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Pyrimidyl-2-selenolates of cadmium and mercury: Synthesis, characterization, structures and their conversion to metal selenide nano-particles

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ABSTRACT

Reactions of $[MCl_2(tmeda)]$ (M = Cd or Hg; tmeda = *N*,*N*,*N*'. tetramethylethylenediamine) with NaSeC₄H(R-4,6)₂N₂ (R = H or Me) gave selenolate complexes of the general formula $[M{SeC_4H(R-4,6)_2N_2}_2 (tmeda)_n]$ (M/R/n = Cd/H/1 (1); Cd/Me/1 (2); Hg/H/1 (3) and Hg/Me/0 (4)). The chloro complexes of general formula, $[MCl{SeC_4H(Me-4,6)_2N_2}(tmeda)]$ (M = Cd (6) or Hg (7)) have been synthesized by redistribution reaction of $[M{SeC_4H(Me-4,6)_2N_2}_2]$ with MCl₂ followed by treatment with tmeda. The complexes have been characterized by elemental analysis, UV–Vis and NMR (¹H, ¹³C, ⁷⁷Se, ¹¹³Cd and ¹⁹⁹Hg) spectroscopy. The molecular structures of $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ and $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ were established by single crystal X-ray diffraction. The complex, $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ comprises of an octahedral cadmium atom containing chelating, two SeC₄H(4,6-Me)N₂ and one tmeda, ligands. The complex, $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ has a linear structure with monodentate selenolate ligand. Thermolysis of $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ and $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ three days afforded CdSe and HgSe nanoparticles which were characterized by UV–Vis, XRD, SEM, EDX and TEM.

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1. Introduction

Metal complexes of hemilabile bidentate ligands containing chalcogen atom and nitrogen donor have been of considerable interest for the last 15 years or so [1-3]. Such ligands offer possibilities to design metal complexes with new structural motifs [4-7] and also assist in suppressing polymerization of metal chalcogenolate precursors used in chemical vapor deposition (CVD) [3,8]. Metal complexes derived from such ligands have been used as catalyst in C-C coupling reactions [9-13] and have also emerged as promising single source precursors for the synthesis of mono-dispersed metal chalcogenide naoparticles [14-17].

Several different families of hemilabile bidentate chalcogen ligands, viz. *N*,*N*-dimethylalkylchalcogenolate [8,18,19], 2-pyridyl-chalcogenolate [3], etc., have been extensively investigated. 2-Pyrimidyl chalcogenolate ligands (1) constitute yet another interesting group of hemilabile bidentate chalcogenolate ligands. Although metal complexes of 2-thiopyrimidine group (I, E = S) have been investigated during last few years [20–23], the complexes with heavier chalcogen ligands (I, E = Se or Te) have hardly received any attention [24]. Thus we have studied 2-pyrimidylse-lenolates of cadmium and mercury and have used them as single

source molecular precursors for the preparation of metal selenide nanoparticles.

$$R \xrightarrow{R} (E = S, Se, Te and R = H or Me)$$

2. Experimental

2.1. Materials and methods

Metal chlorides, *N*,*N*,*N*'-tetramethylethylenediamine (tmeda), oleylamine (OA), tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylphosphine (TOP) and other solvents were obtained from commercial sources. [Se-C₄H₃N₂]₂ (¹H NMR (CDCl₃) δ : 7.03 (t, 4.5 Hz, CH-5); 8.51 (d, 4.5 Hz, CH-4,6). ¹³C{¹H} NMR (CDCl₃) δ : 118.3 (CH-5); 157.9 (CH-4,6); 166.4 (C-2). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 2.37 (s, 490 ppm) and [Se-C₄H(Me-4,6)₂N₂]₂ (¹H NMR (CDCl₃) δ : 2.37 (s, Me); 6.71 (s, CH-5). ¹³C{¹H} NMR (CDCl₃) δ : 23.7 (Me); 117.2 (CH-5); 165.7 (C-2); 167.5 (C-4,6). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 486 ppm) were prepared according to literature method [24].





Inorganica Chimica Acta

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	$[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)] (2)$	$[Hg{SeC_4H(Me-4,6)_2N_2}_2] (4)$
Chemical formula Formula weight Crystal size (mm) Crystal system/space group	$\begin{array}{l} C_{18}H_{30}CdN_6Se_2 \\ 600.80 \\ 0.10 \times 0.02 \times 0.01 \\ monoclinic/P2/m \end{array}$	C ₁₂ H ₁₄ HgN4Se ₂ 572.78 0.40 × 0.30 × 0.10 monoclinic/P21/c
Unit cell dimensions a (Å) b (Å) c (Å) $\beta^{(\circ)}$ V (Å ³) Z $D_{calc} (g cm^{-3})$ $\mu (mm^{-1})/F(000)$ Limiting indices	17.0200(11) 7.7520(5) 17.3313(10) 94.154(5) 2280.7(2) 4 1.750 11.431/1184 $-20 \le h \le 20$ $-9 \le k \le 9$ $-20 \le l \le 20$	$\begin{array}{c} 11.346(7)\\ 9.761(4)\\ 14.964(6)\\ 108.31(4)\\ 1573.4(13)\\ 4\\ 2.418\\ 14.400/1048\\ -14 \leqslant h \leqslant 13\\ -12 \leqslant k \leqslant 0\\ -10 \leqslant l \leqslant 19 \end{array}$
θ Range of data of collection No. of reflections collected/unique No. of data/restraints/parameters Final R_1 , ωR_2 indices $[I > 2\sigma(I)]$ R_1 , ωR_2 (all data) Goodness-of-fit (GOF) on F^2	5.12-67.47 5149/6831 6831/0/254 0.0857, 0.2208 0.1010, 0.2306 1.000	2.53–27.49 1852/3611 3611/0/176 0.0574, 0.1524 0.1449, 0.1977 1.000

Table 1

 $\label{eq:crystallographic and structural determination details for [Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)] (\textbf{2}) and [Hg{SeC_4H(Me-4,6)_2N_2}_2] (\textbf{4}).$

Elemental analyses were carried out on a Thermo Scientific Flash EA1112 elemental analyzer. ¹H, ¹³C{¹H}, ⁷⁷Se{¹H}, ¹¹³Cd{¹H} and ¹⁹⁹Hg{¹H} NMR spectra were recorded on a Bruker Avance-II-300 NMR spectrometer operating at 300, 75.47, 57.24, 66.66 and 53.76 MHz, respectively. Chemical shifts are relative to internal chloroform peak for ¹H and ¹³C{¹H} spectra, external Ph₂Se₂ (δ 463 ppm relative to Me₂Se), Cd(OAc)₂.2H₂O in CH₃OD and Ph₂Hg in CDCl₃ (δ = -745 ppm relative to Me₂Hg) for ⁷⁷Se{¹H}, ¹¹³Cd{¹H} and ¹⁹⁹Hg{¹H} NMR spectra. UV–Vis absorption spectra were recorded on a JASCO V-630 double beam UV–Vis spectrophotometer.

Thermogravimetric analyses (TGA) were carried out on a Nitzsch STA 409 PC-Luxx TG-DTA instrument, which was calibrated with CaC₂O₄.H₂O. The TG curves were recorded at a heating rate of 10 °C min⁻¹ under a flow of argon. X-ray powder diffraction patterns were obtained on a Philips PW-1820 powder diffractometer using Cu K α radiation. SEM and EDX measurements were carried out on ULTRA 55 FESEM of Zeiss and Oxford Inca instruments, respectively. A JEOL-2000FX transmission electron microscope operating at accelerating voltages up to 200 kV was used for TEM studies. The samples for TEM and SAED were prepared by placing a drop of sample dispersed in acetone on a carbon coated copper grid.

Intensity data for $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ (2) and $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ (4) were measured as on a Rigaku AFC7S diffractometer fitted with Mo K α radiation so that $\theta_{max} = 27.5^{\circ}$. The unit cell parameters (Table 1) were determined from 25 reflections measured by a random search routine. The intensity data were corrected for Lorentz, polarization and absorption effects with an empirical procedure [25]. The structures were solved by direct methods using SHELX-97 [26] and refined by full-matrix least squares methods [27]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed in their calculated positions. Molecular structures were drawn using ORTEP [28].

2.2. Syntheses of complexes

2.2.1. Preparation of $[Cd(SeC_4H_3N_2)_2(tmeda)]$ (1)

To a freshly prepared NaSe–C₄H₃N₂ [from toluene–methanol solution of $(SeC_4H_3N_2)_2$ (123 mg, 0.39 mmol) and NaBH₄ (33 mg, 0.87 mmol) in methanol], CdCl₂.tmeda (116 mg, 0.39 mmol) was added with stirring which continued for 3 h at room temperature. The solvents were evaporated under vacuum. The residue was

washed thoroughly with diethyl ether and extracted with dichloromethane and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from dichloromethane-hexane mixture to yield yellow crystals (170 mg, 80%), m.p. 124 °C. *Anal.* Calc. for C₁₄H₂₂CdN₆Se₂: C, 30.87; H, 4.07; N, 15.42%. Found: C, 30.7; H, 3.78; N, 15.3%. UV–Vis λ_{max} (CH₂Cl₂): 287 nm. ¹H NMR (CDCl₃) δ : 2.41 (s, NMe₂); 2.61 (s, NCH₂–); 6.87 (t, 5 Hz, CH-5); 8.22 (d, 5 Hz, CH-4,6) (ring protons). ¹³C{¹H} NMR (CDCl₃) δ : 45.5 (NMe₂); 56.9 (NCH₂); 114.7 (CH-5); 155.7 (CH-4,6); (C-2 not detected) (ring carbons). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 214. ¹¹³Cd{¹H} NMR (CDCl₃) δ : 352.

2.2.2. Preparation of $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ (2)

Prepared in a similar fashion to **1** and the complex was recrystallized from dichloromethane in 73% yield as pale yellow crystals, m.p. 184 °C. *Anal.* Calc. for C₁₈H₃₀CdN₆Se₂: C, 35.98; H, 5.03; N, 13.98%. Found: C, 35.49; H, 4.83; N, 13.76%. UV–Vis λ_{max} (CH₂Cl₂): 287 nm. ¹H NMR (CDCl₃) δ : 2.34 (s, Me); 2.41(s, NMe₂); 2.62 (s, NCH₂–); 6.57 (s, ring proton). ¹³C{¹H} NMR (CDCl₃) δ : 23.6 (Me); 46.8 (NMe₂); 56.7 (NCH₂); 114.7 (CH-5); 166.1 (C-4,6); 176.3 (C-2) (ring carbons). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 331. ¹¹³Cd{¹H} NMR (CDCl₃) δ : 213.

2.2.3. Preparation of $[Hg(SeC_4H_3N_2)_2(tmeda)]$ (3)

Prepared in the same way as **1** by employing HgCl₂.tmeda and NaSeC₄H₃N₂ and the complex was recrystallized from dichloromethane-hexane mixture as colorless crystals (yield 160 mg, 65%), m.p. 110 °C (dec.). *Anal.* Calc. for C₁₄H₂₂HgN₆Se₂: C, 26.57; H, 3.50; N, 13.28%. Found: C, 26.28; H, 3.32; N, 13.89%. UV–Vis λ_{max} (CH₂Cl₂): 270, 306 (sh) nm. ¹H NMR (CDCl₃) δ : 2.30 (s, NMe₂); 2.48 (s, NCH₂–); 6.98 (t, 4.8 Hz, CH-5); 8.31 (d, 4.8 Hz, CH-4,6) (ring protons). ¹³C{¹H} NMR (CDCl₃) δ : 45.6 (NMe₂); 57.1 (NCH₂); 116.0 (CH-5); 156.0 (CH-4,6); 162.3 (C-2) (ring carbons). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 254.

2.2.4. Preparation of $[Hg{SeC_4H(Me-4,6)_2N_2\}_2]$ (4)

The reaction of either HgCl₂.tmeda or HgCl₂ with NaSeC₄H(Me-4,6)₂N₂ invariably yielded the title complex (**4**) which was recrystallized from dichloromethane–hexane as colorless crystals (yield 360 mg, 78%), m.p. 154 °C (decomp.). *Anal.* Calc. for C₁₂H₁₄HgN₄₋ Se₂: C, 25.16; H, 2.46; N, 9.78%. Found: C, 25.33; H, 2.49; N, 10.17%. UV–Vis λ_{max} (CH₂Cl₂): 266, 302 (sh) nm. ¹H NMR (CDCl₃) δ: 2.28 (s, Me); 6.76 (s, ring proton). ¹³C{¹H} NMR (CDCl₃), δ: 23.6 (Me); 116.6 (CH-5); 166.8 (C-4,6); 171.6 (C-2) (ring carbons). ⁷⁷Se{¹H} NMR (CDCl₃) δ: 342. ¹⁹⁹Hg{¹H} NMR (CDCl₃), δ: -1521.

2.2.5. Preparation of $[Cd{SeC_4H(Me-4,6)_2N_2}_2]$ (5)

To a freshly prepared NaSeC₄H(Me-4,6)₂N₂ [from toluenemethanol solution of [$\{SeC_4H_3(Me-4,6)_2N_2\}_2$] (300 mg, 0.81 mmol) and NaBH₄ (66 mg, 1.74 mmol) in methanol], CdCl₂ (145 mg, 0.79 mmol) was added with stirring which continued for 2 h at room temperature. The solvents were evaporated under vacuum. The residue was thoroughly washed with water followed by acetone and dried under vacuum to yield yellow powder (318 mg, 83%), m.p. 200 °C. *Anal.* Calc. for C₁₂H₁₄CdN₄Se₂: C, 29.74; H, 2.91%. Found: C, 29.06; H, 2.93%.

2.2.6. Preparation of $[CdCl{SeC_4H(Me-4,6)_2N_2}(tmeda)]$ (6)

To a suspension of **5** (250 mg, 0.52 mmol) in toluene–methanol mixture, solid CdCl₂ (95 mg, 0.52 mmol) was added and after stirring for 3 h at room temperature, tmeda in excess was added in the solution and stirred for 30 min. The solvent was evaporated in vacuum and the residue was extracted from dichloromethane and recrystallized similar to **1** (357 mg, 77%), m.p. 148 °C. *Anal.* Calc. for C₁₂H₂₃CdClN₄Se: C, 32.01; H, 5.15%. Found: C, 32.43; H, 4.89%. UV–Vis λ_{max} (CH₂Cl₂): 285 nm. ¹H NMR (CDCl₃) δ : 2.35 (s, Me); 2.48 (s, NMe₂); 2.63 (s, NCH₂–); 6.63 (ring proton). ¹³C{¹H} NMR (CDCl₃) δ : 23.5 (Me); 47.1 (NMe₂); 56.6 (NCH₂); 114.8 (CH-5); 166.2 (C-4,6); 175.8 (C-2) (ring carbons). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 198. ¹¹³Cd{¹H} NMR (CDCl₃) δ : 342.

2.2.7. Preparation of $[HgCl{SeC_4H(Me-4,6)_2N_2}(tmeda)]$ (7)

Prepared in a similar fashion to **6** employing [Hg{SeC₄H(Me-4,6)₂N₂]₂] (360 mg, 0.63 mmol), HgCl₂ (171 mg, 0.63 mmol) and tmeda (excess) and the resulting complex was recrystallized from dichloromethane–hexane as colorless crystals (yield 561 mg, 83%), m.p. 124 °C. *Anal.* Calc. for C₁₂H₂₃ClHgN₄Se: C, 26.78; H, 4.31%. Found: C, 27.01; H, 4.72%. UV–Vis λ_{max} (CH₂Cl₂): 266 nm. ¹H NMR (CDCl₃) δ : 2.30 (s, Me); 2.44 (s, NMe₂); 2.61 (s, NCH₂–); 6.70 (ring proton). ¹³C{¹H} NMR (CDCl₃) δ : 23.6 (Me); 46.5 (NMe₂); 56.8 (NCH₂); 116.0 (CH-5); 166.5 (C-4,6); 171.2 (C-2) (ring carbons). ⁷⁷Se{¹H} NMR (CDCl₃) δ : 247. ¹⁹⁹Hg{¹H} NMR (CDCl₃) δ : –1218.

2.3. Preparation of metal selenide nanoparticles

To a pre-heated (250 °C) TOPO (3 g) in a three necked flask, a solution of $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ (2) (100 mg, 0.17 mmol) in OA (3 ml) was injected rapidly with vigorous stirring under flowing argon (experiment 1). The temperature was dropped to 220 °C, was raised to and maintained at 230 °C for 30 min. The hot solution was cooled down rapidly to 70 °C and methanol (20 ml) was added to get a reddish precipitate, which was washed thoroughly with methanol, followed by centrifuging and drying under vacuum. Red CdSe was extracted in toluene and evaporated under vacuum. Similar experiment was also performed in OA (experiment 2).

Similarly, $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ (**4**) (90 mg, 0.16 mmol) was pyrolysed in OA (3 ml)/OA (3 ml) (experiment 3) at 100 °C for 30 min and black precipitate was washed with methanol, followed by centrifuging and drying under vacuum to give a black powder.

3. Results and discussion

3.1. Synthesis and spectroscopy

Treatment of $[CdCl_2(tmeda)]$ with two equivalents of sodium salts of 2-pyrimidyl selenolate, $NaSeC_4H(R-4,6)_2N_2$ (prepared

in situ by reduction of Se–Se bond in [{SeC₄H(R-4,6)₂N₂}₂] in toluene–methanol by a methanolic solution of NaBH₄ under an argon atmosphere) gave selenolate complexes, [Cd{SeC₄H(4,6-R)₂N₂}₂ (tmeda)] (Eq. (1)). Similar reaction with HgCl₂.tmeda gave [Hg(SeC₄H₃N₂)₂(tmeda)] and [Hg{SeC₄H(Me-4,6)₂N₂}₂] depending on the substituent in the pyrimidyl ring. The latter and its cadmium analog can be prepared readily by the reaction between MCl₂ (M = Cd or Hg) and NaSe-C₄H(Me-4,6)N₂ (Eq. (2)). Redistribution reaction between [M{Se-C₄H(Me-4,6)N₂}₂] and MCl₂ followed by treatment with tmeda afforded heteroleptic complexes, [MCl{SeC₄H(Me-4,6)₂N₂}(tmeda)] (Eq. (3)).

$$\begin{split} & [CdCl_2(tmeda)] + 2 \ NaSeC_4H(R-4,6)N_2 \\ & \longrightarrow \left[Cd\{SeC_4H(R-4,6)_2N_2\}_2(tmeda)\right] + 2NaCl \end{split} \tag{1}$$

where R = H, Me

$$\begin{split} & [\text{MCl}_2/\text{HgCl}_2(\text{tmeda})] + 2 \text{ NaSeC}_4\text{H}(\text{Me-4},6)_2\text{N}_2 \\ & \longrightarrow & [\text{M}\{\text{SeC}_4\text{H}(\text{Me-4},6)_2\text{N}_2\}_2] + 2\text{NaCl} \end{split} \tag{2}$$

where M = Cd, Hg

$$\begin{split} & \left[M\{\text{SeC}_4H(\text{Me-4},6)_2N_2\}_2 \right] + MCl_2 + tmeda \\ & \longrightarrow 2 \left[MCl\{\text{SeC}_4H(\text{Me-4},6)_2N_2\}(tmeda) \right] \end{split} \tag{3}$$

where M = Cd, Hg

Electronic spectra of these complexes in dichloromethane showed single absorption band in the region 266-287 nm with a shoulder at ~ 304 nm only in mercury derivatives (**3**, **4**). The observed absorption can be assigned to ligand-to-ligand charge transfer transition in the selenolate ligand.

The ¹H and ¹³C{¹H} NMR spectra displayed expected resonances. The CH-5 proton and carbon-13 resonance are shielded in complexes with respect to the corresponding resonance for the diselenides. Similarly CH-4,6 proton and carbon NMR resonances of **1** and **3** are shielded. The ⁷⁷Se NMR spectra exhibited a single resonance in the region 214–342 ppm as expected for selenolate complexes. The resonance for Hg complex appeared at lower field as compared to the corresponding signals for cadmium derivatives (e.g., ⁷⁷Se NMR δ : 214 (**1** Cd) versus 254 (**3** Hg) ppm and 331 (**2** Cd) versus 342 (**4** Hg)). The ⁷⁷Se NMR resonances for the chloro complexes (**6**, **7**) showed significant shielding with respect to the corresponding bis derivatives (**2** and **4**) due to the presence of chloro ligand. Both ¹¹³Cd{¹H} and ¹⁹⁹Hg{¹H} NMR spectra showed single resonances indicating the presence of a single molecular

Table 2	
Selected bond lengths (Å) and angles (°)) for $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ (2).

Molecule a		Molecule b	
Cd1–Se1	2.6247(10)	Cd2–Se2	2.6123(10)
Cd1-N1	2.428(7)	Cd2-N4	2.426(9)
Cd1-N2	2.651(8)	Cd2-N5	2.672(9)
Se1-C4	1.907(9)	Se2-C13	1.895(9)
Se1-Cd1-Se1 ⁱ	140.15(6)	Se2-Cd2-Se2 ⁱⁱ	139.81(6)
Se1-Cd1-N1	105.37(18)	Se2-Cd2-N4	106.62(19)
Se1-Cd1-N1 ⁱ	105.88(19)	Se2–Cd2–N4 ⁱⁱ	104.9(2)
Se1-Cd1-N2	62.92(19)	Se2-Cd2-N5	62.48(19)
Se1–Cd1–N2 ⁱ	95.99(18)	Se2-Cd2-N5 ⁱⁱ	96.27(19)
Se1 ⁱ -Cd1-N1	105.88(19)	Se2 ⁱⁱ -Cd2-N4	104.9(2)
Se1 ⁱ -Cd1-N1 ⁱ	105.37(18)	Se2 ⁱⁱ -Cd2-N4 ⁱⁱ	106.62(19)
Se1 ⁱ -Cd1-N2	95.99(18)	Se2 ⁱⁱ -Cd2-N5	96.27(19)
Se1 ⁱ -Cd1-N2 ⁱ	62.92(18)	Se2 ⁱⁱ -Cd2-N5 ⁱⁱ	62.49(19)
N2-Cd1-N1	85.0(3)	N5-Cd2-N4	85.3(3)
N2-Cd1-N1 ⁱ	154.3(3)	N5-Cd2-N4 ⁱⁱ	153.2(3)
N2-Cd1-N2 ⁱ	118.0(4)	N5 ⁱⁱ -Cd2-N5	118.2(4)
N1-Cd1-N2 ⁱ	154.3(3)	N4-Cd2-N5 ⁱⁱ	153.2(3)
N2 ⁱ –Cd1–N1 ⁱ	85.0(3)	N5 ⁱⁱ -Cd2-N4 ⁱⁱ	85.3(3)
N1-Cd1-N1 ⁱ	75.5(4)	N4 ⁱⁱ -Cd2-N4	75.6(4)





Fig. 1. (a) ORTEP drawing of [Cd{SeC₄H(Me-4,6)₂N₂}₂(tmeda)] (2) with atomic number scheme. Ellipsoids are drawn with 25% probability and hydrogen atoms are omitted for clarity. (b) and (c) packing along b and c axis.



Fig. 2. (a) ORTEP drawing of [Hg{SeC₄H(Me-4,6)₂N₂]₂] (4) with atomic number scheme. Ellipsoids are drawn with 50% probability and hydrogen atoms are omitted for clarity. (b) Packing diagram showing inter molecular interaction. Selected interatomic parameters : Hg1- Se1, 2.463(2) Å; Hg1- Se2, 2.454(2) Å; Se1- C1, 1.933(13) Å; Se2- C7, 1.918(14) Å. Se1- Hg1- Se2, 169.22(6)°; C1- Se1- Hg1, 91.3(4)°; C7- Se2- Hg1, 91.9(5)°.



Fig. 3. XRD pattern of CdSe nanoparticles obtained by pyrolysis [Cd{SeC₄H(Me $4,6)_2N_2$]₂(tmeda)] (2) in OA/TOPO at 230 °C for 30 min.

species in solution. The resonance for chloro complexes are significantly deshielded than the corresponding bis derivatives (e.g., ¹¹³Cd{¹H} NMR δ : 213 (for **2**) and 352 (for **6**); ¹⁹⁹Hg{¹H} NMR δ : –1521 (for **4**) and –1218 (for **7**) ppm) owing to the strong – I effect of the chloro ligand. The observed ¹¹³Cd{¹H} and ¹⁹⁹Hg{¹H} NMR chemical shifts are within the expected region of metal chalcogenolates [17,29,30].

3.2. Molecular structures

The crystal and molecular structures of $[Cd\{SeC_4H(Me-4,6)_2N_2\}_2(tmeda)]$ (2) and $[Hg\{SeC_4H(Me-4,6)_2N_2\}_2]$ (4) were determined by single crystal X-ray diffraction analyses. Selected bond lengths and angles are given in Table 2, while ORTEP drawings with crystallographic numbering scheme are shown in Figs. 1 and 2. All C-C, C-N, and C-Se distances are similar to those reported in literature [31].

There are two independent molecules of [Cd{SeC₄H(Me-4,6)₂ N_2 ₂(tmeda)] (2) (Fig. 1a) in the crystal lattice each of them have a similar configuration, but differ slightly in various interatomic parameters. It acquires a distorted octahedral configuration in which cadmium atom is surrounded by three chelating ligands, viz. two SeC₄H(Me-4,6)₂N₂ through N, Se and "tmeda". The overall configuration is similar to analogus 2-selenopyridine complex, [Cd(SeC₅H₄N)₂(tmeda)] [17]. The Cd–Se bond lengths (2.6247 Å and 2.6123 Å) are shorter than reported in $[Cd(SeC_5H_4N)_2(tmeda)]$ (2.73 Å) [17] and slightly longer than that reported in [Cd(Se COPh)₂(tmeda)] (2.5859(6) Å) [32] and [Cd(SeOx)₂] (Ox = 2-(4, 4dimethyl-2-oxazolinyl)benzene) (~2.55 Å) [33]. The Cd-N (pyrimidyl) bond length (av 2.66 Å) is longer than Cd–N(tmeda) (2.427 Å) which may due to strain in four-membered ring in the former as compared to the five membered ring in the later. The packing diagram shows short contacts/interactions (N2-H1A-C1 = 2.744 Å and N5–H10A-C10 = 2.786 Å) between the methylene goup of tmeda



Fig. 5. XRD patten of HgSe NPs obtained by pyrolysis $[Hg\{SeC_4H(Me-4,6)_2N_2\}_2]$ (4) in OA at 100 $^\circ C$ for 30 min.

of one molecule and the nitrogen atoms of pyrimidine rings of neighboring molecule (Fig. 1b) molecule leading to the formation of infinite stack (Fig. 1c). The stacks are mutually perpendicular.

The molecular structure of $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ (4) (Fig. 2a) is similar to $[Hg{SeC_5H_3(Me-3)N_2}_2]$ [17] but shows deviation from linearity. The Se–Hg–Se angle is 169.22° while in the latter this angle is 180°. There are short contacts between N2 of one of the pyrimidine rings of one molecule and Hg (N2–Hg = 2.914 Å) of another molecule, whereas other pyrimidine ring is aligned with one of the pyrimidine rings of another molecule through π – π stacking (inter planar distance 3.528 Å). The deviation of the Se–Hg–Se angle from linearity may be due to the repulsions between the π cloud of pyrimidine ring on one side and lone pairs of Se1 and Se2 on other side. The Hg–Se bond length (2.4585 Å) are smaller than that reported in [Hg(SeC₅H₄N)₂(tmeda)] (2.4955 Å) [17] and [Hg{SeC₅H₃(Me-3)N₂] (2.4629 Å) [17].

3.3. Thermal studies

The TG analysis (supplementary information) of $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ (2) under flowing argon showed that the complex underwent a two-step decomposition. The first step corresponds to loss of tmeda (weight loss found: 17.3%, calcd. for tmeda: 19.3%) and the second step shows formation of CdSe (weight loss found: 48.8%, calcd. for the formation of CdSe: 43%).

3.4. Metal selenide nanomaterials

Thermolysis of $[Cd{SeC_4H(Me-4,6)_2N_2}_2(tmeda)]$ (2) in OA/ TOPO or OA were carried out at 230 °C under an argon atmosphere afforded a red precipitate which was characterized as hexagonal phase of CdSe from XRD pattern [JCPDS File No. 08-0459] (Fig. 3) and EDX analysis [Se/Cd atom ratios are 1.05 and 1.07 in OA/TOPO and OA, respectively]. The diffraction peaks at 23.9, 25.3, 27.1, 42.0,



Fig. 4. (a) TEM image and (b) SAED pattern of CdSe nanoparticles obtained by pyrolysis [Cd{SeC₄H(Me-4,6)₂N₂]₂(tmeda)] (2) in OA/TOPO at 230 °C for 30 min.



Fig. 6. (a) TEM image and (b) SAED patten of HgSe NPs obtained by pyrolysis [Hg{SeC₄H(Me-4,6)₂N₂]₂] (4) in OA at 100 °C for 30 min.

45.8 and 49.7 can be assigned to the (100), (002), (101), (110), (103) and (112) planes of bulk hexagonal phase of CdSe. The broadening of the diffraction peaks indicates that the sample is nanosized. The average diameters estimated by Scherrer formula¹ for the CdSe particles prepared in OA/TOPO and OA are 15 and 20 nm, respectively. The TEM image (Fig. 4a) of cadmium selenide obtained from OA/TOPO revealed irregular size with a diameter of 8-20 nm while in OA a mixture of spherical and elliptical shaped morphologies with minor axis of 15 nm and major axis of 20-30 nm is formed (supplementry information). The SAED pattern (Fig. 4b) revealed that NPs are polycrystalline in nature. SAED patterns showed set of lattice planes, (205), (112), (110) corresponding to hexagonal phase which are consistent with the phases determined by XRD. The absorption spectra of OA/TOPO and OA/ OA capped NPs obtained by pyrolysis of **2** at 230 °C displayed broad peak at 650 and 665 nm, respectively which are blue shifted with respect to the bulk CdSe (λ_{max} = 713 nm).

The thermolysis of $[Hg{SeC_4H(Me-4,6)_2N_2}_2]$ (4) in OA at 100 °C yields a black residue, XRD pattern (Fig. 5) of which displayed broad peaks corresponding to cubic phase of HgSe (JCPDS File No. 73-1668, EDX analysis: Se/Hg atom ratio: 0.98). The average particle size estimated from Scherrer formula is 15 nm. The TEM image (Fig. 6a) of HgSe nanoparticles revealed agglomerated chunks composed of rod like morphology with an average diameter of 22 nm and a length of 20–40 nm. The lattice planes (511), (311) and (220) observed in SAED pattern (Fig. 6b) are in conformity with the cubic phase of HgSe as inferred from XRD pattern.

4. Conclusion

Cadmium and mercury 2-pyrimidyl selenolates have been isolated as air stable monomeric complexes. Unlike analogous 2-pyridylslenolate complexes, the pyrimidyl derivatives show weak secondary interactions leading to stacking of molecules. The utility of these complexes as single source precursors has been demonstrated for the preparation of monophasic metal selenide nano particles.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.11.018. CCDC 949678 and 949677 for [Cd{SeC4H(Me-4,6)2N2}2(tmeda)] (**2**) and [Hg{SeC4H(Me-4,6)2N2}2] (**4**), respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223/336 033; E mail: deposit@ccdc.cam.ac.uk].

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¹ *A* = 0.94/cos, where *A* = coherence length; β = full-width at half maximum (fwhm) of the diffraction peak; λ = (1.5418 Å) wavelength of Cu K α X-ray radiation; θ = angle of diffraction.

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