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Construction of heterobimetallic Cd(Hg)/Cu(Ag)/S(Se) complexes from homoleptic [Hg(EPh)₂] molecules and $[Cd(EPh)_4]^{2-}$ anions (E = S, Se)

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ABSTRACT

Treatment of [Hg(EPh)₂] with 2 equivalents of [Cu(PPh₃)₂Cl] gave the trinuclear Hg/Cu/S(Se) complexes $[Hg(\mu-EPh)_2[CuCl(PPh_3)_2]]$ (E = S 1, Se 2) in which the two copper centers are ligated by the [PhE]⁻ ligands of the [Hg(EPh)₂]. A similar reaction of [Hg(EPh)₂] with [Ag(PPh₃)₂Cl] gave rise to isolation of the dinuclear compounds $[Hg(SePh)(\mu-SePh)(\mu-Cl)Ag(PPh_3)_2]$ (E = S 3, Se 4) in which the coordination geometry of the mercury atom is a slightly distorted T-shape. Reactions of the homoleptic tetrahedral species $[Cd(EPh)_4]^{2-}$ with 2 equivalents of $[Cu(PPh_3)_2NO_3]$ afforded the neutral linear trinuclear complexes $[Cd(\mu-EPh)_4[Cu(PPh_3)_2]_2]$ (E = S 5, Se 6) in which two $[Cu(PPh_3)_2]^+$ fragments bind with the opposite edges of a tetrahedral $[Cd(EPh)_4]^{2-}$ moiety via the sulfur or selenium atoms of the PhE⁻ ligands. A similar reaction of [Me₄N]₂[Cd(SPh)₄] with 2 equivalents of [Ag(PPh₃)₂NO₃] gave an analogous complex $[Cd(\mu-SPh)_4[Ag(PPh_3)_2]_2]$ (7), whereas the reaction of $[Me_4N]_2[Cd(EPh)_4]$ with an equivalent amount of $[Ag(PPh_3)_2NO_3]$ under similar conditions afforded the neutral heptanuclear complexes $[Cd_3(\mu-EPh)_6]$ $(\mu_3-\text{EPh})_4(\text{AgPPh}_3)_4$ (E = S 8, Se 9) which comprise three $[(\text{AgPPh}_3)]^+$ fragments side-ligated and one $[(AgPPh_3)]^+$ fragment side-capped with the trinuclear cadmium-thio(seleno)phenolate $[Cd_3(\mu-EPh)_9]$ $(\mu_3$ -EPh)]^{4–} moleties *via* the sulfur atoms of thiophenolates in **8** and the selenium atoms of selenophenolates in 9. The nonlinear optical properties of two neutral heptanuclear complexes 8 and 9 have been examined by z-scan techniques with 7-ns pulses at 532 nm.

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1. Introduction

The study of transition-metal chalcogenolate chemistry has been actively investigated in two decades [1], motivated primarily by the bonding diversity [2], reactivity [3], and potential use as precursors for the binary and ternary metal-chalcogenide materials [4]. Remarkably, the search for the new metal-chalcogen containing building blocks is of current interest because of their capability to manipulate single-source precursors for nano-crystalline photovoltaic materials [5], as well as other materials and biological applications [6]. In contrast to well-documented binary metalchalcogenides, there are relatively few reports on the preparation of ternary metal-chalcogenides which have found widespread application in optical and electronic devices [7]. Recently, reactions of tetrathio- and tetraseleno-metalates $[MQ_4]^{2-}$ (M = Mo, W; Q = S, Se) with coinage-metal ions resulted in the syntheses and structures of many types of hetero-transition-metal clusters [8]. The variation of structural types of these heterometal clusters mainly depends on the number of coinage-metal atoms bound to the tetrahedral $[MQ_4]^{2-}$ moiety with six MQ₂ edges [9]. The successful isolation of those clusters offers an opportunity to study the structure-property relationships of inorganic cluster materials [10]. The indium- and gallium-tetrathiolates $[M(SR)_4]^-$ (M = In, Ga) obtained by treatment of metal trichloride with sodium alkylthiolate react with copper- or silver-phosphine species to produce ternary Cu(Ag)/In(Ga)/S complexes which can be effective single-source precursors to nanocrystalline photovoltaic materials [5]. The electron-rich sulfur affinity and their less steric hindrances probably provide the ability of homoleptic $[M(SR)_4]^-$ (M = In, Ga) anions as metalloligands towards coinage-metals [5a,11]. Similarly, the active sulfur atoms of the neutral spirocyclic [Sn(edt)₂] (edt = ethane-1,2-dithiolate) are capable of binding copper atoms to form heterometallic Cu/Sn/S complexes such as linear trinuclear [(Ph₃P)Cu]₂Sn(edt)₂ and the bottle-shaped heptanuclear $[Cu_4Sn_3(edt)_6(\mu_3-O)(PPh_3)_4](ClO_4)_2$ with strong luminescent properties [12]. Brennan and co-workers reported the syntheses and structural characterization of the series of heterometallic chalcogenolate complexes having the general formula $MM'(EPh)_x(L)_y$ [M = Zn, Cd, Hg; M' = divalent (x = 4) or trivalent (x = 5) rare earth; E = S, Se, Te; L = THF, pyridine] [13]. These heterometallic Ln-group 12 chalcogenolates have a broad range of potential applications in the rapidly developing field of rare earth-doped

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semiconductor technology [14]. Corrigan and coworkers synthesized a series of ternary Zn/Cd(Hg)/E (E = S, Se, Te) clusters by controlling modulation of crystalline size and reduction of polydispersity, since silyl reagents, like $Se(SiMe_3)_2$ and $RSeSiMe_3$, finding extensive use as a source of Se^{2-} and RSe^{-} in the synthesis of metal-selenide nanoclusters and colloids [15]. By way of a similar synthetic route, Fenske and co-workers have successfully isolated series of ternary chalcogenide high-nuclear clusters containing groups 11 and 13 metals [16]. Thus, the development of new approaches to synthesize ternary heterometallic chalcogenides as precursors to the according nanoparticles is still an attractive pursuit.

It is well known that synthetic routes for ternary heterometallic clusters used in the present days are not many, which stimulates many synthetic chemists to find useful metal-complexes as synthons to construct the ternary clusters. One of the notable examples is the use of $[Hg(EPh)_2](E = Se, Te)$ as a precursor for the preparation of nanoclusters using redistribution reactions [17]. A considerable degree of variation in mercury coordination geometries transferred from two to three or four coordination, accordingly, the resulting homoleptic $[Hg(ER)_n]^{m-}$ (n = 2, 3, 4; m = 0, 1, 2) species lead to variable compositions and structures of the clusters [18]. Lang and coworkers have successfully isolated a series of heterometallic clusters $[Hg_6Ag_4(TePh)_{16}]$, $[Hg_6Ag_4Te(TePh)_{14}]_n$ and $[Hg_8Te(TePh)_{12}Cl_4]Q$ $[Q = \{Co(DMF)_6\}^{2^+}, \{Ni(DMF)_6\}^{2^+}]$, which were obtained by the reaction of $[Hg(TePh)_2]$ with M' salts (M' = Ag^I, Co^{II}, Ni^{II}) and stabilized by different phosphines (PPh3 or PMe2Ph), in dimethylformamide (DMF) [17,19]. The analogous $[Cd(ER)_2]$ (E = S, Se; R = alkyl or aryl) can act as single-source compounds to yield Cd-E clusters via a 'bottom up' strategy, however, the propensity of the solid state structures of those compounds shows to possess a three-dimensional nonmolecular polyadamantoid or superdiamondoid network. In fact, crystalline products [Cd(EPh)₂] (E = S, Se) are inorganic polymers consisting of [Cd₄(EPh)₆] adamantane-like cages [20], which was further supported by formation of tetranuclear adamantanoid-type clusters $[Cd_4(SePh)_x(PPh_3)X]_n$ (X = Cl, Br; x = 6, 7) obtained from the reaction of [Cd(SePh)₂] with CdX₂ in the presence of PPh₃ [21]. In this connection, we are realizing the coordination behavior of mononuclear cadmium(II) complexes $[Cd(EPh)_{d}]^{2-}$ (E = S, Se) that contain the distorted tetrahedral CdE₄ chromophore, which may be reasonably speculated to coordinate to coinage-metals via sulfur atoms of thiophenolates and selenium atoms of selenophenolates. Thus, the ability of homoleptic $[Cd(EPh)_4]^{2-}$ anions as metallo-ligands towards coinage-metals is due to the electron-rich sulfur and selenium affinity and the deviations of the E-Cd-E angles from tetrahedral symmetry [22]. In order to prepare heterobimetallic Cd(Hg)/Cu(Ag)/S(Se) complexes, we selected homoleptically neutral $[Hg(EPh)_2]$ and anionic $[Cd(EPh)_4]^{2-}$ (E = S, Se) complexes as precursors to coordinate with the $[M(PPh_3)_2Q]$ (M = Cu, Ag; $Q = Cl^{-}, NO_{3}^{-}$) species which then gave a series of new neutral bimetallic complexes. Their structural characterizations and spectroscopic properties are described and the nonlinear optical properties (NLO) of two novel heptanuclear Cd/Ag/S(Se) complexes were also investigated in this paper.

2. Experimental

2.1. Materials and measurements

All syntheses were performed in oven-dried glassware under a purified nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by conventional methods and degassed prior to use. [Hg(SPh)₂] [23], [Hg(SePh)₂] [18c], [Me₄N]₂[Cd(SPh)₄] [22], [Me₄N]₂[Cd(SePh)₄] [22], [Cu(PPh₃)₂Cl] [24], [Ag(PPh₃)₂Cl] [24], [Cu(PPh₃)₂NO₃] [25], and [Ag(PPh₃)₂NO₃] [25] were prepared by the literature methods. PhSH, PhSeSePh, and PPh₃ were purchased from Alfa Aesar and used without further purification. All

elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyzer. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Infrared spectra were recorded on a Digilab FTS-40 spectrophotometer with use of pressed KBr pellets. Positive FAB mass spectra were recorded on a Finnigan TSQ 7000 spectrometer. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 121.5 MHz for ¹H and ³¹P, respectively, and chemical shift (δ , ppm) were reported with reference to SiMe₄ (¹H) and H₃PO₄ (³¹P).

2.2. Preparation of $[Hg(\mu-SPh)_2\{CuCl(PPh_3)_2\}]$ ·2dmf (**1**·2dmf)

To a solution of [Hg(SPh)₂] (105 mg, 0.25 mmol) in MeCN (10 mL) was added [Cu(PPh₃)₂Cl] (312 mg, 0.50 mmol) in CH₂Cl₂ (10 mL) with stirring. The mixture was stirred at room temperature for 45 min. Fine white solids were gradually observed. The precipitates were collected by suction filtration and washed twice with 10 mL portions of diethyl ether. White air-stable solids were further recrystallized from DMF/MeCN to give colorless block crystals of **1** 2dmf in three days. Yield: 287 mg (64%). Anal. Calc. for $C_{84}H_{70}$ Cl₂P₄S₂HgCu₂·2(C₃H₇NO): C, 59.6; H, 4.67; N, 1.55. Found: C, 59.5; H, 4.62; N, 1.53%. UV–Vis (DMF, λ_{max}/nm , $10^{-3} \epsilon/M^{-1} cm^{-1}$): 263 (9.6), 346 (1.4). IR (KBr disc, cm^{-1}): v(C-H) 3055 (m), v(C=O)1667 (s), v(P-C) 1081 (s), v(C-S) 691 (s), v(Cu-P) 448 (w) and 439 (w). ¹H NMR (DMSO- d_6 , ppm): δ 2.98 (s, 6H, Me_2 NCHO), δ 2.86 (s, 6H, Me₂NCHO), 7.15-7.54 (m, 70H, Ph), 8.03 (s, 2H, CHO). ³¹P NMR (DMSO- d_6 , ppm): δ -3.78 (s). MS (FAB): m/z 1666 (M⁺), 1631 (M⁺-Cl), 1596 (M⁺-2Cl).

2.3. Preparation of $[Hg(\mu-SePh)_2\{CuCl(PPh_3)_2\}_2]\cdot 2dmf(\mathbf{2}\cdot 2dmf)$

The method was similar to that used for 1·2dmf, employing [Hg(SePh)₂] (128 mg, 0.25 mmol) in instead of [Hg(SPh)₂]. Colorless blocks were obtained. Yield: 243 mg (51%). *Anal.* Calc. for C₈₄ H₇₀Cl₂P₄Se₂HgCu₂·2(C₃H₇NO): C, 56.7; H, 4.44; N, 1.47. Found: C, 56.2; H, 4.41; N, 1.42%. UV–Vis (DMF, λ_{max}/nm , 10⁻³ ε/M^{-1} cm⁻¹): 263 (9.6), 359 (1.4), 368 (sh). IR (KBr disc, cm⁻¹): ν (C–H) 3053 (m), ν (C=O) 1665 (s), ν (P–C) 1081 (s), ν (C–Se) 663 (s), ν (Cu–P) 445 (w) and 432 (w). ¹H NMR (DMSO-*d*₆, ppm): δ 2.96 (s, 6H, *Me*₂NCHO), 2.84 (s, 6H, *Me*₂NCHO), 7.13–7.57 (m, 70H, *Ph*), 8.01 (s, 2H, *CHO*). ³¹P NMR (DMSO-*d*₆, ppm): δ –3.21 (s). MS (FAB): *m/z* 1760 (M⁺), 1725 (M⁺–Cl), 1690 (M⁺–2Cl).

2.4. Preparation of $[Hg(SPh)(\mu-SPh)(\mu-Cl)Ag(PPh_3)_2] \cdot dmf(\mathbf{3} \cdot dmf)$

The method was similar to that used for **1**·2dmf, employing [Ag(PPh₃)₂Cl] (334 mg, 0.50 mmol) in instead of [Cu(PPh₃)₂Cl]. Colorless blocks were obtained. Yield: 169 mg (58%). *Anal.* Calc. for C₄₈H₄₀ClP₂S₂HgAg·(C₃H₇NO): C, 52.8; H, 4.08; N, 1.21. Found: C, 52.5; H, 4.07; N, 1.19%. UV–Vis (DMF, λ_{max}/nm , 10⁻³ ε/M^{-1} cm⁻¹): 267 (10.2), 349 (1.6). IR (KBr disc, cm⁻¹): ν (C–H) 3051 (m), ν (C=O) 1663 (s), ν (P–C) 1084 (s), ν (C–S) 692 (s), ν (Ag–P) 420 (w) and 412 (w). ¹H NMR (DMSO-*d*₆, ppm): δ 2.99 (s, 3H, *Me*₂NCHO), 2.85 (s, 3H, *Me*₂NCHO), 7.17–7.62 (m, 35H, *Ph*), 8.02 (s, 1H, CHO). ³¹P NMR (DMSO-*d*₆, ppm): δ –3.94 (s). MS (FAB): *m/z* 1086 (M⁺), 1051 (M⁺–Cl).

2.5. Preparation of $[Hg(SePh)(\mu-SePh)(\mu-Cl)Ag(PPh_3)_2] \cdot dmf(\mathbf{4} \cdot dmf)$

The method was similar to that used for **3**-dmf, employing [Hg(SePh)₂] (128 mg, 0.25 mmol) in instead of [Hg(SPh)₂]. Colorless blocks were obtained. Yield: 169 mg (58%). *Anal.* Calc. for C₄₈H₄₀ClP₂Se₂HgAg·(C₃H₇NO): C, 48.9; H, 3.78; N, 1.12. Found: C, 48.4; H, 3.73; N, 1.11%. UV–Vis (DMF, λ_{max}/nm , 10⁻³ ε/M^{-1} cm⁻¹): 269 (10.7), 353 (1.8). IR (KBr disc, cm⁻¹): ν (C–H) 3054 (m), ν (C=O) 1665 (s), ν (P–C) 1081 (s), ν (C–Se) 665 (s), ν (Ag–P) 422 (w) and 411

(w). ¹H NMR (DMSO- d_6 , ppm): δ 2.98 (s, 3H, Me_2 NCHO), 2.88 (s, 3H, Me_2 NCHO), 7.15–7.67 (m, 35H, Ph), 8.05 (s, 1H, CHO). ³¹P NMR (DMSO- d_6 , ppm): δ –3.48 (s). MS (FAB): m/z 1080 (M⁺), 1145 (M⁺–Cl).

2.6. Preparation of $[Cd(\mu - SPh)_4 \{Cu(PPh_3)_2\}_2]$ (5)

To a solution of $[Me_4N]_2[Cd(SPh)_4]$ (140 mg, 0.20 mmol) in MeCN (10 mL) was added $[Cu(PPh_3)_2NO_3]$ (260 mg, 0.40 mmol) in CH₂Cl₂ (10 mL) with stirring. The mixture was stirred at room temperature for 30 min. Fine white solids were observed. The precipitates were collected by suction filtration and washed twice with 10 mL portions of diethyl ether. White air-stable solids were obtained and further recrystallized from DMF/MeCN to give colorless block crystals of **5** after 3 days. Yield: 225 mg (65%). Anal. Calc. for C₉₆H₈₀P₄S₄CdCu₂: C, 66.8; H, 4.67. Found: C, 66.2; H, 4.64%. UV–Vis (DMF, λ_{max}/nm , 10⁻³ ε/M^{-1} cm⁻¹): 268 (11.4), 343 (1.9). IR (KBr disc, cm⁻¹): v(P-C) 1079 (s), v(C-S) 694 (s), v(Cu-P) 446 (w) and 435 (w). ¹H NMR (DMSO- d_6 , ppm): δ 7.20–7.56 (m, 80H, *Ph*). ³¹P NMR (DMSO- d_6 , ppm): δ -3.71 (s). MS (FAB): m/z 1725 (M⁺).

2.7. Preparation of $[Cd(\mu-SePh)_4[Cu(PPh_3)_2]_2]$ (6)

The method was similar to that used for **5**, employing $[Me_4N][Cd(SePh)_4]$ (177 mg, 0.20 mmol) in instead of $[Me_4N]_2[Cd(SPh)_4]$. Colorless blocks were obtained. Yield: 207 mg (54%). *Anal.* Calc. for $C_{96}H_{80}P_4Se_4CdCu_2$: C, 60.3; H, 4.22. Found: C, 60.1; H, 4.18%. UV–Vis (DMF, λ_{max}/nm , $10^{-3} \varepsilon/M^{-1} cm^{-1}$): 266 (9.7), 355 (1.2), 367 (sh). IR (KBr disc, cm⁻¹): ν (P–C) 1086 (s), ν (C–Se) 662 (s), ν (Cu–P) 443 (w) and 436 (w). ¹H NMR (DMSO- d_6 , ppm): δ 7.21–7.54 (m, 80H, *Ph*). ³¹P NMR (DMSO- d_6 , ppm): δ –3.68 (s). MS (FAB): m/z 1913 (M⁺).

2.8. Preparation of $[Cd(\mu-SPh)_4[Ag(PPh_3)_2]_2]$ (7)

The method was similar to that used for **5**, employing $[Ag(PPh_3)_2NO_3]$ (278 mg, 0.40 mmol) in instead of $[Cu(PPh_3)_2NO_3]$. Colorless blocks were obtained. Yield: 178 mg (49%). *Anal.* Calc. for $C_{96}H_{80}P_4S_4CdAg_2$: C, 63.6; H, 4.44. Found: C, 63.2; H, 4.43%. UV–Vis (DMF, λ_{max}/nm , 10⁻³ ε/M^{-1} cm⁻¹): 261 (10.3), 345 (1.6). IR (KBr disc, cm⁻¹): v(P-C) 1084 (s), v(C-S) 691 (s), v(Ag-P) 423 (w) and 415 (w). ¹H NMR (DMSO- d_6 , ppm): δ 7.24–7.60 (m, 80H, *Ph*). ³¹P NMR (DMSO- d_6 , ppm): δ –4.85 (s). MS (FAB): m/z 1814 (M⁺).

2.9. Preparation of $[Cd_3(\mu$ -SPh)₆ $(\mu_3$ -SPh)₄(AgPPh₃)₄].0.5dmf (**8**.0.5dmf)

To a solution of $[Me_4N]_2[Cd(SPh)_4]$ (280 mg, 0.40 mmol) in MeCN (15 mL) was added [Ag(PPh₃)₂NO₃] (278 mg, 0.40 mmol) in CH₂Cl₂ (15 mL) with stirring. The mixture was stirred at room temperature for 45 min. Fine white solids gradually formed and then suspension solution was stirred for additional 2 h. The precipitates were collected by suction filtration and washed twice with 10 mL portions of diethyl ether. White air-stable solids were further recrystallized from DMF/MeCN to give colorless block crystals of 8.0.5dmf in a week. Yield: 153 mg (38%). Anal. Calc. for $C_{132}H_{110}P_4S_{10}-Cd_3Ag_4\cdot 0.5(C_3H_7NO):\ C,\ 54.4;\ H,\ 3.88;\ N,\ 0.24.$ Found: C, 54.2; H, 3.83; N, 0.23%. UV–Vis (DMF, λ_{max}/nm , $10^{-3} \epsilon/$ M⁻¹ cm⁻¹): 264 (11.4), 350 (2.1), 361 (sh). IR (KBr disc, cm⁻¹): v(C-H) 3051 (m), v(C=O) 1669 (s), v(P-C) 1081 (s), v(C-S) 694 (s), v(Ag-P) 419 (w) and 411 (w). ¹H NMR (DMSO- d_6 , ppm): δ 2.96 (s, 1.5H, Me₂NCHO), 7.12-7.64 (m, 110H, Ph), 8.01 (s, 0.5H, CHO). ³¹P NMR (DMSO- d_6 , ppm): δ –4.86 (s). MS (FAB): m/z 2909 (M^{+}) , 2647 $(M^{+}-PPh_{3})$, 2385 $(M^{+}-2PPh_{3})$, 2123 $(M^{+}-3PPh_{3})$, $1861 (M^+ - 4PPh_3).$

2.10. Preparation of $[Cd_3(\mu$ -SePh)₆ $(\mu_3$ -SePh)₄ $(AgPPh_3)_4]$ ·0.5dmf (**9**·0.5dmf)

The method was similar to that used for **8**, employing $[Me_4N]_2[Cd(SePh)_4]$ (354 mg, 0.40 mmol) in instead of $[Me_4N]_2$ [Cd(SPh)_4]. Colorless blocks were obtained. Yield: 178 mg (49%). *Anal.* Calc. for C₁₃₂H₁₁₀P₄Se₁₀Cd₃Ag₄·0.5(C₃H₇NO): C, 47.0; H, 3.35; N, 0.20. Found: C, 46.4; H, 3.31; N, 0.18%. UV–Vis (DMF, $\lambda_{max}/nm, 10^{-3} \varepsilon/M^{-1} \text{ cm}^{-1}$): 261 (10.1), 352 (2.5), 368 (sh). IR (KBr disc, cm⁻¹): v(C–H) 3053 (m), v(C=O) 1666 (s), v(P–C) 1084 (s), v(C–Se) 664 (s), v(Ag–P) 421 (w) and 413 (w). ¹H NMR (DMSO-*d*₆, ppm): δ 2.98 (s, 1.5H, *Me*₂NCHO), 7.11–7.57 (m, 110H, *Ph*), 8.03 (s, 0.5H, *CHO*). ³¹P NMR (DMSO-*d*₆, ppm): δ –4.42 (s). MS (FAB): *m/z* 3378 (M⁺), 3116 (M⁺–PPh₃), 2854 (M⁺–2PPh₃), 2592 (M⁺–3PPh₃), 2330 (M⁺–4PPh₃).

2.11. X-ray crystallography

Crystallographic data and experimental details for $[Hg(\mu-SPh)_2]$ {CuCl(PPh₃)₂}·2dmf (1·2dmf), [Hg(μ -SePh)₂{CuCl(PPh₃)₂}·2dmf $(2 \cdot 2 dmf)$, and $[Hg(SPh)(\mu-SPh)(\mu-Cl)Ag(PPh_3)_2] \cdot dmf$ $(3 \cdot dmf)$ in Table 1 and those for $[Cd(\mu-SPh)_4[Cu(PPh_3)_2]]$ (5), $[Cd(\mu-SePh)_4]$ $\{Cu(PPh_3)_2\}$ (6), $[Cd(\mu-SPh)_4[Ag-(PPh_3)_2]$ (7), $[Cd_3(\mu-SPh)_6(\mu_3-$ SPh)₄(AgPPh₃)₄] \cdot 0.5dmf (**8** \cdot 0.5dmf), and [Cd₃(μ -SePh)₆(μ ₃-SePh)₄ $(AgPPh_3)_4$ 0.5dmf (9.0.5dmf) in Table 2 are summarized. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromated MoK α radiation (λ = 0.71073 Å) at 293(2) K. The collected frames were processed with the software SAINT [26]. The data was corrected for absorption using the program sadabs [27]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [28]. The metal, phosphorous, sulfur, selenium, and chloride atoms in the complexes were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3} -H = 0.96 and C_{sp2} -H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon or nitrogen atoms before the final cycle of leastsquares refinement. The solvent molecules in 3.dmf and 7.0.5dmf were isotropically refined without hydrogen atoms due to disorder. The phenyl rings of ligands in complexes 5-7 were refined with bond-length restraints. The Flack parameter values of 0.00(5), 0.01(2) and -0.04(13) for 5, 6 and 7, respectively, indicate that the correct enantiomorphs have been selected in the structures. The largest peak in the final difference map had height of 3.839 e $Å^{-3}$ in **4** is in the vicinity of the Hg atom. Atomic coordinates, complete bond distances and angles, and anisotropic thermal parameters of all non-hydrogen atoms for all three clusters are available as Supplementary materials.

2.12. Optical measurements

A DMF solution of 1.48×10^{-4} mol dm⁻³ of **8** or **9** was placed in a 1 mm quartz cuvette for optical measurements. The optical limiting characteristics along with nonlinear absorption and refraction was investigated with a linearly polarized laser light (λ = 532 nm, pulse width = 7 ns) generated from a Q-switched and frequencydoubled Nd:YAG laser. The spatial profiles of the optical pulses were nearly GAUSSIAN. The laser beam was focused with a 25-cm focal-length focusing mirror. The radius of the laser beam waist was measured to be 30 ± 5 µm (half-width at $1/e^2$ maximum in irradiance). The incident and transmitted pulse energy were measured simultaneously by two Laser Precision detectors (RjP-735 energy probes) communicating to a computer *via* an IEEE interface [29,30], while the incident pulse energy was varied by a Newport Com. Attenuator. The interval between the laser pulses was chosen

Tabla	1
Table	

 $Crystallgraphic data and experimental details for [Hg(\mu-SPh)_2{CuCl(PPh_3)_2}_2]-2dmf (1-2dmf), [Hg(\mu-SePh)_2{CuCl(PPh_3)_2}_2]-2dmf (2-2dmf), and [Hg(SPh)(\mu-Cl)Ag(PPh_3)_2]-dmf (3-dmf).$

	1.2dmf	2 ·2dmf	3 ∙dmf
Formula	$C_{90}H_{84}N_2O_2Cl_2P_4S_2HgCu_2$	C ₉₀ H ₈₄ N ₂ O ₂ Cl ₂ P ₄ Se ₂ HgCu ₂	C ₅₁ H ₄₇ NOClP ₂ S ₂ HgAg
Formula weight	1812.16	1905.96	1159.87
Unit cell dimensions			
a (Å)	10.8500(4)	10.9161(2)	10.8157(2)
b (Å)	12.9693(4)	12.9737(3)	13.3522(2)
c (Å)	14.9390(5)	14.9262(3)	17.8945(3)
α (°)	78.964(2)	79.535(1)	111.674(1)
β (°)	82.705(2)	82.877(1)	90.566(1)
γ (°)	88.327(2)	88.893(1)	95.747(1)
V (Å ³)	2046.57(12)	7062.67(7)	2386.36(7)
Ζ	1	1	2
Crystal system	triclinic	triclinic	triclinic
Space group	ΡĪ	ΡĪ	ΡĪ
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.470	1.534	1.614
Number of reflections	37974	38441	44650
Number of independent reflections	9397	9451	10957
$[I > 2.0\sigma(I)]$	$R_1 = 0.0213, wR_2 = 0.0529$	$R_1 = 0.0222, wR_2 = 0.0523$	$R_1 = 0.0290, wR_2 = 0.0757$
All data	$R_1 = R1, 0.0257, wR_2 = 0.0551$	$R_1 = 0.0296, wR_2 = 0.0554$	$R_1 = 0.0358$, $wR_2 = 0.0792$

Table 2

Crystallgraphic data and experimental details for $[Cd(\mu-SPh)_4(Cu(PPh_3)_2)_2]$ (**5**), $[Cd(\mu-SPh)_4(Cu(PPh_3)_2)_2]$ (**6**), $[Cd(\mu-SPh)_4(Ag(PPh_3)_2)_2]$ (**7**), $[Cd_3(\mu-SPh)_6(\mu_3-SPh)_4(AgPPh_3)_4]$ -0.5dmf (**8**-0.5dmf), and $[Cd_3(\mu-SPh)_6(\mu_3-SPh)_4(AgPPh_3)_4]$ -0.5dmf (**9**-0.5dmf).

	5	6	7	8 ·0.5dmf	9 ·0.5dmf
Formula Formula weigh Unit cell dimensions	C ₉₆ H ₈₀ P ₄ S ₄ CdCu ₂ 1725.20	C ₉₆ H ₈₀ P ₄ Se ₄ CdCu ₂ 1912.80	$C_{96}H_{80}P_4S_4CdAg_2$ 1813.86	$\begin{array}{c} C_{133.5}H_{113.5}N_{0.5}O_{0.5}P_4S_{10}Cd_3Ag_4\\ 2945.91\end{array}$	$\begin{array}{c} C_{133.5}H_{113.5}N_{0.5}O_{0.5}P_{4}Se_{10}Cd_{3}Ag_{4}\\ 3414.91 \end{array}$
a (Å) b (Å)	15.1926(2)	15.2747(3)	15.3743(2)	15.7185(3) 17.2345(3)	15.8257(6) 17.3414(7)
$c(\mathbf{\hat{A}}) \\ \alpha(\mathbf{\hat{o}}) \\ \beta(\mathbf{\hat{o}}) $	18.1694(7)	18.2172(8)	18.2442(6)	27.4075(7) 98.770(1) 94.265(1)	27.5999(11) 77.186(2) 85.709(2)
γ (°) V (Å ³) Z	4193.77(18) 2	4250.4(2) 2	4312.37(16) 2	117.089(1) 6445.1(2) 2	63.513(2) 6608.1(5) 2
Crystal system	tetragonal	tetragonal	tetragonal	triclinic	triclinic
Space group	$P-42_1/c$	$P-42_1/c$	$P-42_1/c$	ΡĪ	PĪ
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.366	1.495	1.397	1.518	1.716
Number of reflections Number of independent reflections	15213 2649	15569 2613	16139 2731	121007 29419	123 031 30 206
$[l > 2.0\sigma(l)]$	$R_1 = 0.0515,$ $wR_2 = 0.0986$	$R_1 = 0.0367,$ $wR_2 = 0.0619$	$R_1 = 0.0464,$ $wR_2 = 0.1235$	$R_1 = 0.0420, \ wR_2 = 0.0944$	$R_1 = 0.0745, wR_2 = 0.1564$
All data	$R_1 = 0.1022,$ $wR_2 = 0.1168$	$R_1 = 0.0546,$ $wR_2 = 0.0835$	$R_1 = 0.0944,$ $wR_2 = 0.1651$	$R_1 = 0.0766, wR_2 = 0.1097$	$R_1 = 0.0939, wR_2 = 0.1785$
Flack value	0.00(5)	0.01(2)	-0.04(13)	-	-

to be 10 s to avoid the influence of thermal and long-term effects. The details of the set-up can be found elsewhere [31,32].

3. Results and discussion

3.1. Syntheses and reactions

[Hg(EPh)₂] (E = S, Se, Te) as the starting materials can generate new compounds such as the binary and ternary clusters [17–19]. For example, the sulfide and selenide derivatives react with equimolar amounts of HgCl₂ in pyridine (py) to give the metallacyclic compounds [Hg₄Cl₄(μ -ER)₄(py)_n] (E = S, R = ^tBu, n = 2; E = Se, R = Et, n = 4; E = Se, R = ^tBu, n = 4) [18e,f]. Similarly, the reaction of [Hg(TePh)₂] with HgBr₂ in pyridine produces the large cluster [Hg₆(μ -Br₂)Br₂(μ -TePh)₈(py)₂] with six-membered rings [Hg₃(μ -TePh)₃] [17b]. Interestedly, the reaction of [Hg(TePh)₂] with [Ag(L)_nX] (X = Cl⁻, NO₃⁻; L = PMePh₂, PPh₃, DMF) in a ratio of 1:2 at room temperature affords the cluster [Hg₆Ag₄(TePh)₁₆] with incorporation of Ag(1) into the cluster structure [17a]. Treatment of $[Hg(EPh)_2]$ with 2 equivalents of $[Cu(PPh_3)_2Cl]$ in $CH_2Cl_2/MeCN$ resulted in formation of the white precipitates which were recrystallized from DMF/MeCN to afford the trinuclear Hg/Cu/S(Se) compounds $[Hg(\mu-EPh)_2[CuCl(PPh_3)_2]_2]$ (E = S **1**, Se **2**) [see Eq. (1)].

$$\begin{split} [Hg(EPh)_2] + 2[Cu(PPh_3)_2Cl] \rightarrow & [Hg(\mu\text{-}EPh)_2\{CuCl(PPh_3)_2\}_2] \\ & E = S\mathbf{1} \\ & Se\mathbf{2} \end{split}$$

(1)

As expected, $[Hg(EPh)_2]$ as a precursor binds to $[Cu(PPh_3)_2Cl]$ species *via* the sulfur or selenium atoms of the PhE⁻ moieties whilst the coordination geometry of the central mercury atom was kept. Reaction of $[Hg(EPh)_2]$ with $[Cu(PPh_3)_2NO_3]$ in $CH_2Cl_2/$ MeCN also gave the large white precipitates intermediately, indicative of formation of polynuclear hetero-metallic complexes. Unfortunately, it is very difficult to recrystallize these complexes existing insoluble precipitates. A similar reaction of $[Hg(EPh)_2]$ with $[Ag(PPh_3)_2Cl]$ gave rise to isolation of the dinuclear compounds $[Hg(SePh)(\mu-SePh)(\mu-Cl)Ag(PPh_3)_2]$ (E = S **3**, Se **4**) [see Eq. (2)] in which the coordination geometry of the mercury atom changes from two to three coordinate due to the chloride of the $[Ag(PPh_3)_2CI]$ specie involved in coordination with the mercury atom. It is very difficult to recrystallize the white precipitates formed a quick mixture of $[Hg(EPh_2)_2]$ and $[Ag(PPh_3)_2NO_3]$, suggestive of the polynuclear heterometallic Hg/Ag/S(Se) clusters probably existing in insoluble precipitates.

$$[\text{Hg}(\text{EPh})_2] + [\text{Ag}(\text{PPh}_3)_2\text{CI}] \rightarrow [\text{Hg}(\text{EPh})(\mu\text{-EPh})(\mu\text{-CI})\text{Ag}(\text{PPh}_3)_2]$$
$$E = S \mathbf{3}$$
Se **4**

 $Cd_3(\mu_3$ -EPh) core. Subsequently, coordination of four $[Ag(PPh_3)]^+$ fragments with the $[Cd_3(\mu_3$ -EPh)(EPh)_9]^{4-} anion *via* sulfur and selenium atoms of the peripheral thiophenolates and selenophenolates gave the heptanuclear complexes **8** and **9**, respectively [see Eq. (4)]. Complexes **1–9** are air-stable in both the solid-state and solution, and soluble in very polar solvents such as dimethyl sulfoxide (DMSO) and dimethylformide (DMF) and slightly soluble in CH₂Cl₂.

$$[Cd(EPh)_{4}]^{2-} + 2[M(PPh_{3})_{2}]^{+} \rightarrow [Cd(\mu-EPh)_{4}\{M(PPh_{3})_{2}\}_{2}]$$

$$E = S \quad M = Cu \mathbf{5}$$

$$Se \quad Cu \mathbf{6}$$

$$S \quad Ag \mathbf{7}$$

$$(3)$$



(4)

The analogous $[Cd(EPh)_2]$ has been used to react with CdX_2 (X = Cl, Br) in the presence of PPh₃ to give the tetranuclear adamantanoid-type clusters $[Cd_4(SePh)_x(PPh_3)X]_n$ (X = Cl, Br; x = 6, 7) [21], however, no heterometallic compound with [Cd(EPh)₂] as a precursor has been reported yet. Nevertheless, attempts to synthesize the heterometallic Cd/Cu(Ag)/S(Se) complexes by reacting $[Cd(EPh)_2]$ with $[M(PPh_3)_2NO_3]$ (M = Cu, Ag) species were unsuccessful. The possible reason may be due to the crystalline product [Cd(EPh)₂] itself being inorganic polymer with the typical [Cd₄(EPh)₆] adamantane-like cage [20]. To isolate the heterometallic Cd/Cu(Ag)/S(Se) compounds successfully, the homoleptic tetrahedral species $[Cd(EPh)_4]^{2-}$ (E = S, Se) were used to react with 2 equivalents of [Cu(PPh₃)₂NO₃]. As expected, two [Cu(PPh₃)₂]⁺ fragments chelate to the opposite edges of a tetrahedral $[Cd(EPh)_4]^{2-}$ moiety via the sulfur or selenium atoms of the PhE⁻ species, resulting in formation of the neutral linear trinuclear complexes $[Cd(\mu-EPh)_4]$ ${Cu(PPh_3)_2}_2$ (E = S 5, Se 6). A similar reaction of $[Me_4N]_2$ [Cd(SPh)₄] with 2 equivalents of [Ag(PPh₃)₂NO₃] gave an analogous trinuclear complex $[Cd(\mu-SPh)_4[Ag(PPh_3)_2]_2]$ (7) [see Eq. (3)], whereas the reaction of [Me₄N]₂[Cd(EPh)₄] with an equivalent amount of [Ag(PPh₃)₂NO₃] in the similar conditions surprisingly afforded the neutral heptanuclear complexes $[Cd_3(\mu-EPh)_6(\mu_3-EPh)_4(AgPPh_3)_4]$ (E = S 8, Se 9). These are the first examples of high nuclearity cadmium-silver complexes with thiolate and selenolate ligands. In the present system, it seems that the self-assembly of three $[Cd(EPh)_4]^{2-}$ anions, under the displacement of two PhE⁻ species, constructs a new $[Cd_3(\mu_3-EPh)(EPh)_9]^{4-}$ anion with a stable

3.2. Spectroscopic properties

The characteristic bands for the thiophenolato complexes 1.2dmf, 3.dmf, 5, 7, and 9.0.5dmf were found at 1079-1084 and 691–694 cm⁻¹ in the IR spectra, whereas the corresponding bands for the selenophenolato complexes 2.2dmf, 4.dmf, 6 and 8.0.5dmf were observed at 1081–1086 and 662–665 cm^{-1} in the IR spectra. The respective former bands are assignable to the mode of phenyl ring coupled with C-S or C-Se and the respective latter bands are due to C-S or C-Se bonds. The Cu-P stretching modes of the complexes can be identified as weakly sharp peaks in the range of 435–448 cm⁻¹ in the spectra of complexes **1**·2dmf, **2**·2dmf, **5** and 6, while the Ag–P stretching modes of the complexes can be identified as weakly sharp peaks in the range of 413-425 cm⁻¹ in the spectra of complexes 3.dmf, 4.dmf, 7, 8.0.5dmf, and 9.0.5dmf. The metal-sulfur or -selenium stretching modes of the thio- and seleno-metallic complexes can be identified since they appear as weaker bands in the low-wavenumber region below 400 cm⁻¹ in the IR spectra. The weak bridging M-S and M-Se vibrations are observed in the ranges of 310-325 and 285-300 cm⁻¹, respectively, in the IR spectra of the above complexes. The broad bands at ca. 1665 cm⁻¹ for v(C=0) in the IR spectra indicated the presences of the lattice dimethylformides in the crystalline products 1 2dmf, 2 2dmf, 3 dmf, 4 dmf, 8 0.5 dmf, and 9 0.5 dmf. The main features in the electronic absorption spectra in DMF solution at room temperature are structured bands at 261–269 nm, to which aromatic $\pi \rightarrow \pi^*$ transitions make the major contribution, and low energy absorption bands at 342–359 nm which are assigned to sulfur or selenium-tocopper or silver charge transfer [33].

The ¹H NMR spectra for all complexes are quite similar to those of the free ligands and solvent molecules, indicating that all complexes are diamagnetic. The ³¹P{¹H} NMR resonances for complexes **1–9** show a single peak downfield from that of the free PPh₃ ligand, which may be ascribed to the different phosphorus atoms in each complex with the same coordination environment. The ³¹P resonances slightly shift upfield by the comparison of copper complexes with silver complexes with same structural types. The FAB⁺ mass spectra of compounds **1–9** exhibit molecular ions corresponding to M⁺, (M⁺–halides) and (M⁺–PPh₃) with the characteristic isotopic distribution patterns.

3.3. Crystal structures

The crystal structures of 1.2dmf, 2.2dmf, 3.dmf, 5, 6, 7, 8.0.5dmf, and 9.0.5dmf have been established by X-ray crystallography. Selected structural parameters for 1.2dmf, 2.2dmf, 3.dmf, 5, 6 and 7 are complied in Table S1 for comparison, and selected bond lengths and angles for 8.0.5dmf and 9.0.5dmf are given in Tables S2 and S3, respectively. The asymmetric unit in the crystal structures of 1.2dmf and 2.2dmf consists of one neutral complex and two solvent molecules. Molecular structures of the neutral complexes 1 and 2 possess a symmetric center through the mercury atom (see Fig. 1). Both structures can be described as constituted by [Hg(EPh)₂] units symmetrically ligated by two copper atoms via the sulfur atoms of the PhS⁻ ligands in **1** and the selenium atoms of the PhSe⁻ ligands in 2, forming the new trinuclear heterometallic complexes. The coordination spheres of the mercury atoms in both structures are kept with linearity and mercury atoms are coordinated by two sulfur atoms in 1.2 dmf (Hg–S = 2.3699(4)Å) and two selenium atoms in $2 \cdot 2 \text{dmf}$ (Hg–Se = 2.4740(2) Å) related by the twofold axes. Both S-Hg-S and Se-Hg-Se angles are 180.0°. The coordination geometry of the copper atom in **1**.2dmf or **2**-2dmf is highly distorted tetrahedral with the angles around copper atom ranging from 89.27(2)° to 122.63(2)° in **1** 2dmf and from $89.30(2)^{\circ}$ to $122.93(2)^{\circ}$ in **2**·2dmf. The Cu–S bond length and the Hg–S–Cu angle in 1.2 dmf are 2.4341(5) Å and $99.14(2)^\circ$, respectively, while the Cu-Se bond length and the Hg-Se-Cu angle in 2.2dmf are 2.5450(3) Å and 95.81(1)°, respectively.

Fig. 2 shows a perspective view of complex **3**. The asymmetric unit of the crystal structure consists of one neutral complex and one solvent molecule in the lattice. Compound **3** is a dinuclear heterometallic complex with a non-planar HgSAgCl four-membered ring. In the ring, the Hg(1)–S(1) and Hg(1)–Cl(1) bond lengths are 2.3382(10) and 2.8316(8) Å, respectively, accordingly, the Ag(1)–S(1) and Ag(1)–Cl(1) bond lengths are 2.7030(8) and



Fig. 1. Molecular structure of $[Hg(\mu-SePh)_2\{CuCl(PPh_3)_2\}_2]$ (**2**), showing 30% thermal ellipsoids. The carbon atoms are represented as sticks for clarity.



Fig. 2. Molecular structure of $[Hg(SPh)(\mu$ -SPh)(μ -Cl)Ag(PPh₃)₂] (**3**), showing 30% thermal ellipsoids. The carbon atoms are represented as sticks for clarity.

2.6079(8) Å, respectively. There is an obvious deviation among four angles in the ring $[S(2)-Hg(1)-Cl(1) = 85.72(2)^{\circ}, S(2)-Ag(1) Cl(1) = 84.61(2)^{\circ}$, $Hg(1)-S(2)-Ag(1) = 89.71(2)^{\circ}$ and Hg(1)-Cl(1)- $Ag(1) = 83.00(2)^{\circ}$]. The coordination about mercury atom is slightly distorted T-shape, the three sites being occupied by one bridging sulfur atom, one bridging chloride atom and one terminal sulfur atom. The terminal Hg-S bond length of 2.3382(10) Å is obviously shorter than the bridging Hg-S bond length of 2.4042(8) Å. The S(1)–Hg(1)–S(2) angle is 162.87(3)°, which obviously deviates from the flat angle in [Hg(SPh)₂] due to the coordination of chloride atom to the mercury atom. The Cl-Hg-S angle involving the terminal PhS⁻ moiety (106.97(4)°) is significantly bigger than that involving the bridging PhS^- moiety (85.72(2)°). The coordination around the silver atom is a distorted tetrahedron, main distortions are due to the Cl(1)-Ag(1)-S(2) and P(1)-Ag(1)-P(2) angles of 84.61(2)° and 125.03(3)°. respectively. The average Ag–P bond length of 2.4524(7) Å in **3** dmf is in the expected range. The two metal atoms are 3.608(2) Å apart and are thus nonbonded.

Heterobimetallic Cd/Cu/S(Se) complexes **5** and **6** are isostructural with heterobimetallic Cd/Ag/S complex **7**. Figs. 3 and 4 show perspective views of complexes **6** and **7**, respectively. Quite few structurally characterized heterobimetallic complexes containing the $[Cd(EPh)_4]^{2-}$ (E = S, Se) anions and coinage metals have been synthesized to date [34]. Related coinage metal heterometalates $[(\mu-WSe_4)\{M(PMe_2Ph)_2\}_2]$ (M = Cu, Ag, Au) with symmetric



Fig. 3. Molecular structure of $[Cd(\mu$ -SePh)₄ $\{Cu(PPh_3)_2\}_2]$ (5), showing 30% thermal ellipsoids. The carbon atoms are represented as sticks for clarity.



Fig. 4. Molecular structure of $[Cd(\mu-SPh)_4{Ag(PPh_3)_2}_2]$ (7), showing 30% thermal ellipsoids. The carbon atoms are represented as sticks for clarity.

[M(PMe₂Ph)₂]⁺ fragments have been previously reported by Ibers and co-workers [35]. A similar linear metal skeleton has been observed in some heterometallic trinuclear complexes with transition metal as the central metal, such as $[M(\mu-SAr)_6(CuPPh_3)_2]$ $(M = W, Mo, U, Sn; Ar = Ph, p-C_6H_4Me, p-C_6H_4F, p-C_6H_4Cl, p$ C_6H_4Br) [12b.36]. The solid-state structures of complexes 5-7 contain two symmetry-related $[(PPh_3)_2M(\mu-EPh)_2]$ (M = Cu, Ag; E = S, Se) units with the cadmium at the center of inversion. The geometry around the central cadmium atoms in three complexes is highly distorted tetrahedral, indicated by the S-Cd-S bond angles ranging from 88.25(15)° to 121.02(9)° in 5, the Se-Cd-Se bond angles ranging from $91.80(7)^{\circ}$ to $118.97(4)^{\circ}$ in **6**, and the S-Cd-S bond angles ranging from 98.1(2)° to 115.42(11)° in 7. The Cd–S bond distances of 2.563(3) Å in 5 and 2.540(4) Å in 7 are compared with that of 2.541(3) Å (av.) in $[Me_4N]_2[Cd(SPh)_4]$. Similarly, the Cd–Se bond distance of 2.6593(15)Å in 6 is compatible with that of 2.649(3) Å (av.) in [Me₄N]₂[Cd(SePh)₄] [22]. All coinage metals in three complexes have a distorted tetrahedral geometry, being bonded to two phosphorus of the PPh₃ ligands and two sulfur or selenium atoms of PhE⁻ groups. The Cu-S, Cu-Se and Ag-S bond



Fig. 5. Molecular structure of $[Cd_3(\mu-SePh)_6(\mu_3-SePh)_4(AgPPh_3)_4]$ (**9**), showing 30% thermal ellipsoids. All phenyl rings were omitted for clarity.

lengths are 2.417(3), 2.534(2) and 2.654(4) Å for **5**, **6** and **7**, respectively. Accordingly, the Cu–S–Cd, Cu–Se–Cd and Ag–S–Cd angles are 88.29(9), 85.19(5) and 84.63(12)° for **5**, **6** and **7**, respectively. Similar to other linear trinuclear heterometallic complexes, the three metal atoms in complexes **5–7** are collinear. Furthermore, the Cu–Cd distances are 3.470(2) in **5** and 3.516(2) Å in **6**, and the Ag–Cd distance is 3.498(2) Å in **7**, which are too long to be metal–metal interaction.

Complex 8.0.5dmf is isostructural with complex 9.0.5dmf. The molecular structures consist of the neutral heptanuclear heterobimetallic complexes and lattice solvents. A perspective view of the Cd/Ag/Se complex 9, as represented, is shown in Fig. 5. The structures of the neutral complexes 8 and 9 may be described as three [(AgPPh₃)]⁺ fragments side-ligated and one [(AgPPh₃)]⁺ fragment side-capped with the trinuclear cadmium-thio(seleno)phenolate $[Cd_3(\mu-EPh)_6(\mu_3-EPh)_4]^{4-}$ moieties via the sulfur atoms of thiophenolates in **8** and the selenium atoms of selenophenolates in **9**. Each cadmium atom is coordinated to two μ -EPh and two μ_3 -EPh species in a distorted tetrahedral geometry, which is indicated by the S-Cd-S angles in the ranges of 96.36(3)-126.60(4)° for 8 and the Se-Cd-Se angles in the ranges of $94.50(5)-126.24(7)^{\circ}$ for **9**. The average Cd– μ_3 -S bond length of 2.603(1) Å is longer than the average Cd- μ_2 -S bond length of 2.492(1) Å in **8**, similarly, the average Cd- μ_3 -Se bond length of 2.793(2) Å is also longer than the average Cd– μ_2 -Se bond length of 2.596(2) Å in **9**. The coordination geometry of the silver atoms remains a highly distorted tetrahedral, with the band angles in the ranges 92.30(3)-124.77(4)° and 91.74(6)-123.26(12)° for 8 and 9, respectively. The Ag-P bond lengths, in the range of 2.447(1)-2.473(4) Å, are not clearly influenced by the different silver coordination environments in both complexes. It is interesting to note that there are three CdE₂Ag approximately co-planar four-membered rings, three CdE₃Ag₂ and three Cd2E3Ag non-planar six-membered rings in both complexes. Similar to 7 and other related Cd/Ag/S(Se) complexes, the distances of Ag. Cd separation in 8 (3.379(5)Å) and in 9 (3.377(2) Å) are too long for the metal-metal bond.

3.4. NLO properties

Complexes **1–9** have a low absorbance at 532 nm, which may promise low intensity loss and small temperature changes by photon absorption when the laser pulse propagates in these heterometallic complexes. It has been noted that the neutral polynuclear argento-selenometallic compounds with σ -donating phosphine ligands were found to exhibit the strong nonlinear optical absorptive and refractive effects along with the good photostability [37]. In this connection, the NLO properties of the heptanuclear Cd/Ag/S(Se) complexes **8** and **9** with new structural types were initially selected to be investigated by using the *z*-scan technique [29–31]. The nonlinear absorption component was evaluated under an open aperture configuration. Theoretical curves of transmittance against the *z*-position, Eqs. (5) and (6), were fitted to the observed *z*-scan data

$$T(Z) = \frac{1}{\pi^{1/2}q(Z)} \int_{-\infty}^{\infty} \ln[1+q(z)]e^{-\tau^2}d\tau$$
(5)

$$q(Z) = \alpha_2 I_i(Z) \frac{(1 - e^{-\alpha 0L})}{\alpha_0}$$
(6)

by varying the effective third-order NLO absorptivity α_2 value, where the experimentally measured α_0 (linear absorptivity), *L* (the optical path of sample) and $I_i(Z)$ (the on-axis irradiance at *z*-position) were adopted. The solid line in Fig. S5 (up) is the theoretical curve calculated with $\alpha_2 = 5.26 \times 10^{-4}$ cm/W for the concentration of 1.48×10^{-4} M for **8** in a DMF solution. The non-linear refractive

component of **8** was assessed by dividing the normalized z-scan data obtained in the close-aperture configuration by those obtained in the open-aperture configuration. The nonlinear refractive component plotted with the filled squares in Fig. S4 (down) was assessed by dividing the normalized *z*-scan data obtained under the closed aperture configuration by the normalized z-scan data obtained under the open aperture configuration. The valley and peak occur at about equal distances from the focus. It can be seen that the difference in valley–peak positions δZ_{V-P} is 7.52 mm and the difference between normalized transmittance values at valley and peak positions $\delta T_{V-P} = 0.41$ for **8**. These results suggest an effectively strong third-order optical nonlinearity [31,32]. The solid curve is an eye guide for comparison where the effective nonlinear refractivity n_2 value estimated therefore is 3.47×10^{-9} esu for **8**. Similarly, the solid line in Fig. S5 (up) is the theoretical curve calculated with $\alpha_2 = 7.13 \times 10^{-4}$ cm/W for the concentration of 1.48×10^{-4} M for **9** in a DMF solution. The difference in valley-peak positions δZ_{V-P} is 8.24 mm and the difference δT_{V-P} between normalized transmittance values at valley and peak positions is 0.51 for 9 [see Fig. S5 (down)]. The solid curve is an eye guide for comparison where the effective nonlinear refractivity n_2 value estimated therefore is 5.61×10^{-9} esu for **9**.

It may be seen that the NLO behaviors of the heptanuclear heterobimetallic complexes 8 and 9 are comparable to those of the neutral tetranuclear complex $[(\mu_3-WSe_4)Ag_3(\mu_3-I)(\mu-dppm)_2]$ and hexanuclear complex $[(\mu_3-WSe_4)_2Ag_4(\mu-dppm)_3]$ (dppm = bis (diphenylphosphino)methane) [37], and obviously stronger than those of the neutral linear trinuclear complexes $[(\mu-WSe_4)]$ $(AgPCy_3)_2$] (Cy = cyclohexyl) [37] and [(μ -WSe₄)(AgPPh₃){Ag $(PPh_3)_2$ [38] and cubane-like tetrahedral complexes $[(\mu_3-X)$ WSe_4 $Ag_3(PR_3)_3$ (X = Cl, I; R = Ph, Cy) with relative less-nuclearity [37,39]. The NLO properties of higher nuclearity metal clusters are usually larger than those of the lower nuclearity complexes. It is thus understood that polynuclearity of heterobimetallic clusters may effectively enhance nonlinear optical absorptive and refractive effects. The positive values of nonlinear refractions in 8 and **9** indicate that there are self-focusing effects in NLO behaviors of the present heptanuclear complexes [40]. Comparing the NLO data of 8 and 9, both non-linear absorption and refractive effects of selenium-containing complex 9 are obviously stronger than those of sulfur-containing complex 8. Such significant improvements of non-linear optical effects by replacing skeletal selenium atoms with sulfur atom simply the heavy atom effect, which is similar to those observed in the cubane-like structure complexes $[(\mu_3 -$ X)(μ_3 -MQ₄)M'₃(PPh₃)₃] (M = Mo, W; M' = Cu, Ag; Q = S, Se; X = Cl, Br, I) [41]. More examples of neutral argento-selenometallic and argento-tellurometallic heterobimetallic complexes with tailored structures and composition will be further designed and synthesized in this laboratory.

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Appendix A. Supplementary data

CCDC 827733, 827734, 827735, 827736, 827737, 827738, 827739 and 827740 contain the supplementary crystallographic data for 1.2dmf, 2.2dmf, 3.2dmf, 5, 6, 7, 8.0.5dmf and 9.0.5dmf. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.11.046.

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