Synthesis and X-Ray Single Crystal Structures of Cadmium(II) Complexes: $\text{CdCl}_2[\text{CS}(\text{NHCH}_3)_2]_2$ and $\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHC}_6\text{H}_5)_4$ - Single Source Precursors to CdS Nanoparticles

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Abstract: Two new cadmium(II) complexes $\text{CdCl}_2[\text{CS}(\text{NHCH}_3)_2]_2$ (**1**) and $\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHC}_6\text{H}_5)_4$ (**2**) have been synthesized and characterized by spectroscopic and x-ray crystallographic methods. Both compounds are monomers in the solid state with the four and six coordinate and their coordination geometries based on distorted tetrahedron and distorted octahedron respectively. The thiourea ligands behave as monodentate in both compounds with the binding through sulfur. Complex (**2**) is one of the few examples of monomeric six coordinate Cd(II) complexes with four monodentate thiourea and two chloride ligands. The Cd-S bond proved useful as a source of preparing nanoparticles using these complexes as single source precursor at a temperature of 250 °C in trioctylphosphine oxide (TOPO).

Keywords: Cadmium(II) complexes, Thiourea derivatives, CdS nanoparticles.

Introduction

The chemistry of the substituted thiourea derivatives has attracted attention because of their potential for biological use and as highly selective reagents for separation of metal cations¹. Biological applications involve their use as antibacterial^{2,3}, antiviral⁴ and antifungal agents^{5,6}. In addition to their applications, they are ligands of interest as they possess various potential donor sites: the sulphur atom of the C-S group and the nitrogen atom of the NH, NHR or

NRR` groups (where R = R` = alkyl or aryl groups). Their coordination chemistry led to their interest as potential precursors for cadmium sulfide nanoparticles, which has potential applications in the microelectronic industry.

Semiconductor nanoparticles fall into the size regime such that bulk properties give way to those of the individual assembly. At these critical size dimensions so called quantum confinement effects dominate the electronic properties and result in a blue shift in the band gap. This effect makes it possible the tuning of the absorption and potentially the emission of electromagnetic radiation. Semiconductor nanomaterials can exhibit **3-d** quantum confinement⁷ and have potential applications in light emitting diodes⁸⁻¹⁰, solar cells^{11,12}, biological labeling^{13,14} and catalysis¹⁵.

We have reported in the past the synthesis of cadmium sulfide nanoparticles from several different alkylthiourea complexes of cadmium, methyl and ethyl groups^{16,17}. The method produced good yields of quality crystalline CdS nanoparticles, but particles showing tendency to form agglomerates. We report in this paper the single crystal x-ray structures of two novel complexes of cadmium(II) thiourea derivatives, CdCl₂[CS(NHCH₃)₂]₂ (**1**) and CdCl₂(CS(NH₂)NHC₆H₅)₄ (**2**) and the properties as well as the morphology of the CdS particles prepared using the single source precursor route.

Experimental

Cadmium chloride, tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylphosphine (TOP), hexadecylamine (HDA), *N*-phenylthiourea and *N,N*-dimethylthiourea obtained from Aldrich, were used as purchased. Ethanol, methanol, toluene (all analytical grade) were obtained from Aldrich and used without further purification. Both compounds were prepared using a literature method; preparation of complexes¹⁶ and preparation of metal sulfide nanoparticles^{17,18}. The complexes were synthesized by the reaction of the salt, cadmium chloride with alkylthiourea dissolved in ethanol under a reflux for 1 - 2 h in a mole ratio 1:2. All compounds were obtained as white crystalline solids, which were dried under vacuum and used for the deposition of nanocrystals. Crystals were grown overnight, by re-crystallizing the products in ethanol. Slow evaporation of the solvent at room temperature yielded transparent crystals. CdS nanoparticles were prepared using about 10 g of HDA and 0.75 g of the complex at 250 °C for 1 h.

Characterization

Metal complexes

Microanalysis was performed on a CARLO ERBA elemental analyser for C, H, N, S while for Cd, Horizon ICP Fisons elemental analyser was used. Infrared spectra were recorded on FT-IR Perkin Elmer Paragon 1000 spectrophotometer using nujol mull. NMR spectra were recorded on a Varian Associates Inova spectrometer (400 and 300 MHz). X-ray data was collected on an Enraf Nonius CAD-4 diffractometer. The intensity data were collected on a CAD-4 diffractometer and Mo K α radiation (λ 0.71069 Å) using ω -2 θ scan at 180.0(1) K. The unit cell parameters were determined by least-squares refinement on diffractometer angles (**1**, $2.78 \leq \theta \leq 24.94^\circ$ and **2**, $2.49 \leq \theta \leq 24.97^\circ$) for 25 automatically centered reflections¹⁹. All data were corrected for Lorentz-polarization effects by XCAD4²⁰ and for absorption by semi-empirical methods (ψ scan)²¹. The structure was solved by Patterson method using DIRDIF99²² and refined anisotropically (non-hydrogen atoms) by full-matrix least squares on F² using SHELXL-97²³ program. The H atoms were calculated geometrically and refined with a riding model. The program ORTEP-3²⁴ PLATON²⁵ was used for drawing the molecules. WINGX²⁶ used to prepare material for publication. Experimental data is given in Table 1.

Table 1. Crystal data and detailed structure refinement for complex **1** and **2**.

	1	2
Empirical formula	C ₆ H ₁₆ Cd Cl ₂ N ₄ S ₂	C ₂₈ H ₃₂ Cd Cl ₂ N ₈ S ₄
Formula weight	391.65	792.16
Temperature	293(2) K	160(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	Aa	I 2/a
Unit cell dimensions	a = 12.791(3) Å b = 8.992(2) Å c = 13.271(3) Å	a = 25.098(6) Å b = 8.133(2) Å c = 16.768(3) Å
Volume	1446.2(6) Å ³	3341.2(13) Å ³
Z	4	4
Density (calculated)	1.799 Mg/m ³	1.575 Mg/m ³
Absorption coefficient	2.146 mm ⁻¹	1.097 mm ⁻¹
F(000)	776	1608
Crystal size	0.40 x 0.20 x 0.20 mm ³	0.40 x 0.30 x 0.20 mm ³
Theta range for data collection	2.78 to 24.94°.	2.49 to 24.97°.
Index ranges	-15 ≤ h ≤ 14, -3 ≤ k ≤ 10, -2 ≤ l ≤ 15	0 ≤ h ≤ 29, 0 ≤ k ≤ 9, -19 ≤ l ≤ 19
Reflections collected	1386	3070
Independent reflections	1330 [R(int) = 0.0046]	2934 [R(int) = 0.0135]
Completeness to θ = 24.94°	99.7 %	99.9 % (θ = 24.97°)
Max. and min. transmission	0.6736 and 0.4807	0.8104 and 0.6681
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	1330 / 2 / 140	2934 / 0 / 172
Goodness-of-fit on F ²	1.075	1.127

Nanoparticles

A Perkin Elmer Lambda 20 UV-Vis Spectrophotometer was used to carryout the optical measurements and the samples were placed in silica cuvettes (1 cm, path length), using toluene as a reference solvent. A Jobin Yvon-spex-Fluorolog-3-Spectrofluorimeter with a xenon lamp (150 W) and a 152 P photomultiplier tube as a detector was used to measure the photoluminescence of the particles. The samples were placed in quartz cuvettes (1 cm path length). The HRTEM images and SAED patterns were obtained using a Philips CM 200 compustage electron microscope operated at 200 kV with a EDS analyser. The samples were prepared by placing a drop of a dilute solution of sample in toluene on a copper grid (400 mesh, agar). The samples were allowed to dry completely at room temperature. X-Ray diffraction patterns on powdered samples were measured on Phillips X'Pert materials research diffractometer using secondary graphite monochromated CuK_α radiation ($\lambda = 1.54060$ Å) at 40 kV/ 50 mA. Samples were supported on glass slides. Measurements were taken using a glancing angle of incidence detector at an angle of 2° , for 2θ values over 20° - 60° in steps of 0.05° with a scan speed of $0.01^\circ 2\theta.s^{-1}$.

Results and Discussion

Both complexes crystallized in ethanol by slow evaporation at room temperature to give transparent cube-shaped crystals. Both are air stable with melting points higher than 200 °C. ORTEP diagrams of complexes **1** and **2** with the atomic labeling scheme are shown in Figure 1 and 2, respectively. Selected bond lengths and angles are given in Table 2.

Figure 1. ORTEP drawing of complex **1**, $(\text{CdCl}_2[\text{CS}(\text{NHCH}_3)_2]_2)$ (a) and its packing diagram (b).

Figure 2. ORTEP drawing of complex **2**, $\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHC}_6\text{H}_5)_4$.

The molecular structure of complex **1** is based on a monomer where cadmium is bonded to two chloride ions (Cd-Cl 2.4443 and 2.4782 Å) and two sulfur atoms from the thiourea ligands (Cd-S 2.5010 and 2.5212 Å; C-S 1.7963 and 1.6425 Å). The co-ordination geometry around cadmium can be described as a distorted tetrahedron. The bond angles are close to those of a perfect tetrahedron, S(2)-Cd(1)-S(1) 108.43°, S(2)-Cd(1)-Cl(1) 110.57°, S(1)-Cd(1)-Cl(1) 108.10°, Cl(2)-Cd(1)-Cl(1) 108.83°, Cl(2)-Cd(1)-S(1) 110.12° and Cl(2)-Cd(1)-S(2) 110.75° around cadmium ion. In a unit cell, the methyl groups in each thiourea ligand lie closer to the sulfur atoms of the neighboring compound, due to the existence of hydrogen bond interactions. These hydrogen bond interactions exist also between the chloride ions and the other methyl group.

The cadmium(II) ion in complex **(2)** is bonded to two chloride ions (Cd-Cl 2.7557 and 2.4782 Å) and four sulfur atoms from the thiourea ligands (Cd-S 2.6282 and 2.7429 Å; C-S 1.7095 and 1.7214 Å), hence the co-ordination geometry around it can be described as a distorted octahedron. The bond angles are close to those of a perfect octahedron, S(2)-Cd(1)-S(1) 91.19°, S(2)-Cd(1)-Cl(1) 90.28°, S(1)-Cd(1)-Cl(1) 87.49°, Cl(1)#1-Cd(1)-Cl(1) 180.0°, S(1)-Cd(1)-S(1)#1 180.0°, S(2)-Cd(1)-S(2)#1 180.0°, Cl(1)#1-Cd(1)-S(1) 92.51°, Cl(1)#1-Cd(1)-S(2) 89.72°, S(1)-Cd(1)-S(2)#1 88.81° and Cl(1)#1-Cd(1)-S(2) 89.72° around cadmium.

Table 2. Selected bond distances (Å) and bond angles (°) for complex **1** and **2**.

Bond distances (Å)			
2		1	
Cd(1)-Cl(1)	2.7556 (9)	Cd(1)-Cl(1)	2.472 (8)
Cd(1)-Cl(1)#1	2.7556 (9)	Cd(1)-Cl(2)	2.450 (9)
Cd(1)-S(1)	2.6282 (8)	Cd(1)-S(1)	2.502 (7)
Cd(1)-S(1)#1	2.6282 (8)	Cd(1)-S(2)	2.521 (7)
Cd(1)-S(2)	2.7429 (7)	S(1)-C(1)	1.81 (2)
Cd(1)-S(2)#1	2.7429 (7)	S(2)-C(4)	1.63 (2)
S(1)-C(1)	1.708 (2)	N(1)-C(1)	1.33 (3)
S(2)-C(8)	1.722 (2)	N(3)-C(4)	1.30 (3)
N(1)-C(1)	1.324 (3)	N(2)-C(1)	1.22 (4)
N(3)-C(8)	1.323 (3)	N(4)-C(4)	1.44 (3)
N(2)-C(1)	1.338 (3)		
N(4)-C(8)	1.333 (3)		
Bond angles (°)			
S(1)-Cd(1)-S(2)	91.19 (2)	S(1)-Cd(1)-S(2)	108.43 (10)
S(1)-Cd(1)-Cl(1)#1	92.51 (2)	S(1)-Cd(1)-Cl(2)	110.3 (2)
S(2)-Cd(1)-Cl(1)#1	89.72 (2)	S(2)-Cd(1)-Cl(2)	111.0 (3)
Cl(1)-Cd(1)-Cl(1)#1	180.00 (15)	Cl(1)-Cd(1)-Cl(2)	108.83 (13)
Cl(1)-Cd(1)-S(2)	90.28 (2)	Cl(1)-Cd(1)-S(2)	110.4 (3)
Cl(1)-Cd(1)-S(1)	87.49 (2)	Cl(1)-Cd(1)-S(1)	107.9 (3)
S(1)-Cd(1)-S(2)#1	88.81 (2)		
S(1)-Cd(1)-S(1)#1	180.00 (2)		
S(2)-Cd(1)-S(1)#1	88.81 (2)		
S(2)#1-Cd(1)-S(1)#1	91.19 (2)		
S(2)-Cd(1)-S(2)#1	180.00		
S(1)#1-Cd(1)-Cl(1)#1	87.49 (2)		
S(2)#1-Cd(1)-Cl(1)#1	90.28 (2)		
S(2)#1-Cd(1)-Cl(1)	89.72 (2)		

Symmetry transformations used to generate equivalent atoms: # -x + 1/2, -y + 1/2, -z + 1/2

The common feature in the two structures is the coordination behavior of the thiourea ligands in that both are mono-coordinated by sulfur atoms to the cadmium atom. The geometry for complex **2** is similar to the polymeric complex, $\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHCH}_3)_2$, whereas complex **1** shares the geometry with the compound, $\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHCH}_2\text{CH}_3)_2$ reported recently by our group¹⁶. The bond lengths variations and the geometries around the cadmium ion in these compounds are consistent with other similar *N*-alkyl substituted thiourea cadmium compounds¹⁶ and the bis(thiourea)cadmium halides²⁷. The C-S bond lengths lie on either range associated with C-S single bonds (1.70 – 1.80 Å)²⁸ for complex **1**, whereas for complex **2**, they lie at the lower end. The phenyl groups in complex **2** adopt a

pseudo-anti-periplanar arrangement in order to minimize their steric crowding. The C-N bond lengths of the amide group of the thiourea ligands are intermediate between a single and a double bond (1.3182 - 1.3403 Å) in complex **2**, whereas they lie on either end of the single or double bond (1.2428 - 1.4185 Å) in complex **1**. This is attributed to the delocalization of electrons in the amide bond of the thiourea ligands.

Synthesis of cadmium sulfide nanoparticles

Following the successful use of the *N*-methyl- and *N*-ethylthiourea cadmium complexes to prepare good quality TOPO-capped CdS nanoparticles, the complexes *N*-phenyl and *N*-dimethylthiourea were also thermolysed in TOPO to provide particles with less agglomeration although larger at this temperature, 250 °C. The blue shift was observed for these two precursors in relation to the bulk, 484 nm (**1**) and 493 nm (**2**), with the good distribution of sizes of particles as observed from the emission spectra with maxima 491 and 517 nm for precursor **1** and **2** respectively.

Figure 3. Optical and emission spectra of TOPO-capped CdS nanoparticles prepared from complex **1** (a) and **2** (b) at 250 °C.

The preparation of CdS nanoparticles shows predominance of the formation of either as the cubic or hexagonal phase. The XRD patterns of the present CdS particles are entirely consistent with a predominantly hexagonal phase. The (100), (101) and (002) planes are the most intense in all samples and are clearly distinguishable in the patterns as planes of hexagonal CdS phase. The selected area electron diffraction (SAED) patterns (Figure 4) consist of broad diffuse rings, which are indicative of the small size of the particles. The diffraction rings can be indexed to the (100), (002), (110) and (004) planes confirming the wurtzite phase. The broadening of the peaks on the diffractogram (Figure 4) obtained from the precursors is consistent with the particle sizes 8.8 nm (**1**) and 10.3 nm (**2**) at 250 °C.

Figure 4. XRD patterns for the CdS nanoparticles from the complex **2** (a) and **1** (b) and their SAED patterns.

Figure 5. TEM image of CdS nanoparticles from complex **1**.

The CdS nanoparticles show a tendency to agglomerate as they settle on the carbon-coated copper grid (Figure 6a) although clearly crystalline nanoparticles are obtained as shown by the high-resolution TEM image (Figure 6b). These high-resolution TEM images show the crystallinity of the particles confirmed by the lattice planes observed on the images.

Figure 6. TEM (a) and HRTEM (b) images showing lattice planes of CdS nanoparticles from complex **II**.

Conclusion

Two cadmium complexes of thiourea derivatives, **1** and **2**, have been synthesized and characterized by single x-ray crystal methods. Both structures are monomeric with a distorted tetrahedral geometry for complex **1** and a distorted octahedral geometry for complex **2**. In both cases the thiourea ligands were coordinated to the metal atom by sulphur atoms. The complexes proved successful in preparing CdS nanoparticles using the single source precursor method. The CdS nanoparticles prepared were hexagonal with lattice planes and blue shift in their absorption spectra typical of nanocrystalline materials.

Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 201442 for $(\text{CdCl}_2[\text{CS}(\text{NHCH}_3)_2]_2)$ and CCDC No. 201443 for $\text{CdCl}_2(\text{CS}(\text{NH}_2)\text{NHC}_6\text{H}_5)_4$. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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