Bis(1-methylimidazolyl)diselenide and 1-Methylimidazole-2-selenolate Complexes of Zinc, Cadmium, and Mercury: Synthesis, Characterization, and Their Conversion to Metal Selenide Quantum Dots

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Treatment of a methanolic solution of metal acetate with bis(1-methylimidazolyl)diselenide, [(MeImSe)₂], yields complexes of composition [M(OAc)₂{(MeImSe)₂}] (M = Zn, Cd, or Hg) whereas reactions of [MX₂(Me₂NCH₂CH₂-NMe₂)] (X = Cl or OAc) with sodium 1-methylimidazole-2-selenolate gave selenolate complexes of the general formula [M(MeImSe)₂] (M = Zn or Cd). The complexes were characterized by elemental analysis, IR, UV-vis, NMR (1 H, 13 C, and 77 Se) data. The crystal structure of [Cd(OAc)₂{(MeImSe)₂}] was established by single-crystal X-ray diffraction. The cadmium atom adopts a distorted octahedral configuration defined by asymmetrically chelated acetate groups and chelating diselenide ligand. Thermal behavior of adducts was studied by thermogravimetric analysis. Pyrolysis in hexadecylamine/tri-n-octylphosphine oxide gave MSe quantum dots, which were characterized by UV-vis, photoluminescence, XRD, EDAX, SAED, and TEM.

The compound semiconductor nanoparticles of II–VI materials have received considerable attention in the past 15 years or so. This is primarily due to their shape and size-dependent optoelectronic properties which can be and have been used for a variety of optoelectronic and bioengineering applications. ^{1–5} To meet these objectives, a convenient synthesis of nanoparticles with desirable shape and composition is of paramount importance. A wide variety of synthetic routes for amine/thiols/ phosphates capped and uncapped II-VI nanomaterials have been developed. 6-22 These include reactions of group II source (e.g., metal oxides, metal alkyls (Et₂Zn and R₂Cd), or metaloorganic derivatives such as Cd(OAc)2) with a group VI carrier (e.g., organophosphine chalcogenide (R₃PE) or bis(trimethylsilyl)chalcogenide) in an appropriate coordinating solvent, 6-8 controlled precipitation method involving treatment of a metal salt (MO and M(OAc)₂) with ammonium/sodium sulfide, H₂S;^{9,10} reduction of sulfur/selenium with KBH₄ and the corresponding metal salt at room temperature, 11,12 ultrasonic synthesis from Zn(OAc)₂ and selenourea, ¹³ biological methods using yeasts, ¹⁴ and pyrolysis of single source precursors. ^{19–21} The later technique has been quite successful and straight forward in terms of synthesis of both the precursors as well as high quality nanoparticles on a gram scale. The chemistry of numerous homo- and heteroleptic single source precursors, such as [M(SeCOAr)₂(tmen)], [M(SeCH₂CH₂CH₂NMe₂)₂], $[M(S_2CAr)_2(tmen)]$ $(M = Zn, Cd, and Hg; tmen = Me_2-$ NCH₂CH₂NMe₂), etc. derived from simple and internally functionalized chalcogenolate ligands has been explored. 19-24 Cadmium complexes with simple chalcogenolate ligands tend to polymerize^{25,26} whereas mercury complexes quite often lead to the formation of dichalcogenide and mercury metal.²⁷ As in other preparative routes where the metal and chalcogen sources are independently brought together during the course of reaction, it was of interest to design single source precursor molecules without M–E linkages and evaluate their suitability for the preparation ME nanoparticles.

Experimental

Materials and Methods. Zinc, cadmium, and mercury acetates, N,N,N',N'-tetramethylethylenediamine (tmen), hexadecylamine (HDA), and tri-n-octylphosphine oxide (TOPO) were obtained from commercial sources. The compounds [M(OAc)₂-(tmen)], [MCl₂(tmen)] (M = Zn and Cd), ¹⁹ and bis(1-methylimidazolyl)diselenide, [(MeImSe)₂], [mp 144 °C, UV-vis (CH₃OH) λ_{max} : 216, 295 nm, ¹H NMR (CDCl₃) δ 3.58 (s, Me), 6.99 and 7.09 (each s, CH=CH); ¹³C{¹H} NMR (CDCl₃) δ 34.8 (s, Me), 124.0, 129.9 (s), and 133.6 (each s, ring carbons); ⁷⁷Se{¹H} NMR (in CDCl₃) δ 380]²⁸ were prepared according to the literature method.

 $^1H,\ ^{13}C\{^1H\},\ and\ ^{77}Se\{^1H\}\ NMR\ spectra\ were\ recorded\ on\ a\ Bruker\ DPX-300\ NMR\ spectrometer\ operating\ at\ 300,\ 75.47,\ and\ 57.23\ MHz,\ respectively. Chemical shifts are\ relative to internal chloroform peaks at <math display="inline">\delta$ 7.26 for 1H and δ 77.0 for $^{13}C\{^1H\}$ or methanol peaks ($^1H\ \delta$ 4.78 (OH); $^{13}C\ \delta$ 49.0) and external $Ph_2Se_2\ (\delta$ 463 relative to $Me_2Se)$ in $CDCl_3$ for $^{77}Se\{^1H\}.$ IR spectra were recorded as Nujol mulls between CsI plates on a Bomem MB-102 FT-IR spectrometer. Electronic spectra were recorded in methanol on a Chemito Spectrascan UV 2600 double beam UV–vis spectro-

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Table 1. Crystallographic and Structural Determination Data for [Cd(OAc)₂{(MeImSe)}₂]•2H₂O

Chemical formula	$C_{12}H_{20}CdN_4O_6Se_2$	
Formula weight	586.64	
Crystal size/mm ³	$0.30 \times 0.25 \times 0.20$	
Temperature/K	298(2)	
Wavelength/Å	0.71073	
Crystal system/space group	Orthorhombic/Pbca	
Unit cell dimensions a/Å	30.464(10)	
	14.870(7)	
$b/ m \AA$ $c/ m \AA$	8.420(6)	
Volume/Å ³	3814(3)	
Z	8	
$D_{\rm calcd}/{ m gcm^{-3}}$	2.043	
μ/mm^{-1}	4.997	
F(000)	2272	
Limiting indices	$0 \le h \le 39$; $-10 \le k \le 19$;	
	$-6 \le l \le 10$	
No. of reflections collected/unique	6335/4368	
No. of data/restraints/parameters	4368/7/245	
Final R_1 , ωR_2 indices $[I > 2\sigma(I)]$	0.0363, 0.0692	
$R_1, \omega R_2$ (all data)	0.1077, 0.0851	
Goodness of fit on F^2	1.000	
Largest diff. peak and hole $(e/Å^3)$	0.5900 and -0.8600	

photometer. Fluorescence spectra were recorded using a Hitachi F-4500 FL spectrofluorometer.

Thermogravimetric analyses (TGA) were performed on a Nitzsch STA PC-Luxx TG-DTA instrument. TG curves were recorded at a heating rate of 5 $^{\circ}$ C min $^{-1}$ under a flowing nitrogen atmosphere. X-ray powder diffraction patterns were obtained on a Philips PW-1820 powder diffractometer using Cu K α radiation. EDAX measurements were carried out on a Tescan Vega 2300T/40 instrument. 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 $[Cd(OAc)_2\{(MeImSe)_2\}]$, which crystallizes as a hydrate, were measured on a Rigaku AFC7S diffractometer fitted with Mo K α radiation so that $\theta_{max}=27.5^{\circ}$. The structure was solved by direct methods²⁹ and refinement was on $F^{2\,29}$ using data that had been corrected for absorption effects with an empirical procedure,³⁰ with non-hydrogen atoms modeled with anisotropic displacement parameters, with hydrogen atoms in their calculated positions. Molecular structure was drawn using ORTEP.³¹ Crystallographic and structural determination data are listed in Table 1.

Synthesis of Complexes. Preparation of [**Zn(OAc)**₂-{(**MeImSe)**₂}] (**1a):** To a methanolic solution ($10 \,\mathrm{cm}^3$) of [(MeImSe)₂] ($150 \,\mathrm{mg}$, $0.47 \,\mathrm{mmol}$), a solution of $\mathrm{Zn(OAc)}_2 \cdot 2\mathrm{H}_2\mathrm{O}$ ($101 \,\mathrm{mg}$, $0.47 \,\mathrm{mmol}$) in the same solvent ($10 \,\mathrm{cm}^3$) was added with stirring which continued for 2 h. The solvent was evaporated under vacuum and the yellow residue was recrystallized from methanol–ethyl acetate as yellow needle-shaped crystalline solid (yield $180 \,\mathrm{mg}$, 78%): mp $170 \,^{\circ}\mathrm{C}$; Anal. Calcd for $\mathrm{C_{12}H_{16}N_4O_4Se_2Zn}$: C, 28.6; H, 3.2; N, 11.1%. Found: C, 27.5; H, 3.2; N, 10.6%. UV–vis λ_{max} (CH₃OH): 219, 284 nm; IR: 1620, $1581 \,\mathrm{cm}^{-1}$ (ν C=O); $^1\mathrm{H}\mathrm{NMR}$ (CD₃OD) δ 1.95 (s, OAc), 3.83 (s, Me-), 7.41 and 7.45 (each d, $J=1.3 \,\mathrm{Hz}$); $^{13}\mathrm{C}^{\{1}\mathrm{H}\}\mathrm{NMR}$ (CD₃OD) δ 21.6 (OAc), 35.2 (s, Me), 124.9, 130.7, and 136.4 (ring carbons), 179.0 (C=O);

 77 Se{ 1 H} NMR (CD₃OD) δ 428.

Preparation of [Cd(OAc)₂{(MeImSe)₂}] (1b): Prepared similar to 1a and recrystallized from dichloromethane as orange needle-shaped crystals in 94%: mp 169 °C; Anal. Calcd for C₁₂H₁₆-CdN₄O₄Se₂: C, 26.2; H, 2.9; N, 10.2%. Found: C, 25.2; H, 2.9; N, 9.8%. UV–vis λ_{max} (CH₃OH): 219, 292 nm; IR: 1560 cm⁻¹ (ν C=O); ¹H NMR (CD₃OD) δ 1.99 (s, OAc), 3.81 (s, Me), 7.34 and 7.40 (each d, J = 1.3 Hz); ¹³C{¹H} NMR (CD₃OD) δ 20.5 (s, OAc), 35.2 (s, Me), 125.2, 131.1, and 135.7 (each s, ring carbons), 180.2 (s, C=O); ⁷⁷Se{¹H} NMR (CD₃OD) δ 425.

CCDC-636598 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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 336033; E-mail: deposit@ccdc.cam. ac.uk).

Preparation of [Hg(OAc)₂{(MeImSe)₂}] (1c): Prepared similarly to the zinc adduct and recrystallized in dichloromethane-hexane mixture to obtain light green product in 71% (260 mg); mp 125 °C; Anal. Calcd for C₁₂H₁₆HgN₄O₄Se₂: C, 22.6; H, 2.5; N, 8.8%. Found: C, 21.6; H, 2.5; N, 8.6%. IR: 1661, 1576 cm⁻¹ (C=O); UV-vis λ_{max} (CH₃OH): 224 nm; ¹H NMR (CD₃OD) δ 1.95 (s, OAc), 3.64 (s, Me), 6.61, 7.00 (s); ¹³C{¹H} NMR (CD₃OD) δ 20.4 (s, OAc), 35.7 (s, Me), 123.8, 126.6, and 137.2 (each s, ring carbons), 175.1 (s, C=O).

Preparation of [Zn(MeImSe)₂]_n (2a): To a freshly prepared NaMeImSe (from [(MeImSe)₂] (236 mg, 0.74 mmol) and NaBH₄ (62 mg, 1.63 mmol) in methanol) was added a toluene suspension of [ZnCl₂(tmen)] (182 mg, 0.72 mmol). The whole was stirred at room temperature for 3 h and the solvents were evaporated under vacuum. The residue was extracted with toluene and filtered. The filtrate was concentrated under reduced pressure to yield a cream solid (200 mg, 72%), mp >250 °C; Anal. Calcd for C₈H₁₀N₄Se₂-Zn: C, 24.9; H, 2.6; N, 14.5%. Found: C, 25.9; H, 2.4; N, 14.0%. UV–vis λ_{max} (CH₃OH): 231 nm; ¹H NMR (CDCl₃) δ 3.52, 3.56, 3.59, 3.64, 3.68, and 3.75 (Me), 6.48–6.82 (m), 7.36 (s) (ring protons); ¹³C{¹H} NMR (CDCl₃) δ 35.8 (s, Me), 120.4, 120.8, 126.7, 127.1, 145.3 (s).

Preparation of [Cd(MeImSe)₂]_n (**2b):** To a freshly prepared methanolic solution of NaMeImSe (from (MeImSe)₂ (150 mg, 0.47 mmol) and NaBH₄ (39 mg, 1.03 mmol)) was added a methanolic solution of [Cd(OAc)₂(tmen)] (159 mg, 0.46 mmol) and the whole was stirred for 3 h at room temperature. The solvent was evaporated under vacuum and the white residue was washed with several portions of distilled water followed by acetone and again dried in vacuo (131 mg, 66%), mp >350 °C; Anal. Calcd for C₈-H₁₀CdN₄Se₂: C, 22.2; H, 2.3; N, 12.9%. Found: C, 22.4; H, 2.1; N, 12.7%. Product is insoluble in all common organic solvents, and hence could not be characterized further.

Preparation of Metal Selenide Nanoparticles Using 1: To a pre-heated (210 °C) mixture of HDA (4 g) and TOPO (800 mg) in a three-necked flask, a solution of [Zn(OAc)₂{(MeImSe)₂}] (150 mg, 0.3 mmol) in a mixture of CHCl₃ (1.5 cm³)/CH₃OH (1 cm³) and TOPO (200 mg) was injected rapidly with vigorous stirring under flowing argon. The temperature dropped to 170 °C and was raised to and maintained at 200 °C for 30 min. The hot solution was cooled down rapidly to 70 °C and methanol (20 cm³) was added so as to get a cream flocculent precipitate of ZnSe which was washed thoroughly with methanol, followed by centrifuging and drying under vacuum. Similarly, red CdSe quantum dots were prepared by injecting [Cd(OAc)₂{(MeImSe)₂}] at 190 °C and stabilizing at 178 °C for 20 min. The mercury complex was pyrolysed

$$[M(OAc)_2 \cdot nH_2O] + (MeImSe)_2 \longrightarrow [M(OAc)_2\{(MeImSe)_2\}] + nH_2O$$

$$(1)$$

$$[MX_2(tmen)] + 2NaMeImSe \longrightarrow [M(MeImSe)_2] + tmen + 2NaX$$

$$(M = Zn \text{ or } Cd; X = Cl \text{ or } OAc)$$

$$(2)$$

Scheme 1.

in an HDA (1 g) and toluene (5 cm 3) mixture at 95 $^{\circ}$ C for 20 min and processed in a manner similar to ZnSe preparation.

Results and Discussion

Synthesis and Spectroscopy. Treatment of a methanolic solution of metal acetate with bis(1-methylimidazolyl)diselenide afforded readily 1:1 addition complexes of composition $[M(OAc)_2\{(MeImSe)_2\}]$ (1) $(M = Zn \ (1a), \ Cd \ (1b), \ or Hg \ (1c))$. Reaction of $MX_2(tmen)$ $(X = Cl \ or \ OAc)$ with NaMeImSe gave selenolate complexes of composition $[M(MeImSe)_2]$ (2) (Scheme 1).

The ¹H and ¹³C{¹H} NMR spectra displayed expected resonances. The ring proton and carbon resonances appeared at lower field for 1a and 1b from the corresponding signals for the free ligand. The coordination of ring nitrogen (N-3) to the metal atom can be inferred from the chemical shift of C-4 resonance. The signal appeared at lower field (135.7-137.2 ppm) than its position for the free ligand (133.6 ppm). The acetate groups showed single absorptions in the ¹H and ¹³C NMR spectra suggesting their magnetic equivalence. The ⁷⁷Se-{1H} NMR spectra of **1a** and **1c** showed a singlet which was deshielded by ≈45 ppm from its position in free ligand. The nitrogen coordination to metal center may be inducting electron density from the selenium atom consequently resulting in deshielding.³² The ¹H NMR spectrum of 2a showed a complex pattern which may be due to magnetically different ligand moieties in an associated structure.

X-ray Crystallography. The molecular structure of $[Cd(OAc)_2\{(MeImSe)_2\}]$ (**1b**), which crystallized as a hydrate, is shown in Figure 1 and the selected bond lengths and angles are given in Table 2. The coordination environment around the central cadmium atom is distorted octahedral defined by the O_4N_2 core of two asymmetrically chelated acetate groups and the chelating diselenide. The degree of asymmetry of the acetate group in the Cd–O bond distances is slightly different with the difference between the Cd–O bond distances being 0.10-0.23 Å. The Cd–O distances (2.289 and 2.521 Å) are well in agreement with those reported in several cadmium complexes. $^{33-35}$

The diselenide ligand forms a seven-membered chelate ring and binds the metal atom through imidazole nitrogen atoms. There is a marked change in the geometry of the diselenide on coordination. The Se–Se distance (2.336(1) Å) is reduced on complexation (free ligand 2.3568(15) Å); whereas the C–N distances in one of the imidazole rings are marginally reduced while the same in other ring are little affected. The N–C–Se angles $(127.2(4) \text{ and } 125.7(4)^\circ)$ open up marginally on coordination (free ligand $122.8(3)^\circ$). The Cd–N distances are considerably shorter than those reported (2.33-2.44 Å) in $[\text{Cd(SeCOPh)}_2(\text{tmen})]$, $[\text{Cd(Sepy)}_2]_n$, and $[\text{Cd(S}_2\text{COEt)}_2(\text{phen})]$.

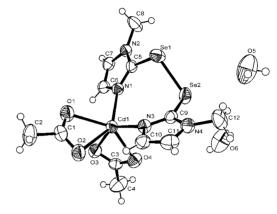


Figure 1. Crystal structure of [Cd(OAc)₂{(MeImSe)₂}]• 2H₂O with atomic numbering scheme. The ellipsoids were drawn at the 25% probability level.

Table 2. Bond Lengths (Å) and Angles (°) for [Cd(OAc)₂-{(MeImSe)₂}]•2H₂O

{(Mennse) ₂ }]•2H ₂ O			
Cd1-N1	2.267(4)	N1-C5	1.323(6)
Cd1-N3	2.230(4)	N2-C5	1.358(6)
Cd1-O1	2.289(4)	N3-C9	1.314(6)
Cd1-O2	2.521(4)	N4-C9	1.352(6)
Cd1-O3	2.435(4)	O1-C1	1.242(6)
Cd1-O4	2.335(4)	O2-C1	1.255(6)
Se1-C5	1.904(5)	O3-C3	1.240(6)
Se2-C9	1.904(5)	O4-C3	1.265(6)
Se2-Se1	2.336(1)		
N3-Cd1-N1	107.57(15)	O3-Cd1-O2	92.75(13)
N3-Cd1-O1	117.36(14)	C5-Se1-Se2	99.09(15)
N1-Cd1-O1	91.23(14)	C9-Se2-Se1	99.81(15)
N3-Cd1-O4	92.37(13)	C5-N1-C6	106.3(4)
N1-Cd1-O4	105.02(14)	C5-N1-Cd1	134.3(3)
O1-Cd1-O4	140.21(13)	C6-N1-Cd1	119.2(3)
N3-Cd1-O3	145.42(14)	C9-N3-Cd1	129.2(3)
N1-Cd1-O3	91.80(14)	C10-N3-Cd1	124.3(4)
O1-Cd1-O3	89.76(13)	O1-C1-O2	122.6(5)
O4-Cd1-O3	54.35(13)	O3-C3-O4	121.1(5)
N3-Cd1-O2	87.54(14)	N1-C5-Se1	127.2(4)
N1-Cd1-O2	144.78(13)	N2-C5-Se1	122.4(4)
O1-Cd1-O2	53.90(13)	N3-C9-Se2	125.7(4)
O4-Cd1-O2	105.94(13)	N4-C9-Se2	123.1(4)

The water molecules are associated with [Cd(OAc₂)-{(MeImSe)₂}] through hydrogen bonding, a view showing such contacts is given in Figure 2. The water molecule forms long O–H···O hydrogen bonds with the oxygen atoms of two acetate groups of neighboring molecules involving O5–H5′···O2 (2.006 Å) and O5–H5″···O4 (2.087 Å) contacts. Additional

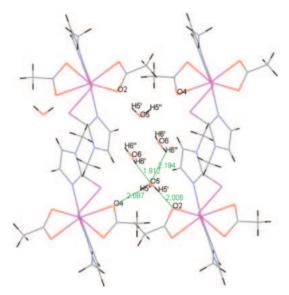


Figure 2. Line diagram of [Cd(OAc)₂{(MeImSe)₂}]. 2H₂O showing intermolecular hydrogen bondings.

contacts of this water molecule involve bonds with two other free water molecules in the lattice (O6–H6′···O5 = $2.1912 \,\text{Å}$) and (O6–H6″···O5 = $2.194 \,\text{Å}$).

Thermal Studies. TG analyses of **1** were carried out to assess their suitability as precursors for the preparation of metal selenides. These complexes underwent two—three step decomposition with onset temperatures of 165 (**1a**), 170 (**1b**), and $105\,^{\circ}\text{C}$ (**1c**). The decomposition led to the formation of metal selenides as inferred from % weight loss and confirmed from the XRD patterns of the residues. The XRD patterns of the residues from **1a** (XRD d values (Å) 3.27, 2.00, and 1.706) and **1c** (XRD d values (Å) 3.51, 2.15, and 1.83) have been interpreted in terms of cubic MSe (M = Zn³⁷ or Hg³⁸) while the pattern of the residue from **1b** was in conformity with the hexagonal CdSe (XRD d values (Å) 3.71, 3.49, 3.28, 2.54, 2.14, 1.97, and 1.83) (Figure 3).³⁹

Having assessed the suitability of 1 as precursors for metal selenide synthesis, it was considered worth exploring their decomposition in coordinating solvents. Thus, solvothermal decomposition of 1a and 1c in HDA/TOPO mixture gave cubic MSe (M = Zn or Hg) quantum dots while **1b** yielded hexagonal CdSe nanoparticles (from XRD). The EDAX analyses (ZnSe: Found: Zn, 46.4; Se, 53.7%. Calcd for ZnSe: Zn, 45.3; Se, 54.7%. CdSe: Found: Cd, 61.1; Se, 38.9%. Calcd for CdSe: Cd, 58.7; Se, 41.3%) was consistent with the MSe composition. The particle sizes estimated from Scherrer formula^{40,41} are 1.6 (ZnSe), 6.6 (CdSe), and 4.6 (HgSe) nm. The TEM images of these particles show that they are spherical in shape (Figure 4) with an average diameter of 6 (ZnSe), 10 (CdSe), and 8 (HgSe) nm. The mismatch between the sizes estimated by XRD and obtained by TEM is because particle size does not determine the line width directly in XRD.⁴² The particles obtained were crystalline as determined by SAED. SAED patterns of nanoparticles revealed that the formation of cubic MSe (M = Zn and Hg) or hexagonal CdSe with diffraction rings corresponding to lattice planes: (111), (220), (311), (400), (331), and (422) (ZnSe); (100), (220), and (311) (HgSe); and (100), (002), (101), (110), and (112) (CdSe). The phases

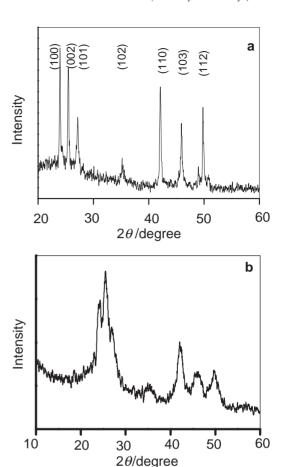


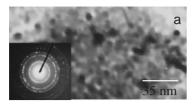
Figure 3. a) XRD pattern of the TG residue of [Cd(OAc)₂-{(MeImSe)₂}] (hexagonal CdSe), b) XRD pattern of CdSe obtained from solvothermal decomposition of the precursor in HDA/TOPO mixture (4:1) at 178 °C for 20 min.

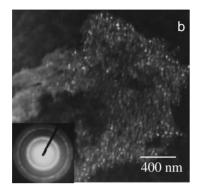
determined from XRD and SAED patterns were in agreement with each other.

Semiconducting materials show quantum confinement effect when their particle size becomes equal or less than the Bohr's radius of that material. The quantum confinement effect is manifested in the absorption spectra where absorption, depending on the size of the particle, is blue shifted from the bulk material value. 43,44 The electronic spectra in methanol (Figures 5 and 6) of metal selenide nanoparticles prepared during this study displayed absorptions at 377 (ZnSe), 608 (CdSe), and 588 (HgSe) nm, which were blue shifted with respect to the absorptions for bulk materials [480 (ZnSe), 713 (CdSe), and 12400 (HgSe) nm]. This suggests that the particles are quantum confined. Absorption spectrum of HgSe particles showed a broad absorption edge tailing into the infrared end of the spectrum. Excitation profiles of these dots displayed maxima at 358 (1a), 603 (1b), and 582 (1c) nm whereas emission profiles showed an emission maxima at 433 (ZnSe), 694 (CdSe), and 674 (HgSe) nm. The narrow fwhm (full width at half maxima) of the emission peaks of ZnSe and CdSe nanoparticles shows their narrow size distribution.

Conclusion

The Group 12 complexes, devoid of any M-Se linkage, of an internally functionalized diselenide have been isolated as





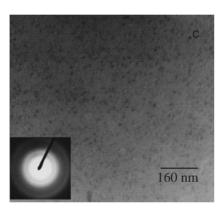


Figure 4. TEM pictures of MSe quantum dots; inset shows SAED pattern of (a) ZnSe, (b) CdSe, and (c) HgSe.

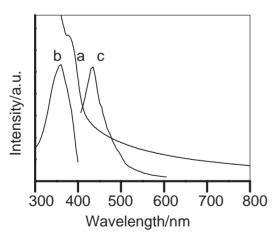


Figure 5. a) Absorption spectrum, b) excitation, and c) emission profiles of ZnSe quantum dots obtained by the thermolysis of [Zn(OAc)₂{(MeImSe)₂}].

monomeric, air stable molecules, which can be stored at room temperature for several months. These molecules have been demonstrated to serve as convenient precursors for the preparation of metal selenide quantum dots. Despite the low temper-

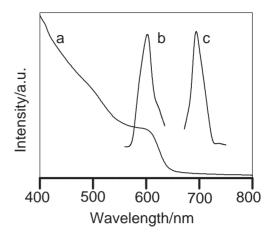


Figure 6. a) Absorption spectrum, b) excitation, and c) emission profiles of CdSe quantum dots obtained by the thermolysis of [Cd(OAc)₂{(MeImSe)₂}].

ature (95 $^{\circ}\text{C})$ and reaction time of synthesis, the HgSe quantum dots obtained were crystalline in nature.

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