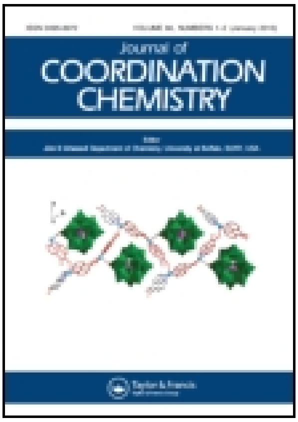

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# Synthesis and spectral studies on nitrogen donor adducts of bis(4-ethylpiperazinecarbodithioato-S,S′)M(II) (M = Zn, Cd) and use of adducts of cadmium dithiocarbamate for the preparation of cadmium sulfide

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[M(4-epzdtc)$_2$(py)], [M(4-epzdtc)$_2$(1,10-phen)], and [M(4-epzdtc)$_2$(2,2′-bipy)] (where M = Zn(II), Cd(II); 4-epzdtc$^-$ = 4-ethylpiperazinecarbodithioate) were synthesized and characterized by IR and NMR ($^1$H, $^{13}$C, HSQC and HMBC) spectra. A single-crystal X-ray analysis was carried out for [Zn(4-epzdtc)$_2$(py)]. The N$^{13}$CS$_2$ chemical shifts of [M(4-epzdtc)$_2$] and its adducts follow the order: [M(4-epzdtc)$_2$] (*ca* 202 ppm) < [M(4-epzdtc)$_2$(py)] (*ca* 204 ppm) < [M(4-epzdtc)$_2$(N,N)] (N,N = 1,10-phen, 2,2′-bipy) (*ca* 206 ppm), due to the change in coordination number. Single-crystal X-ray structural analysis of [Zn(4-epzdtc)$_2$(py)] showed that zinc is five-coordinate with four sulfurs from dithiocarbamate and one nitrogen from pyridine. This complex adopts a geometry intermediate between the tetragonal pyramid ($C_{4v}$) and trigonal bipyramid ($D_{3h}$). [Cd(4-epzdtc)$_2$] and its adducts were used as single source precursors for preparation of CdS. The as-prepared CdS was characterized by powder X-ray diffraction, UV-Vis absorption, and fluorescence spectroscopy. The UV-Vis absorption spectra of CdS particles indicate a blue shift in the absorption spectra due to the quantum size effect.

*Keywords*: 4-Ethylpiperazinecarbodithioate; Sulfide; Cd(II); Crystal structure

## 1. Introduction

A driving force for investigation of Group XII 1,1-dithiolate chemistry is the fact that these materials display a wide range of applications. Dithiocarbamate containing coordination compounds have been widely studied because of their biological, industrial, agricultural, and chemical applications [1]. Dithiocarbamates of many metals tend to reversibly add organic N, O, S, and P-donors to give heteroligand complexes generically called adducts. Because such molecules are usually volatile in vacuum, such adducts are of practical interest as precursors of metal-sulfide films with semiconducting and luminescent properties [2, 3]. Metal dithiocarbamate complexes have proven to be very successful as single source precursors for the

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preparation of EuS, PdS, PtS, PbS, $Bi_2S_3$, NiS, $Ni_3S_2$, CuS, ZnS, and CdS nanoparticles [4]. The phase and morphology of the resultant materials are often influenced by the precursors (as well as by the solvent and thermolysis temperature) [5]. In this work, we have used [$Cd(4epzdtc)_2$], [$Cd(4epzdtc)_2(py)$], [$Cd(4epzdtc)_2$(1,10-phen)], and [$Cd(4epzdtc)_2$(2,2′-bipy)] as single source precursors and ethylenediamine as solvent. We report synthesis and spectral studies on [M(4-epzdtc)$_2$(py)], [M(4-epzdtc)$_2$(1,10-phen)], and [M(4-epzdtc)$_2$(2,2′-bipy)] and the use of adducts of cadmium dithiocarbamates for the preparation of CdS. A single-crystal X-ray structure analysis of [Zn(4-epzdtc)$_2$(py)] is also reported.

## 2. Experimental

All reagents and solvents were commercially available high grade materials (Sigma-Aldrich/Sd fine/Merk) and used as received. Elemental analyses (C, H, and N) were performed on a Perkin Elmer 2400 Series II CHN Instrument. IR spectra were recorded on a Thermo NICOLET AVATAR 330 FT-IR spectrophotometer (range: 400–4000 $cm^{-1}$) as KBr pellets. The NMR spectra were recorded on a BRUKER-NMR spectrometer operating at 500 MHz. CdS is characterized by powder X-ray diffraction using a XPERT-PRO diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.54060$ Å). A Shimadzu UV-1650 PC double beam UV-Vis spectrophotometer was used for recording electronic spectra. Fluorescence spectra were recorded at room temperature with a spectrofluorophotometer (SHIMADZU RF-5301) using 400 nm as the excitation wavelength.

### 2.1. *Preparation of the complexes*

The bis(4-ethylpiperazinecarbodithioato-S,S′)M(II) (M = Zn, Cd) complexes were prepared by using the established procedure [6]. [M(4-epzdtc)$_2$(py)] were prepared by dissolving the parent dithiocarbamates in warm pyridine. The yellow solution obtained was filtered and kept for evaporation. After a few days, both powder and single crystals suitable for X-ray analysis were obtained. [M(4-epzdtc)$_2$(1,10-phen)] and [M(4-epzdtc)$_2$(2,2′-bipy)] were prepared by adding a hot solution of 1,10-phenanthroline (2 mmol) or 2,2′-bipyridine (2 mmol) in ethanol to a hot solution of [M(4-epzdtc)$_2$] (1 mmol) in chloroform. The resulting solution was cooled and then petroleum ether (boiling range: 60–80°C) was added. Yellow precipitate of the adducts separated.

### 2.2. *Preparation of CdS from Cd(4-epzdtc)$_2$ and its adducts*

1.0 g of [Cd(4-epzdtc)$_2$] was dissolved in 15 mL of ethylenediamine in a flask, and then heated to reflux (117°C), and maintained at this temperature for 2 min. The yellowish CdS precipitate was filtered off and washed with methanol. Similar procedure was adopted for the preparation of CdS from [Cd(4-epzdtc)$_2$(py)], [Cd(4-epzdtc)$_2$(1,10-phen)], and [Cd(4-epzdtc)$_2$(2,2′-bipy)].

### 2.3. *Spectral data of the complexes*

**[Zn(4-epzdtc)$_2$].** Yield, 78%. Anal. Calcd for $C_{14}H_{26}N_4S_4Zn$ (%): C, 37.87; H, 5.90; N, 12.62. Found: C, 37.66; H, 5.74; N, 12.48. IR (cm$^{-1}$) 1490 ($\nu_{C\text{–}N}$), 1010 ($\nu_{C\text{–}S}$); $^1$H NMR (ppm): 1.10 (t, $J=7.3$ Hz, 6H, CH$_3$), 2.48 (q, $J=7.0$ Hz, 4H, $C\underline{H}_2CH_3$), 2.56 (t, $J=5.0$ Hz, 8H, H-3), 4.12 (t, $J=5.0$ Hz, 8H, H-2); $^{13}C\{^1H\}$ NMR (ppm): 12.0 (CH$_3$), 51.1 (C-2), 51.8 ($\underline{C}H_2CH_3$), 52.0 (C-3), 202.5 (NCS$_2$).

**[Zn(4-epzdtc)$_2$(py)].** Yield, 65%. Anal. Calcd for $C_{19}H_{31}N_5S_4Zn$ (%): C, 43.62; H, 5.97; N, 13.39. Found: C, 43.41; H, 5.89; N, 13.41. IR (cm$^{-1}$): 1482 ($\nu_{C\text{–}N}$), 1009 ($\nu_{C\text{–}S}$), 1604 (pyridine); $^1$H NMR (ppm): 1.11 (t, $J=7.5$ Hz, 6H, CH$_3$), 2.47 (q, $J=7.0$ Hz, $J=7.5$ Hz, 4H, $C\underline{H}_2CH_3$), 2.55 (t, $J=5.0$ Hz, 8H, H-3), 4.18 (t, $J=5.0$ Hz, 8H, H-2), 7.49 (t, $J=7.0$ Hz, 2H, H-3 (py)), 7.88 (t, $J=7.8$ Hz, 1H, H-4 (py)), 8.99 (d, $J=5.0$ Hz, 2H, H-2 (py)); $^{13}C\{^1H\}$ NMR (ppm): 12.0 (CH$_3$), 51.1 (C-2), 51.9 ($\underline{C}H_2CH_3$), 52.1 (C-3), 124.7, 138.5, 149.5 (pyridine), 204.1 (NCS$_2$).

**[Zn(4-epzdtc)$_2$(1,10-phen)].** Yield, 74%. Anal. Calcd for $C_{26}H_{34}N_6S_4Zn$ (%): C, 50.03; H, 5.49; N, 13.46. Found: C, 49.87; H, 5.38; N, 13.38. IR (cm$^{-1}$): 1467 ($\nu_{C\text{–}N}$), 1009 ($\nu_{C\text{–}S}$), 1627, 1605, 1514 (1,10-phen); $^1$H NMR (ppm): 1.05 (t, $J=7.3$ Hz, 6H, CH$_3$), 2.39 (q, $J=7.0$ Hz, $J=7.5$ Hz, 4H, $C\underline{H}_2CH_3$), 2.46 (t, $J=4.5$ Hz, 8H, H-3), 4.18 (t, $J=5.0$ Hz, 8H, H-2), 7.80 (t, $J=5.0$ Hz, 2H, H-3 (1,10-phen)), 7.88 (s, 2H, H-5 (1,10-phen)), 8.39 (d, $J=7.5$ Hz, 2H, H-4 (1,10-phen)), 9.60 (b, 2H, H-2 (1,10-phen)); $^{13}C\{^1H\}$ NMR (ppm): 12.0 (CH$_3$), 51.0 (C-2), 51.9 ($\underline{C}H_2CH_3$), 52.2 (C-3), 124.6–149.1 (1,10-phen), 206.2 (NCS$_2$).

**[Zn(4-epzdtc)$_2$(2,2′-bipy)].** Yield, 72%. Anal. Calcd for $C_{24}H_{34}N_6S_4Zn$ (%): C, 48.01; H, 5.71; N, 14.01. Found: C, 47.88; H, 5.62; N, 13.89. IR (cm$^{-1}$): 1468 ($\nu_{C\text{–}N}$), 1011 ($\nu_{C\text{–}S}$), 1598 (bipy); $^1$H NMR (ppm): 1.07 (t, $J=7.3$ Hz, 6H, CH$_3$), 2.41 (q, $J=7.0$ Hz, $J=7.5$ Hz, 4H, $C\underline{H}_2CH_3$), 2.48 (t, $J=5.0$ Hz, 8H, H-3), 4.15 (t, $J=5.0$ Hz, 8H, H-2), 7.46 (t, $J=6.0$ Hz, 2H, H-4 (bipy)), 7.92 (t, $J=7.5$ Hz, 2H, H-5 (bipy)), 8.19(d, $J=8.0$ Hz, 2H, H-6 (bipy)), 9.13 (d, $J=4.5$ Hz, 2H, H-3 (bipy)); $^{13}C\{^1H\}$ NMR (ppm): 11.9 (CH$_3$), 51.0 (C-2), 51.9 ($\underline{C}H_2CH_3$), 52.1 (C-3), 120.8–151.5 (2,2′-bipy), 205.2 (NCS$_2$).

**[Cd(4-epzdtc)$_2$].** Yield, 70%. Anal. Calcd for $C_{14}H_{26}N_4S_4Cd$ (%): C, 34.24; H, 5.34; N, 11.41. Found: C, 34.10; H, 5.25; N, 11.27. IR (cm$^{-1}$): 1470 ($\nu_{C\text{–}N}$), 1009 ($\nu_{C\text{–}S}$); $^1$H NMR (ppm): 0.98 (t, $J=7.3$ Hz, 6H, CH$_3$), 2.31 (q, $J=8.0$ Hz, $J=7.0$ Hz, 4H,$C\underline{H}_2CH_3$), 2.37 (t, $J=5.5$ Hz, 8H, H-3), 4.03 (t, $J=5.0$ Hz, 8H, H-2); $^{13}C\{^1H\}$ NMR (ppm): 12.0 (CH$_3$), 51.9 (C-2), 52.1 ($\underline{C}H_2CH_3$), 52.9 (C-3), 203.0 (NCS$_2$).

**[Cd(4-epzdtc)$_2$(py)].** Yield, 60%. Anal. Calcd for $C_{19}H_{31}N_5S_4Cd$ (%): C, 40.03; H, 5.48; N, 12.28. Found: C, 39.97; H, 5.40; N, 12.23. IR (cm$^{-1}$): 1478 ($\nu_{C\text{–}N}$), 1014 ($\nu_{C\text{–}S}$), 1650 (pyridine); $^1$H NMR (ppm): 1.01 (t, $J=7.0$ Hz, 6H, CH$_3$), 2.36 (q, $J=7.5$ Hz, $J=7.3$ Hz, 4H, $C\underline{H}_2CH_3$), 2.42 (t, $J=5.0$ Hz, 8H, H-3), 4.08 (t, $J=5.0$ Hz, 8H, H-2), 7.40 (t, $J=4.5$ Hz, 2H, H-3 (py)), 7.80 (t, $J=7.5$ Hz, 1H, H-4 (py)), 8.59 (d, $J=4.5$ Hz, 2H, H-2 (py)); $^{13}C\{^1H\}$ NMR (ppm): 12.2 (CH$_3$), 51.5 (C-2), 52.2 ($\underline{C}H_2CH_3$), 52.4 (C-3), 124.5, 136.9, 150.0 (pyridine), 204.6 (NCS$_2$).

**[Cd(4-epzdtc)$_2$(1,10-phen)].** Yield, 68%. Anal. Calcd for $C_{26}H_{34}N_6S_4Cd$ (%): C, 46.52; H, 5.11; N, 12.52. Found: C, 46.37; H, 5.06; N, 12.39. IR (cm$^{-1}$): 1467 ($\nu_{C\text{–}N}$), 1008 ($\nu_{C\text{–}S}$), 1619, 1587, 1508 (1,10-phen); $^1$H NMR (ppm): 1.09 (t, $J=7.3$ Hz, 6H, CH$_3$),

Table 1. Crystal data, data collection, and refinement parameters for [Zn(4-epzdtc)$_2$(py)].

| | |
|---|---|
| Empirical formula | $C_{19}H_{31}N_5S_4Zn$ |
| Formula weight | 523.10 |
| Crystal dimensions (mm$^3$) | 0.45 × 0.40 × 0.30 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 10.5660(10) |
| $b$ | 27.3080(10) |
| $c$ | 8.7278(4) |
| $\alpha$ | 90.00 |
| $\beta$ | 90.294(6) |
| $\gamma$ | 90.00 |
| Volume (Å$^3$), $Z$ | 2518.3(3), 4 |
| Calculated density (g cm$^{-3}$) | 1.380 |
| Absorption coefficient (cm$^{-1}$) | 1.322 |
| $F$(000) | 1096 |
| λ (Å) | Mo-Kα (0.71069) |
| $\theta$ range (°) | 4.25–28.94 |
| Index ranges | $-13 \le h \le 13$; $-36 \le k \le 34$; $-11 \le l \le 11$ |
| Reflections collected | 5191 |
| Observed reflections $F_o > 4\sigma(F_o)$ | 2272 |
| Weighting scheme | Calcd $W = 1/(\sigma^2(F_o^2) + (0.0283P)^2 + 0.0000P)$,<br>where $P = (F_o^2 + 2F_c^2)/3$ |
| Number of parameters refined | 262 |
| Final $R$, $R_w$ (all data) | 0.1091, 0.0744 |
| Goodness-of-fit on $F^2$ | 0.759 |

2.43 (q, $J = 7.5$ Hz, $J = 7.0$ Hz, 4H, $C\underline{H}_2CH_3$), 2.49 (t, $J = 5.0$ Hz, 8H, H-3), 4.24 (t, $J = 5.0$ Hz, 8H, H-2), 7.85 (t, $J = 4.0$ Hz, 2H, H-3 (1,10-phen)), 7.92 (s, 2H, H-5 (1,10-phen)), 8.43 (d, $J = 8.0$ Hz, 2H, H-4 (1,10-phen)), 9.44 (b, 2H, H-2 (1,10-phen)); $^{13}C\{^1H\}$ NMR (ppm): 11.9 ($CH_3$), 51.9 (C-2), 52.0 ($\underline{C}H_2CH_3$), 52.2 (C-3), 124.7–149.7 (1,10-phen), 206.7 ($NCS_2$).

**[Cd(4-epzdtc)$_2$(2,2′-bipy)].** Yield, 70%. Anal. Calcd for $C_{24}H_{34}N_6S_4Cd$ (%): C, 44.52; H, 5.30; N, 12.99. Found: C, 44.39; H, 5.21; N, 12.87. IR (cm$^{-1}$): 1470 ($\nu_{C-N}$), 1014 ($\nu_{C-S}$), 1591 (2,2′-bipy); $^1$H NMR (ppm): 1.09 (t, $J = 7.5$ Hz, 6H, $CH_3$), 2.44 (q, $J = 5.0$ Hz, $J = 8.0$ Hz, 4H, $C\underline{H}_2CH_3$), 2.51 (t, $J = 5.0$ Hz, 8H, H-3), 4.23 (t, $J = 5.0$ Hz, 8H, H-2), 7.52 (t, $J = 7.5$ Hz, 2H, H-4 (bipy)), 7.97 (t, $J = 5.0$ Hz, 2H, H-5 (bipy)), 8.17(d, $J = 10.0$ Hz, 2H, H-6 (bipy)), 9.06 (d, $J = 5.0$ Hz, 2H, H-3 (bipy)); $^{13}C\{^1H\}$ NMR (ppm): 12.0 ($CH_3$), 51.9 (C-2), 52.1 ($\underline{C}H_2CH_3$), 52.2 (C-3), 121.2–150.5 (2,2′-bipy), 206.1 ($NCS_2$).

### 2.4. *X-ray crystallography*

Details of the crystal data and structure refinement parameters for [Zn(4-epzdtc)$_2$(py)] are summarized in table 1. Intensity data were collected at ambient temperature on an Xcalibur, Sapphire3 diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by SHELXS-97 [7] and refined by full matrix least square with SHELXL-97 [8]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically. Selected bond distances and angles are presented in table 2.

Table 2. Selected bond distances (Å) and angles (°) of [Zn(4-epzdtc)$_2$(py)].

| | |
|---|---|
| Zn1–N5 | 2.048(2) |
| Zn1–S2 | 2.3307(8) |
| Zn1–S4 | 2.3624(8) |
| Zn1–S3 | 2.5602(10) |
| Zn1–S1 | 2.6066(10) |
| S1–C1 | 1.709(3) |
| S2–C1 | 1.717(3) |
| S3–C8 | 1.700(3) |
| S4–C8 | 1.723(3) |
| N1–C1 | 1.323(3) |
| N3–C8 | 1.330(3) |
| S2–Zn1–S4 | 132.79(3) |
| S2–Zn1–S3 | 98.16(3) |
| S4–Zn1–S3 | 73.08(3) |
| S2–Zn1–S1 | 72.33(3) |
| S4–Zn1–S1 | 102.60(3) |
| S3–Zn1–S1 | 162.95(3) |
| S1–C1–S2 | 117.06(19) |
| S3–C8–S4 | 118.10(18) |

## 3. Results and discussion

### 3.1. *IR spectral studies*

The $\nu_{\text{C–N}}$ has been used as a measure of the contribution of the thioureide form to the complexes [9]. The pyridine, 1,10-phenanthroline and 2,2′-bipyridine adducts of [Zn(4-epzdtc)$_2$] show thioureide $\nu_{\text{C–N}}$ bands at 1482, 1467, and 1468 cm$^{-1}$, respectively. The shift in $\nu_{\text{C–N}}$ values to lower wavenumbers compared to [Zn(4-epzdtc)$_2$] ($\nu_{\text{C–N}} = 1490\,\text{cm}^{-1}$) is due to the change in coordination geometry [10]. [Cd(4-epzdtc)$_2$] adducts do not show observable changes in $\nu_{\text{C–N}}$ values. Relatively larger size of cadmium compared to zinc alleviates the strain involved in the transformation from tetrahedral to octahedral. The characteristic band due to pyridine appears at 1604 cm$^{-1}$ in [M(4-epzdtc)$_2$(py)]. The ring frequencies associated with 1,10-phenanthroline and 2,2′-bipyridine are 1600–1000 cm$^{-1}$ [11, 12]. In this study, [M(4-epzdtc)$_2$(1,10-phen)] adducts show bands around 1620, 1600, and 1510 cm$^{-1}$ whereas [M(4-epzdtc)$_2$(2,2′-bipy)] adducts show bands at 1600 cm$^{-1}$. Other bands due to nitrogen ligands are masked by those due to dithiocarbamate.

### 3.2. *NMR spectral studies*

Structure and numbering of 4-epzdtc is given in figure 1. NMR spectra were recorded at room temperature using TMS as internal reference. DMSO was used as solvent for [Cd(4-epzdtc)$_2$] and [Cd(4-epzdtc)$_2$(py)] and $CDCl_3$ was used as solvent for other complexes.

**3.2.1. $^1$H NMR spectral studies.** The protons at C-2 (adjacent to the $NCS_2$ group) of dithiocarbamate in all the complexes are deshielded (4.00 ppm) due to complexation [13]. Although the magnitude of the deshielding decreases with increase in distance from

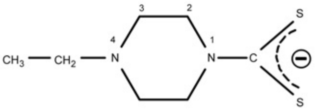
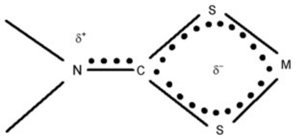


Figure 1. The structure and numbering of 4-epzdtc.



Scheme 1. The charge distribution in a dithiocarbamate group with N–C partial double bond character.

metal center or the thioureide bond, the other proton signals are also slightly deshielded on complexation. The signals observed at 7.46–9.60 ppm are assigned to protons in nitrogen donor ligands.

**3.2.2. $^{13}$C NMR spectral studies.** [M(4-epzdtc)$_2$] complexes and their adducts show N$^{13}$CS$_2$ signals in the region 202.4–206.1 ppm, indicating contribution of double bond character to a formally single N–C bond in the dithiocarbamate, i.e., the admixture of sp$^2$ hybridized state to sp$^3$ orbitals of nitrogen, a considerable $\delta^+$ surplus charge is localized on nitrogen, while $\delta^-$ is delocalized through the four-membered chelate ring $-$CS$_2$M [14] (scheme 1). The N$^{13}$CS$_2$ chemical shift of dithiocarbamate is also affected by coordination of nitrogen donor to metal. The N$^{13}$CS$_2$ carbon sites of adducts are additionally deshielded compared to parent [M(4-epzdtc)$_2$]. Additional coordination of nitrogen donors to metal dithiocarbamates yields a decrease of nitrogen–carbon partial double bond character and, as a result of that, the displacement of electron density from carbon to nitrogen of dithiocarbamate [15]. This explains the additional deshielding of carbon sites in the N$^{13}$CS$_2$ of the adducts. The upfield shift of N$^{13}$CS$_2$ for [M(4-epzdtc)$_2$(py)] from the chemical shift values of [M(4-epzdtc)$_2$(N,N)] (N,N = 1,10-phen, 2,2′-bipy) is due to change in coordination number from five to six.

**3.2.3. 2-D NMR analysis of [Zn(4-epzdtc)$_2$(py)].** To support the assignments made through 1-D NMR and to assign the three methylene carbon signals of 4-epzdtc which appear in the region 51.0–52.9 ppm, 2-D NMR, namely HSQC and HMBC spectra were recorded for [Zn(4-epzdtc)$_2$(py)] and are shown in figures S1, S2, and S3; the correlations for protons in 4-epzdtc are given in table 3. The correlations for three methylene protons in HSQC and HMBC spectra confirm the respective carbon signals.

### 3.3. *Single-crystal X-ray studies*

ORTEP diagram of [Zn(4-epzdtc)$_2$(py)] is shown in figure 2. The structure of [Zn(4-epzdtc)$_2$(py)] contains four discrete monomeric units per unit cell. Zinc is five coordinate with four sulfur atoms from the dithiocarbamate and one nitrogen atom

Table 3. Correlations in HSQC and HMBC spectra of [Zn(4-epzdtc)$_2$(py)].

| $^1$H NMR signal | Correlations in HSQC | Correlations in HMBC |
|---|---|---|
| 1.11 (t, $CH_3$) | 12.0 ($CH_3$) | 51.9 ($\underline{C}H_2CH_3$) |
| 2.47 (q, $C\underline{H_2}CH_3$) | 51.9 ($\underline{C}H_2CH_3$) | 12.0 ($CH_3$) |
| 2.55 (t, H–3) | 52.1 (C–3) | 51.1 (C–2) |
| 4.18 (t, H–2) | 51.1 (C–2) | 52.1 (C–3) |

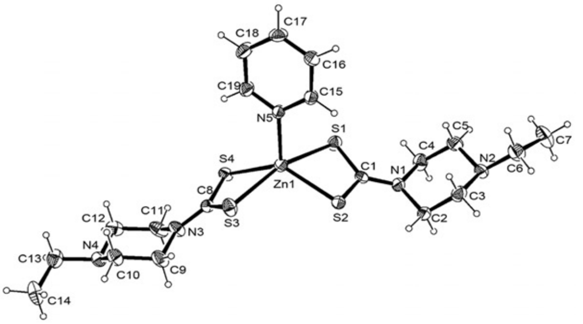


Figure 2. ORTEP diagram of [Zn(4-epzdtc)$_2$(py)].

from pyridine. The geometry of this coordination polyhedron [$ZnS_4N$] is intermediate between tetragonal pyramid and trigonal bipyramid. The structure adopted by this complex is characterized using the $\tau$-descriptor for five coordination suggested by Addison *et al.* [16]. From the $\tau$-value (0.50), the coordination of [Zn(4-epzdtc)$_2$(py)] is described as being 50% along the pathway of distortion from tetragonal pyramid to trigonal bipyramid. The two dithiocarbamate ligands in [Zn(4-epzdtc)$_2$(py)] coordinate in an anisobidentate fashion [Zn–S1 = 2.6066(10) Å, Zn–S2 = 2.3307(8) Å, Zn–S3 = 2.5602(10) Å and Zn–S4 = 2.3624(8) Å]. The C–S distances are slightly asymmetric and the shorter Zn–S bonds are associated with longer C–S distances. The C–S bond lengths [mean: 1.713(3) Å] lie approximately midway between values expected for single and double bonds, i.e., 1.81 and 1.61 Å [17], respectively, and thus have considerable double bond character. The C–N distances similar to other dialkyldithiocarbamate complexes confirm a considerable double bond character in keeping with the IR spectroscopic data. The pyridine and piperazine rings show normal bond parameters. Both six-membered piperazine heterocycles adopt a "chair conformation".

Selected molecular parameters for related zinc compounds are given in table 4. The S–Zn–S bite angle in the present compound is less compared to those observed in [$Zn_2$(dtc)$_4$] (dtc = pipdtc, 4-mpipdtc). Reduction in S–Zn–S angle does not affect the S–C–S angle and C–S distances when compared with similar compounds listed in table 4. The Zn–S distances in [Zn(4-epzdtc)$_2$(py)] are longer than distances observed in [$Zn_2$(dtc)$_4$] complexes. The presence of an additional neutral ligand causes an increase in the Zn–S bond lengths. [Zn(4-epzdtc)$_2$(py)] shows a short Zn–N bond compared to [Zn(dtc)$_2$(N,N)] (N,N = 2,2′-bipy, tmed). The monodentate pyridine is closer to zinc compared to bidentate ligands. The Zn–S, C–S, and C–N and related angles are similar

Table 4. Comparative structural parameters for related zinc and cadmium complexes (Å, °).

| Complex | Coord. No. | M–S | C–S | $S_2C$–N | S–M–S | S–C–S | M–N | Ref. |
|---|---|---|---|---|---|---|---|---|
| $[Zn_2(pipdtc)_4]$ | 4[a] | 2.3733(11) | 1.733(3) | 1.330(4) | 75.86(4) | 117.84(11) | – | [17] |
| $[Zn_2(4\text{-}mpipdtc)_4]$ | 4[a] | 2.371(9) | 1.716(16) | 1.314(4) | 75.62(3) | 117.8(2) | – | [18] |
| $[Zn(4\text{-}epzdtc)_2(py)]$ | 5 | 2.4650(9) | 1.712(3) | 1.327(3) | 72.71(3) | 117.58(19) | 2.048(2) | This work |
| $[Zn(S_2CNMe_2)_2(py)]$ | 5 | 2.466(4) | 1.718(10) | 1.337(13) | 72.9(3) | 118.3(3) | 2.079(6) | [19] |
| $[Zn(S_2CNEt_2)_2(py)]$ | 5 | 2.466(2) | 1.717(7) | 1.331(7) | 73.24(6) | 117.9(4) | 2.076(5) | [20] |
| $[Zn(4\text{-}mpipdtc)_2(py)]$ | 5 | 2.461(1) | 1.731(3) | 1.336(5) | 73.21(3) | 116.71(9) | 2.089(5) | [21] |
| $[Zn(4\text{-}mpipdtc)_2(tmed)]$ | 6 | 2.538(1) | 1.718(3) | 1.327(4) | 70.62(4) | 117.43(18) | 2.273(3) | [22] |
| $[Zn(pipdtc)_2(2,2'\text{-}bipy)]$ | 6 | 2.521(1) | 1.715(4) | 1.343(13) | 71.1(1) | 117.6(2) | 2.196(4) | [23] |
| $[Cd_2(S_2CN(CH_2Ph)_2)_4]$ | 4[a] | 2.5888(7) | 1.729(3) | 1.329(3) | 67.06(2) | 118.78(14) | – | [24] |
| $[Cd(S_2CN(CH_2Ph)_2)_2(py)]$ | 5 | 2.6123(8) | 1.720(3) | 1.333(4) | 69.25(2) | 119.31(17) | 2.317(3) | [25] |
| $[Cd(padtc)_2(tmed)]$ | 6 | 2.6713(8) | 1.707(6) | 1.358(4) | 67.61(5) | 120.7(4) | 2.414(5) | [26] |

Notes: The bond distances and angles are mean values.

[a] It has been suggested that the coordination number is essentially 5 due to the presence of very long Zn–S bond in the dimer.

to those observed in other pyridine adducts of zinc dithiocarbamates [19–21]. Comparison of bond parameters (Table 4) of zinc dithiocarbamate complexes ($[Zn_2(dtc)_4]$, $[Zn(dtc)_2(py)]$, and $[Zn(dtc)_2(tmed)]$) and cadmium dithiocarbamate complexes ($[Cd_2(dtc)_4]$, $[Cd(dtc)_2(py)]$, and $[Cd(dtc)_2(tmed)]$) shows that M–S and M–N bonds are longer, S–M–S angles are smaller, and S–C–S angles are larger in cadmium complexes than that found in zinc complexes due to the large size of cadmium compared to zinc ($Cd^{2+}$: 92 pm (td), 109 pm (oh); $Zn^{2+}$: 74 pm (td), 88 pm (oh)). No significant changes in C–N and C–S bond lengths are found.

### 3.4. *Powder X-ray diffraction studies on CdS*

CdS prepared from $[Cd(4\text{-}epzdtc)_2]$, $[Cd(4\text{-}epzdtc)_2(py)]$, $[Cd(4\text{-}epzdtc)_2(1,10\text{-}phen)]$, and $[Cd(4\text{-}epzdtc)_2(2,2'\text{-}bipy)]$ are represented as CdS**1**, CdS**2**, CdS**3**, and CdS**4**, respectively. The powder X-ray diffraction patterns for CdS**1**, CdS**2**, CdS**3**, and CdS**4** are shown in figure 3. The presence of the (110), (103), and (112) planes in the X-ray diffraction patterns of samples prepared from all four complexes is characteristic of the hexagonal phase of CdS, in good agreement with the reported pattern JCPDS card file No. 41-1049. The presence of XRD peaks at 25° and 53° ($2\theta$) correspond to the crystal planes of wurtzite CdS structure. The absence of XRD peak at $2\theta = 31°$ is due to the lack of zinc blende structure in the samples [27]. For CdS**2**, CdS**3**, and CdS**4**, the observed narrow peak at (002) shows that CdS particles are elongated toward the *c*-axis which is characteristic of wire-shaped particles [28]. The XRD peaks for CdS**1** are broadened compared to CdS**2**, CdS**3**, and CdS**4**, indicating that the CdS particles prepared from $[Cd(4\text{-}epzdtc)_2]$ are smaller.

The mean crystallite sizes of CdS**1**, CdS**2**, CdS**3**, and CdS**4** from the Scherrer formula [29] are 2.7, 6.5, 6.4, and 8.9 nm, respectively. The mean crystallite size of the CdS**1** being smaller than CdS**2**, CdS**3**, and CdS**4**, indicates that the presence of additional neutral ligands in the adducts affects the crystallite size of CdS.

### 3.5. *Optical properties of CdS*

UV-Vis absorption spectra for CdS prepared from different precursors are shown in figure 4. An absorption shoulder or peak is observed at 465, 484, 449, and 487 for CdS**1**,

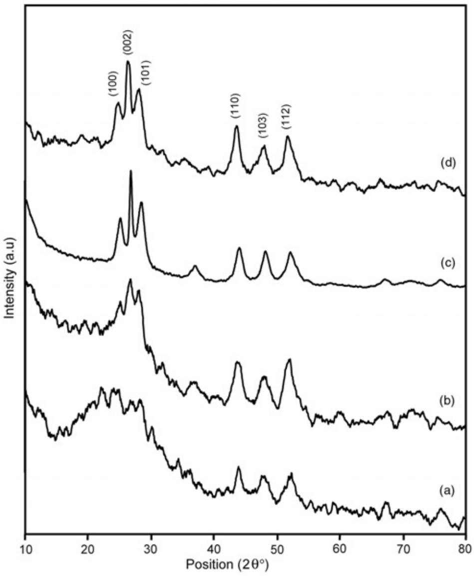


Figure 3. Powder X-ray diffraction patterns of (a) CdS**1**, (b) CdS**2**, (c) CdS**3**, and (d) CdS**4**.

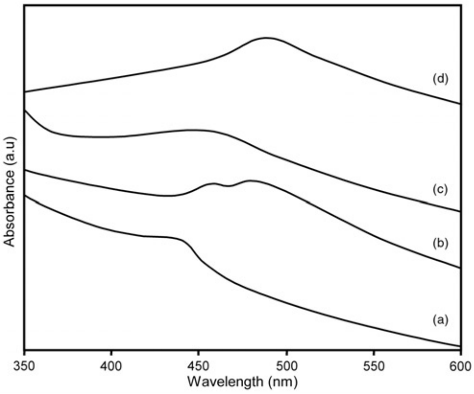


Figure 4. UV-Vis absorption spectra of (a) CdS**1**, (b) CdS**2**, (c) CdS**3**, and (d) CdS**4**.

CdS**2**, CdS**3**, and CdS**4**, respectively. In all the cases, the blue shift of the absorption peak relative to bulk CdS (512 nm) indicates that the cadmium sulfide particles are quantum confined [30].

A fluorescence spectrum of CdS nanoparticles was recorded at excitation wavelength 400 nm at room temperature and the resulting spectra are shown in figure 5. The observed fluorescence peaks at 465–500 nm and at 530 nm for CdS prepared from all the complexes are commonly attributed to the excitonic (or) band edge emission and surface trapped emission, respectively. CdS**2** shows blue shift compared to CdS prepared from other complexes. Due to the quantum confinement effect, the fluorescence peak position of band edge emission of the nanostructure is strongly size

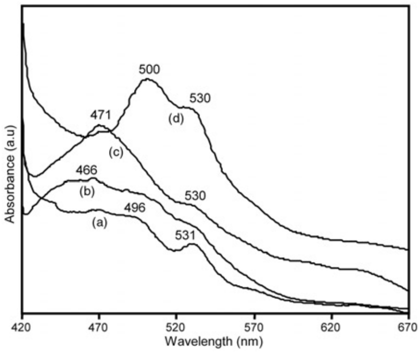


Figure 5. Fluorescence spectra of (a) CdS**1**, (b) CdS**2**, (c) CdS**3**, and (d) CdS**4**.

and shape dependent and usually in the wavelength range of 420–500 nm for CdS. The emission band around 500–800 nm is ascribed to the transition from trap state arising from surface atoms to the ground state [31]. On the other hand, the surface defect emission is caused by surface state vacancies and/or sulfur dangling bonds.

## 4. Conclusion

Pyridine, 1,10-phenanthroline, and 2,2′-bipyridine adducts of bis(4-ethylpiperazinecarbodithioato-S,S′)M(II) (M = Zn, Cd) have been prepared and characterized by IR and NMR spectroscopy. A single-crystal X-ray structure analysis was carried out for [Zn(4-epzdtc)$_2$(py)]. This complex adopts a geometry intermediate between the tetragonal pyramid ($C_{4v}$) and trigonal bipyramid ($D_{3h}$). The cadmium complexes were used as single source precursors to synthesize cadmium sulfide. The presence of nitrogen donors in precursors appears to influence the size of the particles.

## Supplementary material

CCDC-829111 contains the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2, 1EZ, UK; Fax: +44(0)1223-336033. In addition, HSQC and HMBC spectra are also provided as supplementary material.

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