence of a single resonances at δ = 374.9, 364.8, 448.6 and 443.8 ppm, respectively, (Figure S9-S12) and reveals identical coordination of all ligands in each compound.

The composition of complexes $\mathbf{2_H}$-$\mathbf{3_H}$ was further verified by ESI-mass spectrometry (2130.6 for $\mathbf{2_H}$, and 1961.3 for $\mathbf{3_H}$) and an excellent agreement was seen between the theoretical and experimental isotopic patterns of these compounds (Figures S13, S14). However, the molecular ion peak for $\mathbf{4_H}$ and $\mathbf{5_H}$ was not observed in the positive ESI-mass spectrometry. Instead only adduct peaks corresponding to $[Cu_7(H)(Se_2CNR_2)_6(Cu)]^+$ {2129.8 for $[\mathbf{4_H} + Cu]^+$ and 1962.4 for $[\mathbf{5_H} + Cu]^+$ } were identified (Figures S15, S16), which suggested the potential re-formation of $[Cu_8(H)(Se_2CNR_2)_6]^+$ in the gas phase during ESI-mass analysis conditions.[27] Since similar results in the positive ESI-mass spectrum were also identified on their sulfur analogues,[27] these provide an important lesson: the formulation of a molecular composition by using the mass spectrometry must be very cautious not to assign an adduct ion as the actual composition of a species, which is indeed neutral. The molecular formulas of these compounds were also corroborated with their elemental analysis data and indeed the accuracy can be improved with the association of solvent molecules, which were used for purification during the synthesis.

X-ray crystal structures

1: The solid-state structure of compound **1** is analogous to [$Cu_4\{Se_2P(O^iPr)_2\}_4$],[10] and crystallizes in the orthorhombic space group *P*can, with four molecules in the unit cell. The metal skeleton of **1** reveals that four copper atoms are arranged in the tetrahedral framework capped by diselenocarbamate ligands on each trigonal face in a trimetallic triconnective (μ_3; η^1, η^2) pattern.[28] Four of the six Cu···Cu edges of a tetrahedron are shorter (2.632(2) Å, 2.653(2) Å) due to bridging of a selenium atom than the rest of two edges (2.770(2) Å, 2.808(2) Å). This variation in edge lengths is significantly shorter than the analogous [$Cu_4\{Se_2P(O^iPr)_2\}_4$], where selenium-bridged Cu···Cu distances are in the range of 2.711(6) Å to 2.809(6) Å, and the two uncapped distances are 2.899(6) Å and 2.875(5) Å. Obviously, the ligand "bite distance", 3.29(4) & 3.70(5) Å, plays a critical role. However, the Cu-Se bond distances, 2.359(1)-2.397(1) Å, in **1** are almost similar with its analogue (2.355(6)-2.408(5) Å). Besides neutral species **1** and its analogues {[$Cu_4\{Se_2P(O^iPr)_2\}_4$] and [$Cu_4(Se_2P^iPr_2)_4$]}, there are a few reports on the Cu_4 species [$Cu_4\{PPh_2(Se)NP(Se)Ph_2\}_3$]$^+$, [$Cu\{SeC_5H_3(Me\text{-}_3)N\}$]$_4$, and [$Cu_4(SePh)_6$]$^{2-}$ stabilized by selenium-donor ligands.[29] Since the complex [$Cu_4\{Se_2P(O^iPr)_2\}_4$] was demonstrated as an excellent precursor in the synthesis of non-stoichiometric copper selenide nanomaterials,[10] the compound $\mathbf{1_H}$ and other Cu_4 species can also be an alternative target used to study such types of useful materials.

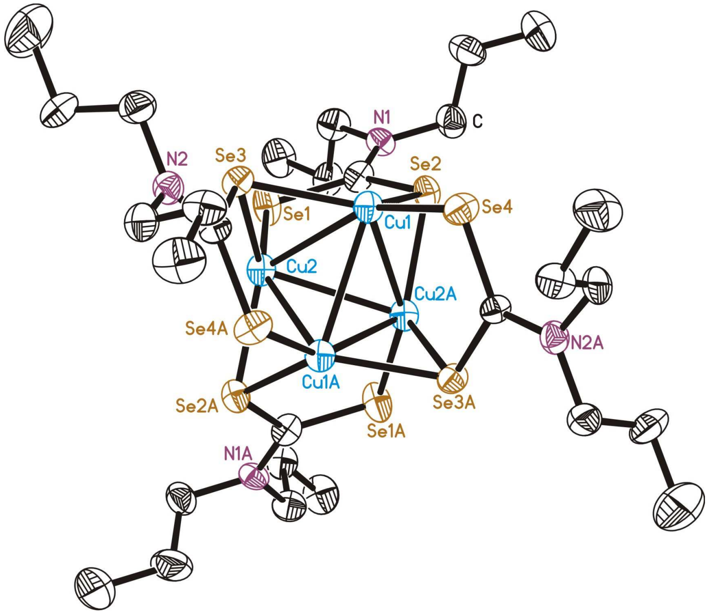


Figure 1. Molecular structure of $[Cu_4(Se_2CN^nPr_2)_4]$, **1**, (30% thermal ellipsoid) and H-atoms are omitted for clarity. Ranges of selected bond lengths [Å] and angles [°]: Cu···Cu 2.632(2)-2.808(2), Cu-Se 2.359(1)-2.397(1), Se···Se (bite) 3.292(1)-3.297(1); Cu-Se-Cu, 66.99(5)-67.50(5), Se-C-Se 122.0(5). Symmetry code A: x, -y, 0.5-z.

$\mathbf{2_H}$ and $\mathbf{3_H}$: Similar to crystallographic study of an octanuclear copper(I) dithiocarbamate cluster,[27] the monocationic octanuclear copper cluster $\mathbf{2_H}$ crystallizes in the trigonal space group, *P*(-)31c. Eight Cu atoms are disordered at 16 positions on both general and special positions, where the four atoms constitute the inner Cu_4 tetrahedron and the other four atoms compose the outer Cu_4 tetrahedron, to generate a tetracapped tetrahedron (Figure 2). The solid-state structure of $\mathbf{2_H}$ shows that eight copper atom are assembled in a tetracapped tetrahedral cage via supporting of six diselenocarbamates ligands in tetrametallic tetraconnective (μ_2-Se;

μ_2-Se) mode, where all the twelve selenium elements constitute a distorted icosahedral array (Figure 2a, b). The tetracapped tetrahedron geometry of Cu_8 cage is revealed due to simultaneous support of both C_2 and C_3 rotational axes to acquire all ligands in equivalent environment in solution state, which is also approved by the ^1H, ^{77}Se NMR spectra of $\mathbf{2_H}$ (*vide infra*). In the Cu_8 cage, Cu3A, Cu4, Cu4A, and Cu4B atoms locate on the vertices (abbreviated as Cu_v) of a tetrahedron unit, are coordinated with an encapsulated hydride and Cu1(C-E), and Cu2 as capping atoms (abbreviated as Cu_{cap}) of a tetracapped unit are plugged on each triangle face of tetrahedron (Figure 2c). The $Cu_v\cdots Cu_v$ edge distances (2.843(3)-2.96(3) Å) of the tetrahedron, are longer than the $Cu_v\cdots Cu_{cap}$ distances (2.58(1)-2.665(5) Å), as found in $[Cu_8(H)\{Se_2P(CH_2CH_2Ph)_2\}_6]^+$ and $[Cu_8(H)\{Se_2P(O^iPr)_2\}_6]^+$.[19,15a] Thus, in these clusters $Cu_v\cdots Cu_{cap}$ distances are generally shorter than the sum of the van der Waals radii for copper (2.80 Å).[30] Each of the six diselenocarbamates ligands places on the top of Cu_4 butterflies, where hinges and wingtips are resembled by the edges of the tetrahedron and capping Cu atoms, respectively (Figure 2b,c). The dihedral angles of the Cu_4 butterflies are in the range of 151.9(5)° to 156.8(6)° and the average length of intraligand Se···Se bite distance is 3.316(2) Å, which is shorter than found in $[Cu_8(H)\{Se_2P(O^iPr)_2\}_6]^+$ (3.749(6) Å). The copper and selenium interactions reveal that there are two types of Cu_v-Se (avg. 2.532(7) Å) and Cu_{cap}-Se (avg. 2.31(3) Å) bond distances. As found in the (^1H, ^2H) NMR spectrum of $\mathbf{2_H}$ and its deuterides analog ($\mathbf{2_D}$), a hydride anion was located at the center of tetrahedron to balance the charge. The average Cu-μ_4-H distance [1.77(8) Å] is comparable with $[Cu_8(H)\{Se_2P(O^iPr)_2\}_6]^+$ (avg. 1.83(1) Å) and slightly longer than those observed in $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ (avg. 1.71(2) Å)[31] and $[Cu_{28}(H)_{15}(S_2CN^nPr_2)_{12}]$ (avg. 1.56(5) Å)[32] certified by the neutron diffraction analysis.

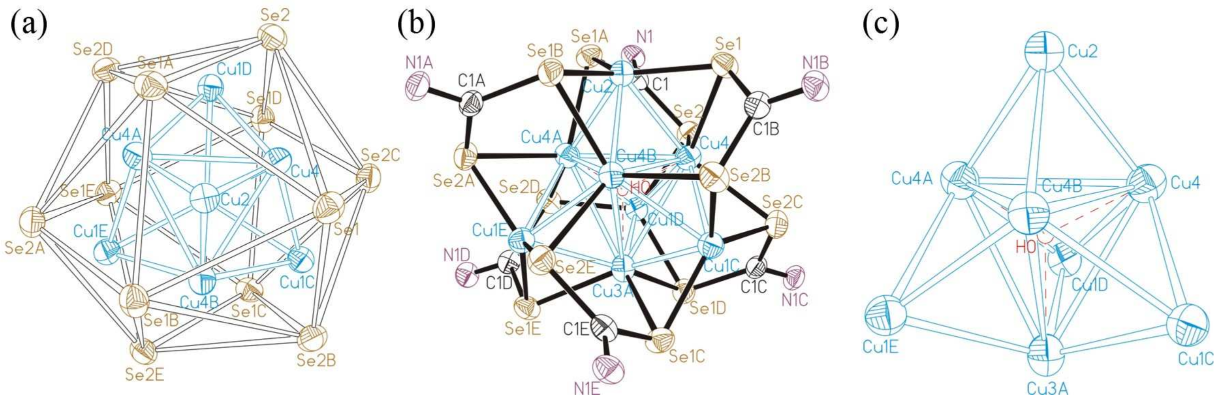


Figure 2. (a) Schematic representation of a Cu_8 core within Se_{12} icosahedron along the C_3 axis. (b) Molecular structure of the $[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_4(Se_2CNR_2)_6]^+$ (R = ^{n}Pr, $\mathbf{2_H}$; Et, $\mathbf{3_H}$), (30% thermal ellipsoid) with alkyl groups omitted for clarity. (c) Tetracapped tetrahedral core with an interstitial hydride $[Cu_8H]$. Ranges of selected bond lengths [Å] and angles [°], $\mathbf{2_H}$: $Cu_v\cdots Cu_v$ 2.843(3)-2.96(3), $Cu_v\cdots Cu_{cap}$ 2.58(1)-2.665(5), Cu_v-Se 2.511(2)-2.549(3), Cu_{cap}-Se 2.282(3)-2.332(3), Se···Se (bite) 3.316(1); Cu-Se-Cu, 64.0(1)-66.7(1), Se-C-Se 122.4(5). $\mathbf{3_H}$: $Cu_v\cdots Cu_v$ 2.892(2)-2.961(2), $Cu_v\cdots Cu_{cap}$ 2.559(2)-2.691(2), Cu_v-Se 2.503(1)-2.555(1), Cu_{cap}-Se 2.283(1)-2.344(1), Se···Se (bite) 3.3081(7)-3.3235(7); Cu-Se-Cu, 63.29(5)-67.68(4), Se-C-Se 121.9(2)-122.2(2). Symmetry code A: -y, x-y, z; B: -x+y, -x, z; C: y, -x+y, 1-z; D: x-y, x, 1-z; E: -x, -y, 1-z.

Even though ethyl homoleptic complex $\mathbf{3_H}$ is isostructural with $\mathbf{2_H}$ (Figure 2), it crystallizes in the tetragonal space group, *P*4/*n*, with eight acetone molecules co-crystallized in each unit cell. The copper framework of $\mathbf{3_H}$ was also disordered in a similar way as $\mathbf{2_H}$, where the tetracapped tetrahedral unit was disordered at two positions, each in 50% occupancy. Whereas $Cu_v\cdots Cu_v$ edge lengths (range 2.892(2)-2.961(2) Å) of tetrahedron, are larger than $Cu_v\cdots Cu_{cap}$ (range 2.559(2)-2.691(2) Å), the variations between these distances are slightly less than those ($Cu_v\cdots Cu_v$ and $Cu_v\cdots Cu_{cap}$) as observed in $\mathbf{2_H}$. Additionally, the avg. Cu_v-Se (2.52(6) Å), avg. Cu_{cap}-Se (2.313(3) Å) and avg. Cu-μ_4-H (1.78(8) Å) bond distances of $\mathbf{3_H}$ are slightly shorter in comparison with similar distances in $\mathbf{2_H}$. Although, in both compounds the dihedral angles (range 151.9(4)-157.9(7)°) of the Cu_4 butterflies and average length 3.316(9) Å of intraligand Se$\cdots$Se bite are quite similar.

$\mathbf{4_H}$: The neutral Cu_7 cage cluster crystallizes in the trigonal, *R*(-)3 space group with three molecules in the unit cell. Seven Cu atoms constituted a tricapped tetrahedral framework are disordered at 16 positions which form two concentric cubes. The sum of inner eight positions is equal to four copper atoms, which form a tetrahedron, and the sum of eight positions of an outer cube is equal to three Cu atoms, each capping on the triangular face of tetrahedron to generate a tricapped tetrahedral geometry of Cu_7 core (Figure 3). This complex can be formed by loss of one capping atom from a tetracapped tetrahedral Cu_8 core of compound $\mathbf{2_H}$ during its further reduction with one equivalent of $[BH_4]^-$. Thus, the solid state structure reveals a tricapped tetrahedral copper skeleton, which is also inscribed inside an icosahedron of 12 Se atoms from six diselenocarbamates ligands and reveals the first reported tricapped tetrahedral Cu_7 cluster inscribed within a Se_{12} icosahedron (Figure 3a, b).[15a] The tetrahedron unit is constituted by Cu4, Cu3(A-B), and Cu3E atoms (abbreviated as Cu_v), and capping unit have three copper Cu1, Cu1C, and Cu1D (abbreviated as Cu_{cap}) atoms (Figure 3c). Therefore, one triangle (Cu3A, Cu3B, and Cu3E atoms) out of four triangles of a tetrahedron is not capped by a copper atom and due to the lack of one capping Cu atom, the coordination patterns of diselenocarbamate ligands in this cluster differs from those of $\mathbf{2_H}$ complex. Out of six diselenocarbamates ligands, each of three is coordinated to two Cu_v and two Cu_{cap} atoms via tetrametallic–tetraconnective (μ_2-Se; μ_2-Se) bonding mode on each of three Cu_4 butterflies and the rest three ligands are each coordinated to two Cu_v and one Cu_{cap} via trimetallic, triconnective (μ_2-Se; μ_1-Se) bonding mode on three triangles made up of two copper atoms of a tetrahedron and one capping copper atom. The coordination mode of the dithiophosphate ligands in the homoleptic complex $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{S_2P(O^iPr)_2\}_6]$[33] of $\mathbf{4_H}$ is identical with $\mathbf{2_H}$, but in the dithiocarbamate analogue $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{S_2C(\text{aza-15-crown-5})\}_6]$ complex the coordination mode of aza-15-crown-5-dtc ligands was found slight different due to the three-fold elongation of tetrahedron unit, where only two ligands achieve a tetrametallic–tetraconnective (μ_2-S; μ_2-S) bonding mode and the rest of four dtc ligands exhibit in a trimetallic, triconnective (μ_2-S; μ_1-S) bonding mode.[27] The average of $Cu_v\cdots Cu_v$ distances (2.888(8) Å) are slightly longer than the sum of the van der Waals radii for two copper atoms, 2.8 Å, whereas, the average of $Cu_v\cdots Cu_{cap}$ distances [2.545(8) Å] are shorter as also found in the $\mathbf{2_H}$. The probability of a hydride presence, arising from the ^{1}H and ^{2}H NMR spectrum of $\mathbf{4_H}$ and $\mathbf{4_D}$, was located inside a tetrahedron moiety and the average of Cu-μ_4H distances (1.76(8) Å) is comparable with the neutron diffraction analyzed Cu-μ_4H distance (1.86(2) Å) of $[Cu_4(\mu_4\text{-H})(\mu_3\text{-Cu})_3\{S_2C(\text{aza-15-crown-5})\}_6]$[27] but it is slightly greater than $[Cu_{20}(H)_{11}\{S_2P(O^iPr)_2\}_9]$ (1.71(2) Å)[31] for tetrahedrally coordinated hydrides. The average length of Cu_v-Se bonds, avg. of Cu_{cap}-Se bonds, and the dihedral angle ranges of three Cu_4 butterflies are observed 2.524(5) Å, 2.316(2) Å and 153.7(9)-153.8(2)°, respectively, and those are comparable with $\mathbf{2_H}$ as shown in table 2. The intraligand Se···Se bite distance in the diselenocarbamate ligand is 3.2943(6) Å. Thus an overview of $\mathbf{4_H}$ reveals that the coordination environment of each copper atom of tetrahedron and each capping copper atom is in a tetrahedral Se_3H and trigonal planer Se_3 coordination, respectively.

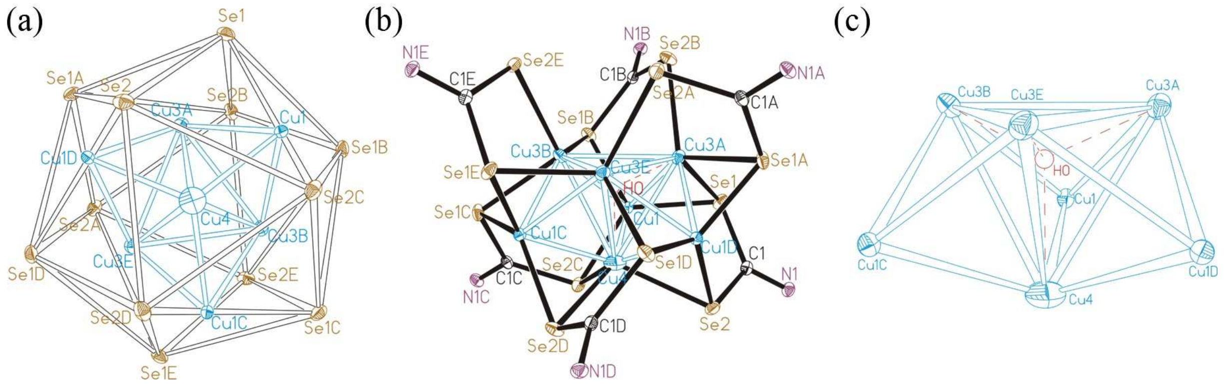


Figure 3. (a) Schematic representation of a Cu_7 core within Se_{12} icosahedron along the C_3 axis. (b) Molecular structure of $[Cu_4(\mu_4\text{-}H)(\mu_3\text{-}Cu)_3\{Se_2CNR_2\}_6]$ (R = ^{n}Pr, $\mathbf{4_H}$; Et, $\mathbf{5_H}$) (30% thermal ellipsoid) with alkyl groups omitted for clarity except the interstitial hydride. (c) Tricapped tetrahedral core with an interstitial hydride $[Cu_7H]$. Rang`es of selected bond lengths [Å] and angles [°], $\mathbf{4_H}$: $Cu_v\cdots Cu_v$ 2.856(1)-2.92(2), $Cu_v\cdots Cu_{cap}$ 2.48(6)-2.580(2), Cu_v-Se 2.4705(9)-2.584(1), Cu_{cap}-Se 2.290(1)-2.331(1), Se···Se (bite) 3.2943(6); Cu-Se-Cu, 61.3(7)-64.97(4), Se-C-Se 121.2(1). $\mathbf{5_H}$: $Cu_v\cdots Cu_v$ 2.803(2)-3.035(2), $Cu_v\cdots Cu_{cap}$, 2.506(2)-2.691(2), Cu_v-Se 2.442(1)-2.693(2), Cu_{cap}-Se 2.298(2)-2.407(2), Se···Se (bite) 3.2776(7)-3.2899(7); Cu-Se-Cu, 61.28(6)-66.47(5), Se-C-Se 120.4(2)-121.6(2). Symmetry code A: -1/3+y, 1/3-x+y, 1/3-z; B: 2/3+x-y, 1/3+x, 1/3-z; C: 1-y, 1+x-y, z; D: -x+y, 1-x, z; E: 2/3-x, 4/3-y, 1/3-z.

$\mathbf{5_H}$: The neutral Cu_7 cage of $\mathbf{5_H}$ cluster crystallizes in the monoclinic, *C*2/c space group. The architecture and structural feature of $\mathbf{5_H}$ is similar to those found in $\mathbf{4_H}$ wherein tricapped tetrahedral metal core is stabilized by the six diselenocarbamates via equally trimetallic-triconnective (μ_2-S; μ_1-S) and tetrametallic–tetraconnective (μ_2-S; μ_2-S) bonding patterns (Figure 3). The ^{2}H NMR spectrum shows a broad resonance at 3.18 ppm related to the presence of hydride and located at the center of tetrahedron (Figure 3).

The averaged Cu_v-Se, Cu_{cap}-Se bond lengths, intraligand Se···Se bite distances, and the dihedral angle ranges of three Cu_4 butterflies are 2.533(5) Å, 2.328(8) Å, 3.283(9) Å and 150.1(2)-157.3(5)°, respectively. Those are comparable with $\mathbf{3_H}$ as shown in Table 2. Compounds $\mathbf{4_H}$ and $\mathbf{5_H}$ reveal the first stabilized tricapped tetrahedral Cu_7 core with diselenocarbamate type of ligands among the known selenium containing ligands. However, a Cu^I_7 core in cubic frame with a missing corner has been stabilized by a central bromide and diselenophosphates (dsep) type of ligands.[34]

With the existence of a hydride at the center of tetracapped- and tricapped-tetrahedral copper cores in the compounds $\mathbf{2_H}$-$\mathbf{5_H}$ permits a structural comparison with their relative derivatives,[15a,19, 33] and their important geometrical parameters as well as ^1H (or ^2H) chemical shifts are listed in Table 2. Although the intraligand Se···Se bite distances $\mathbf{2_H}$-$\mathbf{5_H}$ are much smaller than those observed in other derivatives, the dihedral angles of the butterfly face are comparable. The observed discrepancies in metric parameters and ^1H (or ^2H) chemical shifts may be due to the perturbation of the electronic environment of the ligands.

Table 2. Selected structural parameters, hydride (deuteride) chemical shifts of $\mathbf{2_H}$-$\mathbf{5_H}$ and other related species.

Compounds	Avg. $M_V\cdots M_V$ [Å]	Avg. $M_V\cdots M_{cap}$ [Å]	Avg. M_V-Se [Å]	Avg. M_{cap}-Se [Å]	Avg. Se...Se bite[Å]	dihedral angle [deg][a]	Avg. M-μ_4H[Å]	^{1}H NMR (ppm)	^{2}H NMR[b] (ppm)
$\mathbf{2_H}$	2.90(3)	2.625(2)	2.532(7)	2.31(3)	3.316(2)	151.9(5)-156.8(6)	1.77(8)	3.03(br)	3.03(br)
$\mathbf{3_H}$	2.920(5)	2.62(5)	2.52(6)	2.311(3)	3.316(9)	151.9(4)-157.9(7)	1.78(8)	3.17(br)	3.07(br)
$\mathbf{4_H}$	2.888(8)	2.545(8)	2.524(5)	2.316(2)	3.2943(6)	153.7(9)-153.8(2)	1.76(8)	3.32(br)	3.34(br)
$\mathbf{5_H}$	2.90(9)	2.584(4)	2.533(5).	2.328(8)	3.283(9)	150.1(2)-157.3(5)	1.78(4)	3.24(br)	3.18(br)
$[Cu_8(H)\{Se_2P(O^iPr)_2\}_6]^+$	2.991(2)	2.762(3)	2.560(3)	2.307(2)	3.749(6)	151.5(5)-154.3(1)	1.83(1)	-0.58	-0.54
$[Cu_8(H)\{Se_2P(OEt)_2\}_6]$	2.937(3)	2.717(9)	2.527(1)	2.374(4)	3.749(6)	151.6(6)-154.0(8)	1.79(5)	-0.57	--[c]
$[Cu_8(H)\{Se_2P((CH_2)_2Ph)_2\}_6]^+$	2.915(8)	2.733(4)	2.558(2)	2.294(6)	3.709(6)	151.5(7)-152.6(8)	1.78(6)	-1.93	--[c]

[a] Dihedral angles range of the Cu_4 butterflies, [b] ^{2}H NMR of analogue deuteride species ($\mathbf{2_D}$-$\mathbf{5_D}$). [c] (data are not available).

Photophysical Properties of $\mathbf{2_H}$ and $\mathbf{3_H}$. The photophysical data (UV−vis, excitation and emission) of both ($\mathbf{2_H}$, $\mathbf{3_H}$) complexes in the solid and solution states at 77 K are summarized in Table 3. The spectral characteristics for both complexes are almost identical and only those of complex $\mathbf{2_H}$ are depicted in Figure 4. An intense absorption band for both complexes $\mathbf{2_H}$ and $\mathbf{3_H}$ appeared at 292 (ε = 43000 cm^{-1} M^{-1}) and 290 (ε = 49000 cm^{-1} M^{-1}) nm, respectively, characteristic of ligand-centered transitions.[35] Additionally, a less intense absorption peak is also detected at 367 (ε = 23000 cm^{-1} M^{-1}) and 362 (ε = (24000) cm^{-1} M^{-1}) nm, which can be reasonably assigned as the metal to ligand charge transfer (MLCT) transition due to the presence of an almost identical pattern of their dithiocarbamates analogous.[27] These compounds exhibit an orange emission in both the solid state and solution under UV−irradiation at 77 K. In the frozen state (CH_2Cl_2) of $\mathbf{2_H}$, the emission band is centered at 606 nm (Figure 4c), which is red-shifted about ~36 nm compared to the emission from the solid state (570 nm). Similar observations can also be realized in the liquid frozen state (CH_2Cl_2) of $\mathbf{3_H}$ as shown in Table 3. To the best of knowledge these are the only reports on the emissive properties of any copper(I) diselenocarbamate complexes. However, the photochemistry of Cu(II) diselenocarbamates in various solvents has been well established.[36]

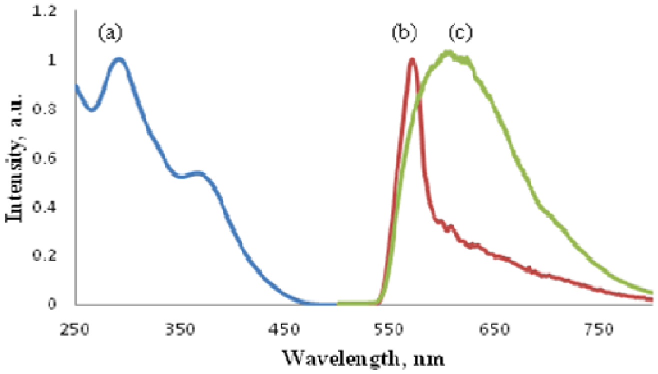


Fig. 4. Normalized spectra of $\mathbf{2_H}$. UV−vis absorption (a), emission spectra at 77K in the solid state (b) and in CH_2Cl_2 glass (c).

Table 3. Photophysical data for $[Cu_8(H)(Se_2CNR_2)_6]^+$ (R = ^{n}Pr, $\mathbf{2_H}$; Et, $\mathbf{3_H}$)

Compd.	State(*T*/K)	λ^{ex}_{max} (nm)	λ^{em}_{max} (nm)	Stoke shift(cm^{-1})	λ^{ab}_{max} (nm)
$\mathbf{2_H}$	CH_2Cl_2 (77)	312-433	606	15600	292(43000), 367(23000)
	Solid (77)	370-430	570		
$\mathbf{3_H}$	CH_2Cl_2 (77)	320-402	608	14800	290(49000), 362(24000)
	Solid (77)	370-400	568		

Preparation of Copper Selenides Nanocomposites

It has been well-documented that the copper selenides have diverse stoichiometric CuE, Cu_2E (E = S or Se), Cu_3Se_2, etc. and nonstoichiometric ($Cu_{2\text{-}X}E$ (E = S or Se)) phases.[37] Temperature-dependent phase transitions as well as composition variation for copper chalcogenides have been reported,[38,39] where phases of copper selenides can be easily differentiated by the powder X-ray diffraction pattern. For instance, Cu_3Se_2 disproportionates into $Cu_{1.8}Se$ and CuSe in the temperature range of 120–135 °C. Similarly CuSe not only undergoes phase transition from hexagonal phase at room temperature to orthorhombic at 48 °C and back to hexagonal phase at 120 °C, but also disproportionates at higher temperature to $Cu_{2\text{-}x}Se$ and selenium.[38, 39] The copper cluster, $[Cu_{20}Se_{13}(PEt_3)_{12}]$ on pyrolysis at 100 °C yields Cu_2Se[13a] whereas $[Cu\{Se_2P(O^iPr)_2\}]_4$ was employed for the synthesis of non-stoichiometric copper selenide nanostructures.[10]

Copper selenide material was synthesized by a solvothermal route employing $\mathbf{2_H}$ as an example among the isolated complexes, **1** ~ **5**. $\mathbf{2_H}$ was charged in a furnace at 200 °C for 1 h to afford black residues. The resulting product was examined by various techniques such as X-ray powder diffraction (XRD), energy dispersive X-ray analysis (EDX), and field emission scanning electron microscopy (FE-SEM) (Figure 5). FE-SEM images show that there was not much regularity in the size features. A high magnification shows the presence of hexagonal nanoplates which had a mean plane size of 80–90 nm (measured edge to edge) along with large size of 229 nm. Low magnified FE-SEM image reveals that the hexagonal plates are self-assembled via end-to-end growth to form hexagonal sheets. Powder X-ray diffraction (XRD) pattern exhibits the diffraction peaks at 26.4, 28.1, 31.1, 46.1, 50.0, and 56.6, corresponding to (101), (102), (006), (110), (108), and (116) planes of hexagonal CuSe, respectively, which are in good agreement with the reported diffraction pattern of hexagonal CuSe (JCPDS No. 34-0171) except one peak at 44 (220), which can be assigned to the cubic $Cu_{2-x}Se$. EDS analysis indicates that yielded material contains Cu and Se with atomic ratio of 55.08:44.92, which deviates from the expected ratio of hexagonal CuSe perhaps due to the presence of cubic $Cu_{2-x}Se$. A possible disproportionation of CuSe at higher temperature yields small amount of $Cu_{2-x}Se$.[38,39] A thermal behavior of copper(I) 2-pyridyl selenolates and tellurolates complexes $[Cu\{EC_5H_3(R\text{-}3)N\}]_4$ (E/R = Se/Me or Te/R; R = H or Me) was also reported to produce both stoichiometric and non-stoichiometric copper chalcogenides under various conditions.[37a]

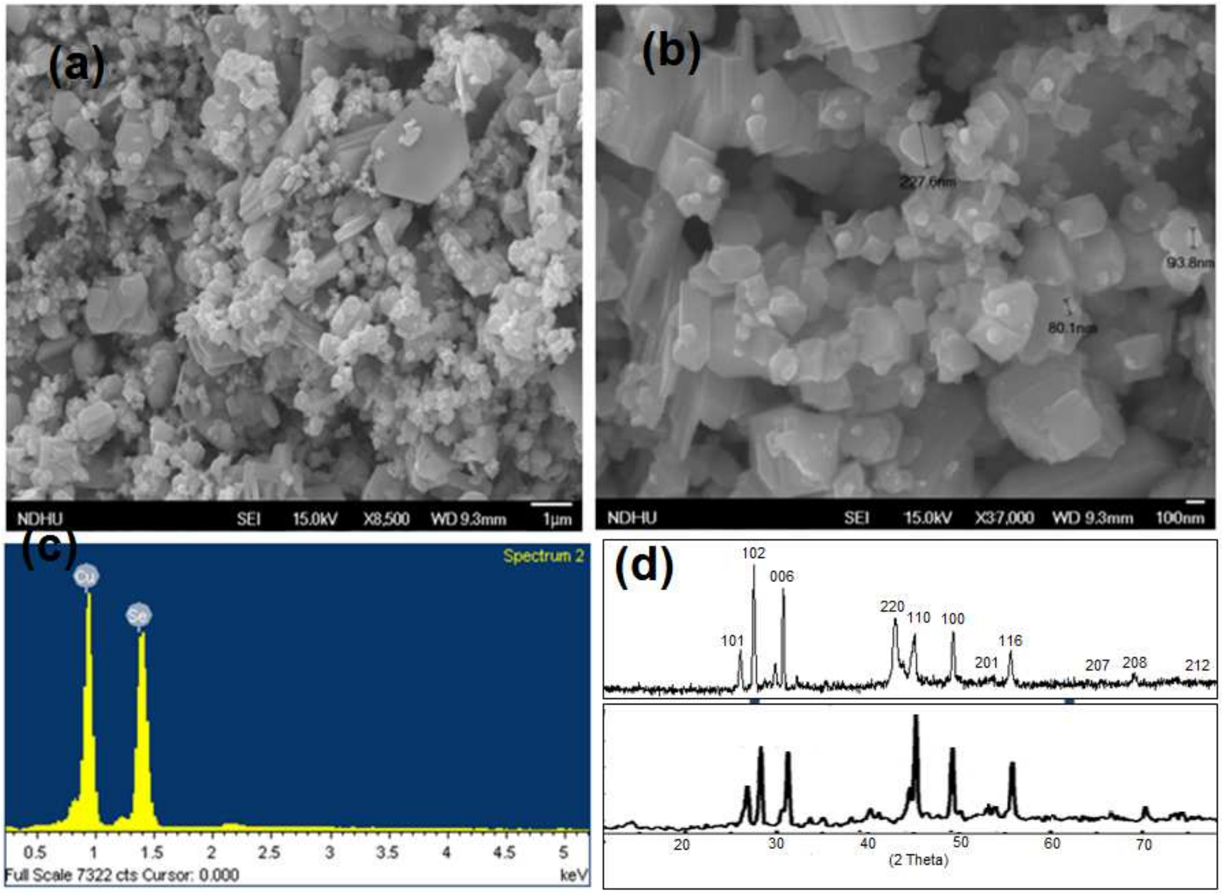


Fig. 5. Analysis of CuSe nanoparticles obtained from $\mathbf{2_{H}}$. SEM images with a low (a) and high (b) magnification. (c) EDS spectrum. (d) Powder XRD patterns (top), standard data for CuSe JCPDS No.: 340171 (bottom).

Conclusions

Hydride-centered hepta- and octa-nuclear (air and moisture stable) and tetranuclear (air sensitive) copper(I) complexes stabilized by diselenocarbamate ligands have been synthesized and structurally characterized for the first time. Even though a few examples of the Cu_4 (tetrahedral) and Cu_8 (tetracapped tetrahedral) cage clusters are known for diselenophosph(in)ate ligands, a Cu_7 (tricapped tetrahedral) cage inside an icosahedral Se_{12} cage has not previously been reported. However, a Cu_7 cage, a cubic structure with a missing vertex, enclosed within an icosahedral Se_{12} cage has been reported, which has a central bromide anion. Additionally, the photophysical properties of Cu_8 species (**2_H**, **3_H**) have been illustrated. The described complexes as single-molecule precursors to produce CuSe (or $Cu_{2-x}Se$ partially) by a solvothermal process were investigated in compound **2_H**. Thus, these hydrido-copper clusters stabilized with diselenocarbamates are beneficial materials in the synthesis of copper selenide nanocomposites.

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