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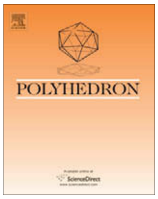

Synthesis and characterization of metal complexes of *N*-alkyl-*N*-phenyl dithiocarbamates

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ABSTRACT

Ammonium *N*-ethyl-*N*-phenyl dithiocarbamate (**L^1**) and *N*-butyl-*N*-phenyl dithiocarbamate (**L^2**), and their group 12 metal complexes formulated as **$Zn_2L^1_4$, CdL^1_2, HgL^1_2, $Zn_2L^2_4$, CdL^2_2, HgL^2_2** have been synthesized and characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR spectroscopy. The crystal structures of the zinc complexes (**$Zn_2L^1_4$** and **$Zn_2L^2_4$**) are also reported. Single crystal analyses of the two complexes revealed the presence of distorted trigonal bipyramidal and tetrahedral coordination geometry about the metal ions. The dithiocarbamate acts as bidentate chelating and bidentate bridging ligands between the metal ions giving centrosymmetric dimeric molecules. The apparent substitution of the ethyl substituents in **L^1** by the butyl groups in **L^2** results in profound change in structure.

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1. Introduction

The dialkyldithiocarbamates anions $-S_2CNR_2$ and its derivatives are used extensively in inorganic and organic chemistry and as active agents in pharmacology, medicinal and biochemistry [1,2]. Dithiocarbamates can act as monodentate, bidentate chelating or bidentate bridging ligands. These binding properties determine the structural organization of the resulting metal complexes [3]. A wide range of chemistry has been developed around them, and seemingly small modifications to the ligand can lead to significant changes in the structure–behavior of the complexes formed with a particular metal. Metal dithiocarbamates have aroused a lot of interests due to their structural features [4,5], and can thus be used as lubricants, antioxidants, accelerators for rubber vulcanization [6], and biocidal applications [7–10]. Dithiocarbamates derived from secondary amines are the most studied ones because they are stable and possess interesting electrochemical and optical properties [11,12].

The dithiocarbamate chemistry of the group 12 elements is well developed and as expected, their chemistry is constrained to the +2 oxidation state. The ease and stability of the complexation reaction is on the fact that group 12 metals act as strong Lewis acids, and hence readily complex to electron-rich sulfur containing ligands in the principle of Hard Soft [Lewis] Acid Base, HSAB [13]. These complexes have been found to be good air-stable precursors for sulfides of Cd, Zn, and Hg and in the construction of new supramolecular structural motifs [14,15]. The bis (dithiocarbamate) complexes $[M(S_2CNR_2)_2]$, where R = alkyl group, are the most common and many studies and reviews have been done on transition and non-transition metals [16,17]. Few reports appear on the corresponding phenyl derivatives probably due to their instability. In order to investigate the structural diversity of alkyl-aryldithiocarbamates complexes, we report the synthesis and characterization of Zn(II), Cd(II) and Hg(II) complexes of *N*-ethyl-*N*-phenyldithiocarbamate and *N*-butyl-*N*-phenyldithiocarbamate.

2. Experimental

All reagents and chemicals were used as obtained. Elemental analyses were performed on a Fisons elemental analyzer at the University of Cape Town, South Africa. FTIR spectra were obtained as KBr discs on Perkin Elmer 2000 FTIR spectrophotometer in the range 4000–370 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz and 101 MHz Bruker NMR spectrophotometers respectively. Chemical shifts are given in ppm (δ scale) relative to tetramethylsilane (for ^{1}H and ^{13}C nuclei).

*2.1. Synthesis of ammonium N-ethyl-N-phenyldithiocarbamate, **L^1***

The ligand ammonium *N*-ethyl-*N*-phenyldithiocarbamate [**L^1**] was prepared according to a reported procedure with some modifications [18]. To a mixture of 6.44 mL (0.05 mol) of *N*-ethyl aniline and concentrated aqueous ammonia (15 mL) in ice, was added 3.00 mL (0.05 mol) of ice cold carbon disulfide. The yellowish green liquid mixture was stirred for 6–7 h given yellowish white solid product which was filtered by suction and rinsed three times with cold ethanol (75 mL) given thermally unstable, moisture and

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air-sensitive, ammonium salt of *N*-ethyl-*N*-phenyldithiocarbamate which was stored in the refrigerator. Attempts to obtain elemental analyses were hindered by rapid decomposition.

Yield: 6.8 g (56%). Selected IR, ν (cm^{-1}) $\mathbf{L^1}$: 1456 (C=N), 1261 (C_2–N), 982, 1056 (S=C = S), 3422 (N–H), 1601 σ(N–H).

2.2. Synthesis of ammonium N-butyl-N-phenyldithiocarbamate, $\mathbf{L^2}$

The ligand, ammonium *N*-butyl-*N*-phenyldithiocarbamate $\mathbf{L^2}$, was prepared using the same procedure for $\mathbf{L^1}$. A mixture of 8.20 mL (0.10 mol) *N*-butyl aniline and concentrated aqueous ammonia (15 mL) was allowed to attain ice temperature in a round bottom flask. To this mixture, 3.00 mL (0.05 mol) of ice cold carbon disulfide was added and stirred for 8 h. The yellowish solid which separated was filtered and rinsed three times with ice cold ethanol (75 mL). The product was stored in the refrigerator.

Yield: 7.5 g (62%). Selected IR, ν (cm^{-1}) $\mathbf{L^2}$: 1456 (C=N), 1254 (C_2–N), 929, 1055 (S=C=S), 3423 (N–H), 1601 σ(N–H).

2.3. Preparation of complexes

The preparation of complexes was carried out at room temperature. About 15 mL aqueous solution of the metal salt (MCl_2, 0.625 mmol) [M = Zn, Cd, Hg], was added to 15 mL aqueous solution of ammonium *N*-alkyl-*N*-phenyldithiocarbamate (1.250 mmol), the white precipitate which immediately formed was stirred for about 45 min. to ensure complete reaction. The solid precipitates were filtered off, rinsed with distilled water and dried at ambient temperature over $CaCl_2$.

$\mathbf{Zn_2L^1_4}$: complex was obtained as white solid. Yield: 0.196 g, (69%), M.p. 210–212 °C.

^{1}H NMR ($CDCl_3$) δ = 7.67–7.32 (m, 4H, C_6H_5), 4.21 (dd, *J* = 14.2, 6.9, 2H, CH_2), 2.17 (s, 1H, CH_3). ^{13}C NMR ($CDCl_3$) δ 129.57, 128.37, 126.70, (C_6H_5), 68.07 (–CH_2), 12.38 (–CH_3).

Selected IR, ν (cm^{-1}): 1456 (C=N), 1157 (C_2–N), 959 (C=S). *Anal.* Calc. for $C_{18}H_{20}N_2S_4Zn$ (457.99): C, 47.21; H, 4.40; N, 6.12; S, 28.00. Found: C, 47.08; H, 4.38; N, 6.14; S, 28.01%. Recrystallization of complex, $\mathbf{Zn_2L^1_4}$, in dichloromethane/methanol (1:1) solvent mixture gave colorless single crystals suitable for X-ray analysis.

$\mathbf{CdL^1_2}$: complex was obtained as white solid. Yield: 0.223 (71%), M.p. 278–280 °C. ^{1}H NMR (DMSO) δ 7.42 (t, *J* = 7.2, 1H, C_6H_5), 7.40–7.20 (m, 2H, C_6H_5), 4.15 (q, *J* = 7.0, 1H, CH_2), 2.50 (d, *J* = 1.7, 8H, CH_3). Selected IR, ν (cm^{-1}): 1454 (C=N), 1159 (C_2–N), 957 (C=S). *Anal.* Calc. for $C_{18}H_{20}N_2S_4Cd$ (505.02): C, 42.81; H, 3.99; N, 5.55; S, 25.39. Found: C, 43.00; H, 4.03; N, 5.63; S, 25.78%.

$\mathbf{HgL^1_2}$: complex was obtained as pale green solid. Yield: 0.240 g (65%), Dec/M.p. 150/210 °C. ^{1}H NMR ($CDCl_3$) δ 7.54–7.21 (m, 8H, C_6H_5), 7.26 (s, 4H, C_6H_5), 4.17 (dd, *J* = 14.2, 7.2, 3H, CH_2), 2.17 (s, 1H, CH_3). ^{13}C NMR ($CDCl_3$) δ 130.01, 129.29, 126.84 (C_6H_5); 56.00 (–CH_2), 12.40 (–CH_3). Selected IR, ν (cm^{-1}): 1455 (C=N), 1281 (C_2–N), 981 (C=S). *Anal.* Calc. for $C_{18}H_{20}N_2S_4Hg$ (593.20): C, 36.45; H, 3.40; N, 4.72; S, 21.62. Found: C, 37.29; H, 3.68; N, 4.96; S, 22.48%.

$\mathbf{Zn_2L^2_4}$: complex was obtained as white solid. Yield: 0.267 g (42%) M.p. 198–200 °C. ^{1}H NMR ($CDCl_3$) δ = 7.40 (dt, *J* = 13.6, 7.2, 5H, C_6H_5), 7.25 (d, *J* = 6.5, 6H, C_6H_5), 4.21–4.05 (m, 3H, CH_2), 2.17 (s, 1H, CH_2), 1.92–1.53 (m, 9H, CH_2), 1.35 (dd, *J* = 14.7, 7.3, 5H, CH_3). ^{13}C NMR ($CDCl_3$) δ 129.51, 128.57, 126.67, (C_6H_5); 58.86 (–CH_2), 29.24 (–CH_2), 19.85(–CH_2), 13.70 (–CH_3). Selected IR, ν (cm^{-1}): 1455 (C=N), 1063 (C_2–N), 940 (C=S). *Anal.* Calc. for $C_{22}H_{28}N_2S_4Zn$ (514.10): C, 51.40; H, 5.49; N, 5.45; S, 24.94. Found: C, 51.07; H, 5.12; N, 5.26; S, 24.46%. Complex $\mathbf{Zn_2L^2_4}$, was recrystallized in dichloromethane/methanol (3:1) solvent mixture given colorless single crystals suitable for X-ray analysis.

$\mathbf{CdL^2_2}$: complex was obtained as white solid and recrystallized in dichloromethane/ethyl acetate (2:1) solvent mixture. Yield: 0.265 g (75%) M.p. 204–206 °C. ^{1}H NMR ($CDCl_3$) δ = 7.57–7.11 (m, 5H, C_6H_5), 4.21 (td, *J* = 16.4, 9.3, 3H, CH_2), 2.17 (s, 1H, CH_2), 1.95–1.64 (m, 2H, CH_2), 1.47–1.07 (m, 7H, CH_3). ^{13}C NMR ($CDCl_3$) δ 130.87, 128.82, 128.27 (–C_6H_5); 68.18 –CH_2), 29.24 (–CH_2), 19.92, (–CH_2), 14.04 (–CH_3). Selected IR, ν (cm^{-1}): 1454 (C=N), 1159 (C_2–N), 950, (C=S). *Anal.* Calc. for $C_{22}H_{28}N_2S_4Cd$ (561.13): C, 47.09; H, 5.03; N, 4.99; S, 22.85. Found: C, 46.78; H, 4.87; N, 5.19; S, 22.62%.

$\mathbf{HgL^2_2}$: complex was obtained as greenish-ash solid. Yield: 0.330 g (81%) M.p. 164–166. ^{1}H NMR ($CDCl_3$) δ = 7.31–7.22 (m, 5H, C_6H_5), 4.19–3.97 (m, 2H, CH_2), 2.17 (s, 1H, CH_2), 1.70 (s, 1H, CH_2), 1.69–0.94 (m, 10H, CH_3). ^{13}C NMR ($CDCl_3$) δ 129.93, 129.05, 126.82 (–C_6H_5), 60.48(–CH_2), 29.54 (–CH_2), 20.27 (–CH_2), 14.10 (–CH_3). Selected IR, ν (cm^{-1}): 1455 (C=N), 1068 (C_2–N), 942 (C=S). *Anal.* Calc. for $C_{22}H_{28}N_2S_4Hg$ (649.31): C, 40.70; H, 4.35; N, 4.31; S, 19.75. Found: C, 41.02; H, 4.12; N, 3.99; S, 19.52%.

2.4. Crystal structure determination and refinement

Crystal structure determinations for the zinc complexes structures were collected on a Nonius Kappa-CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). The strategy for the data collections was evaluated using the Bruker Nonius "COLLECT" program. Data were scaled and reduced using DENZO-SMN software [19]. An empirical absorption correction using the program SADABS [20] was applied. Both structures were solved by direct methods and refined employing full-matrix least-squares with the program SHELXL-97 [21] refining on F^2. Packing diagrams were produced using the program PovRay and graphic interface X-seed [22]. For the structure of $[Zn_2(C_9H_{10}NS_2)_4]$, all non-hydrogen atoms were refined anisotropically. For the structure of $[Zn_2(C_{11}H_{14}NS_2)_4]$, all the non-hydrogen atoms except a number of carbon atoms (C8, C9A, C10A, C9B, C10B and C16) were refined anisotropically. These carbon atoms have relatively high temperature factors ($0.06 < U_{iso} > 0.16$) due to high thermal motions and therefore were refined isotropically. For both two structures, all the hydrogen atoms were placed in idealized positions in a riding model with U_{iso} set at 1.2 or 1.5 times those of their parent atoms and fixed C–H bond lengths. Both structures were refined successfully with final $R = 0.0321$ for $[Zn_2(C_9H_{10}NS_2)_4]$ and $R = 0.0433$ for $[Zn_2(C_{11}H_{14}NS_2)_4]$.

3. Results and discussion

3.1. Synthesis

The ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ are unstable at ambient temperature, and more stable under refrigerator's condition, $\mathbf{L^2}$ is relatively more stable than $\mathbf{L^1}$ at both conditions. The solubility of these ligands was found to reduce with increased number of carbon on the nitrogen atom. Reaction of two molar equivalents of $\mathbf{L^1}$ and $\mathbf{L^2}$ with 1 mol of $ZnCl_2$, $CdCl_2$ and $HgCl_2$ at room temperature gave the respective metal complexes. All compounds are air-stable, soluble in chloroform, and dichloromethane; and insoluble in *n*-hexane, pentane, methanol and 2-propanol. The analytical and spectroscopic data are consistent with the proposed formulation for the complexes.

3.2. Spectroscopic analysis

The infra red spectra of the ligands and their corresponding metal complexes were compared and assigned on the basis of careful comparison. In the ligands, the band in the range 1453–1456 cm^{-1} and 1063–1261 cm^{-1} are attributed to the υ(C–N) and υ(C_2–N)

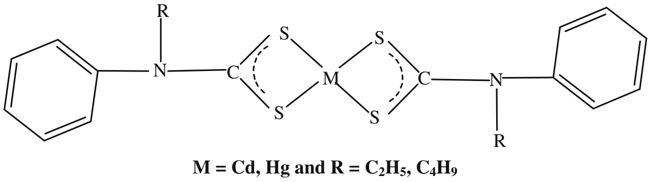

Fig. 1. Proposed structure for some of the complexes.

Table 1
Summary of crystal data and structure refinement.

Compound	$[Zn_2(C_9H_{10}NS_2)_4]$	$[Zn_2(C_{11}H_{14}NS_2)_4]$
Empirical formula	$C_{36}H_{40}N_4S_8Zn_2$	$C_{44}H_{56}N_4S_8Zn_2$
Formula weight	915.94	1028.15
Temperature (K)	173(2)	173(2)
Wavelength	0.71073	0.71073
Space group	$P\bar{1}$	$P21/n$
Unit cell dimensions		
a (Å)	8.7163(3)	11.0542(2)
b (Å)	10.5618(3)	14.8044(3)
c (Å)	12.0172(3)	15.1778(3)
β (°)	66.341(2)	91.7050(10)
γ (°)	79.577(2)	90
Volume (Å^3)	995.26(5)	2482.76(8)
Z	1	2
D_{calc} (Mg/m^3)	1.528	1.375
Absorption coefficient (mm^{-1})	1.657	1.337
F (0 0 0)	472	1072
Crystal size (mm)	0.20 × 0.18 × 0.16	0.14 × 0.12 × 0.08
θ Range (°)	3.10–28.28	3.31–28.27
Limiting indices	$-11 \le h \le 11$, $-14 \le k \le 14$, $-16 \le 1 \le 16$	$-14 \le h \le 14$, $-19 \le k \le 19$, $-20 \le 1 \le 20$
Reflections collected	31 692	93 202
Independent reflection	4931 [R(int) = 0.0341]	6147 [R(int) = 0.0517]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Completeness to θ = 28.28	99.8	99.8
Data/restraints/parameters/	4931/1/246	6147/5/251
Goodness-of-fit on F^2	1.054	1.042
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0321, wR_2 = 0.0676	R_1 = 0.0433, wR_2 = 0.1048
R indices (all data)	R_1 = 0.0427, wR_2 = 0.0728	R_1 = 0.0620, wR_2 = 0.1158
Largest difference in peak and hole (e Å^{-3})	0.670 and −0.739	0.925 and −0.843

Table 2
Selected bond length (Å) and bond angle (°) for $[Zn_2(C_9H_{10}NS_2)_4]$.

Zn(1)–S(4)	2.3501(7)	S(4)–Zn(1)–S(1)	136.12(2)
Zn(1)–S(1)	2.3659(6)	S(4)–Zn(1)–S(3)#1	104.03(2)
Zn(1)–S(3)#1	2.4007(5)	S(1)–Zn(1)–S(3)#1	117.03(2)
Zn(1)–S(2)	2.4421(6)	S(4)–Zn(1)–S(2)	107.33(2)
Zn(1)–S(3)	2.7513(6)	S(1)–Zn(1)–S(2)	75.59(2)
S(1)–C(9)	1.730(2)	S(3)#1–Zn(1)–S(1)	105.43(2)
S(2)–C(9)	1.740(2)	S(4)–Zn(1)–S(3)	70.724(19)
S(3)–C(10)#1	2.4007(5)	S(1)–Zn(1)–S(3)	95.734(19)
N(1)–C(9)	1.334(3)	S(3)#1–Zn(1)–S(3)	88.847(17)
N(1)–C(1)	1.454(3)	S(2)–Zn(1)–S(3)	165.50(2)
N(1)–C(7A)	1.490(4)	C(9)–S(1)–Zn(1)	84.29(8)
N(1)–C(7B)	1.4937(10)	C(9)–S(2)–Zn(1)	82.30(8)
N(2)–C(10)	1.326(3)	C(10)–S(1)–Zn(1)#1	100.73(7)
N(2)–C(13)	1.448(3)	C(10)–S(3)–Zn(1)	78.67(7)
N(2)–C(11)	1.483(3)	Zn(1)#1–S(3)–Zn(1)	91.153(17)
		C(10)–S(4)–Zn(1)	91.70(8)

Table 3
Selected bond length (Å) and bond angle (°) for $[Zn_2(C_{11}H_{14}NS_2)_4]$.

Zn(1)–S(4)	2.3119(7)	S(4)–Zn(1)–S(1)	131.73(3)
Zn(1)–S(1)	2.3353	S(4)–Zn(1)–S(3)#1	106.47(3)
Zn(1)–S(3)#1	2.3607	S(1)–Zn(1)–S(3)#1	117.47(3)
Zn(1)–S(2)	2.4396	S(4)–Zn(1)–S(2)	108.36(3)
S(1)–C(11)	1.732	S(1)–Zn(1)–S(2)	76.32(3)
S(2)–C(11)	1.714	S(3)#1–Zn(1)–S(2)	108.36(3)
S(3)–C(12)	1.741	C(11)–S(1)–Zn(1)	84.30(10)
S(3)–Zn(1)#1	2.3607	C(11)–S(2)–Zn(1)	81.47(9)
S(4)–C(12)	1.719	C(12)–S(3)–Zn(1)#1	103.21(9)
N(1)–C(11)	1.336	C(12)–S(4)–Zn(1)	96.36(9)
N(1)–C(1)	1.444	N(1)–C(11)–S(2)	120.9(2)
N(1)–C(7)	1.478	N(1)–C(11)–S(1)	121.3(2)
N(2)–C(12)	1.328	S(2)–C(11)–S(1)	117.83(16)
N(2)–C(17)	1.450	N(2)–C(12)–S(4)	118.9(2)
N(2)–C(13)	1.483	N(2)–C(12)–S(4)	121.7(2)
		S(4)–C(12)–S(3)	119.32(15)

stretching vibration [23] respectively. Studies on alkyl dithiocarbamates have shown that the lengthening of the alkyl chain is accompanied by a decrease in ν(C–N) although the ν(C–S) remains unaltered as it has been found to be insensitive to the nature of alkyl substituents [24]. The lower values observed in this prominent and characteristic peaks in the ligands can be ascribed to the effect of the size of the butyl group on the nitrogen. The symmetrical and unsymmetrical vibrations observed as two peaks in the range 929–960 and 1054–1056 cm^{-1}, respectively, in the ligands gave way to a single peak in the complexes in the range 940–990 cm^{-1}, belonging to the υ(C–S) stretching vibration [23,25]. This showed that the dithiocarbamates act as bidentate ligands based on the criterion of Bonati and Ugo [23] which uses the number of bands observed in the region 950–1050 cm^{-1} to determine the nature of the coordination of the ligand as either bidentate symmetrical or monodentate asymmetrical. The proposed formulation for the Cd(II) and Hg(II) complexes is shown in Fig. 1.

In the complexes, the observed decrease of about 100 cm^{-1} in the υ(C–S) indicates that the metal ions bond to the dithiocarbamate through the S atom. The absence of the bands around 3422 and 1601 cm^{-1} in the complexes which are attributed to υ(N–H) and σ(N–H) in the ligands confirm the ammonium ion is displaced by the metal atom. The ν(M–S) peaks occurred in the far-IR region, 300–400 cm^{-1}, and depend on the nature of the metal ion and the substituents attached with the nitrogen [26].

The ^{1}H NMR chemical shifts around 2.17 and 4.20 ppm found in all the spectra are ascribed to methyl and methylene carbon linked directly with N atoms of the dithiocarbamates. It is found that the coordinated dithiocarbamate group is more electronegative than in the case where there is no coordination. These could account for the downfield shift of about <1 ppm usually observed when the peaks of the metal complexes are compared with the salts of their appropriate acids [27]. The signals observed in the region d 7.25–7.67 ppm are attributed to the protons of phenyl rings. The coupling constants were not observed in most complexes because the phenyl protons are displayed as a multiplet. A feature of the ^{13}C NMR spectra of all the complexes is the resonances from the alkyl substituents. The nitrogen-bound α-carbon is shifted downfield with respect to the other signals, being found between 55 ppm and 68 ppm. This could be ascribed to the effect of the aromatic ring, pushing the peaks downfield, which typically are found between 43 and 57 ppm in alkyldithiocarbamates. Further methylene groups appear between 20 and 40 ppm, being shifted to higher field upon increasing distance from the nitrogen center, while the end methyl groups are found between 14 and 12 ppm [28]. The aromatic carbons appear between 120 and 130 ppm.

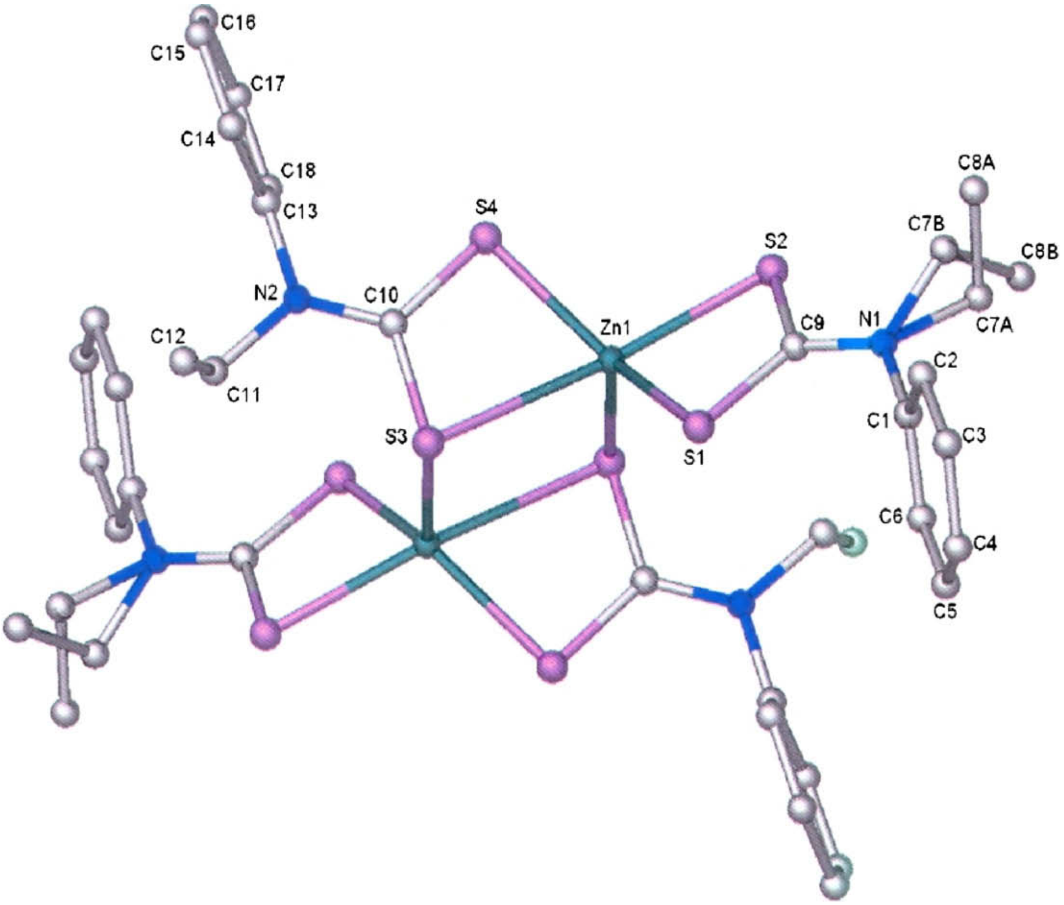

Fig. 2. Crystal structure of $[Zn_2(C_9H_{10}NS_2)_4]$.

3.3. X-ray crystallography

The zinc complexes were structurally determined by X-ray crystallography. The crystallographic and measurement data are shown in Table 1 and representative bond lengths and bond angles are listed in Table 2 and 3. Figs. 2 and 3 present thermal ellipsoid representations of the complexes respectively and the schematic drawing of the crystal packing are presented in Figs. 4 and 5. In dithiocarbamate metal complexes, the planarity of the MS_2CNC_2 unit is a key feature of the crystal structure of metal-bound dithiocarbamates. That is, all seven atoms lie approximately in a plane and thus dithiocarbamates are best considered as being stereochemically rigid hence sterically non-demanding [29]. The $[Zn_2(C_9H_{10}NS_2)_4]$ was crystallized at $P\bar{1}$ with $Z = 1$. The molecule of $[Zn_2(C_9H_{10}NS_2)_4]$ is located at the center of inversion in which one of the C_2H_5 moieties of the asymmetric unit is disordered over two positions with C7A and C8A having site occupancy factor (s.o.f.) of 60.8%, C7B and C8B having s.o.f. of 39.2%. The molecular structure consist of discrete molecular species in which the metal atom is coordinated to two dithiocarbamate molecules and bridge the S-atom of one of the dithiocarbamate on the adjacent molecule. The X-ray structure of $[Zn_2(C_9H_{10}NS_2)_4]$ revealed that the Zn atoms are in a distorted trigonal bipyramidal environment. The distortion of the regular trigonal bipyramidal geometry is mainly due to small bite of the dithiocarbamate ligands, whose S(1)–Zn(1)–S(2) and S(3)–Zn(1)–S(4) chelate angles are 75.59(2)° and 70.724(19)°, respectively, which deviate significantly from 90°. These deviations produce bond angle values that are different from the expected. Therefore the other angles such as S(4)–Zn(1)–S(2) and S(1)–Zn(1)–S(23) with 107.33(2)° and 95.73(2)° are significantly different from the ideal value of 90°. The angles described by atoms in the equatorial positions should be close to 120°; the angles involving S(3)#1 atoms [104.03(2) and 117.03(2)] are smaller than the ideal value (120°) but the S(4)–Zn(1)–S(1) bond angle is somewhat larger, 136.12(2)°, most probably due to steric requirements of the ligands and the S(2)–Zn(1)–S(3) bond angle of 165.50(2)° deviate from the ideal value of 180°.

In $[Zn_2(C_{11}H_{14}NS_2)_4]$, the structure consist of discrete molecular species in which the zinc atom have four coordinate geometry. The $[Zn_2(C_{11}H_{14}NS_2)_4]$ was crystallized in the space group $P2_1/n$ with $Z = 2$. The molecule is located at the center of inversion at position *d*. One of the C_4H_9 moieties of the asymmetric unit is disordered over two positions with 50% s.o.f for C9A and C10A, another 50% s.o.f. for C9B and C10B. The Zn atom is tetrahedrally coordinated to one molecules of butyl-phenyl dithiocarbamate functioning as bidentate ligands through the S-atom. The other sites are occupied by the bridging-chelating dithiocarbamate ligands to give interconnected eight-member rings, each containing two zinc atoms and two bridging dithiocarbamates. The Zn–S(1) [2.3353(8) Å] and Zn–S(2) [2.4396(7) Å] bond distances indicate that the dithiocarbamate acts as a bidentate chelating ligands. The Zn–S bonds vary from 2.3353(8) Å for the non-bridging chelate ligand to 2.3607(7) Å for the bridging-chelating ligand. Two of the shortest metal–sulfur distances are formed by S atoms of one of the chelating moieties while the S atoms of the other chelating-bridging moiety produce both long and short M–S distances. Sharing of an S atom in the complexes gives rise to a dimeric unit in which one of the ligand form a chelate ring and the other is coordinated to two Zn^{2+} ions.

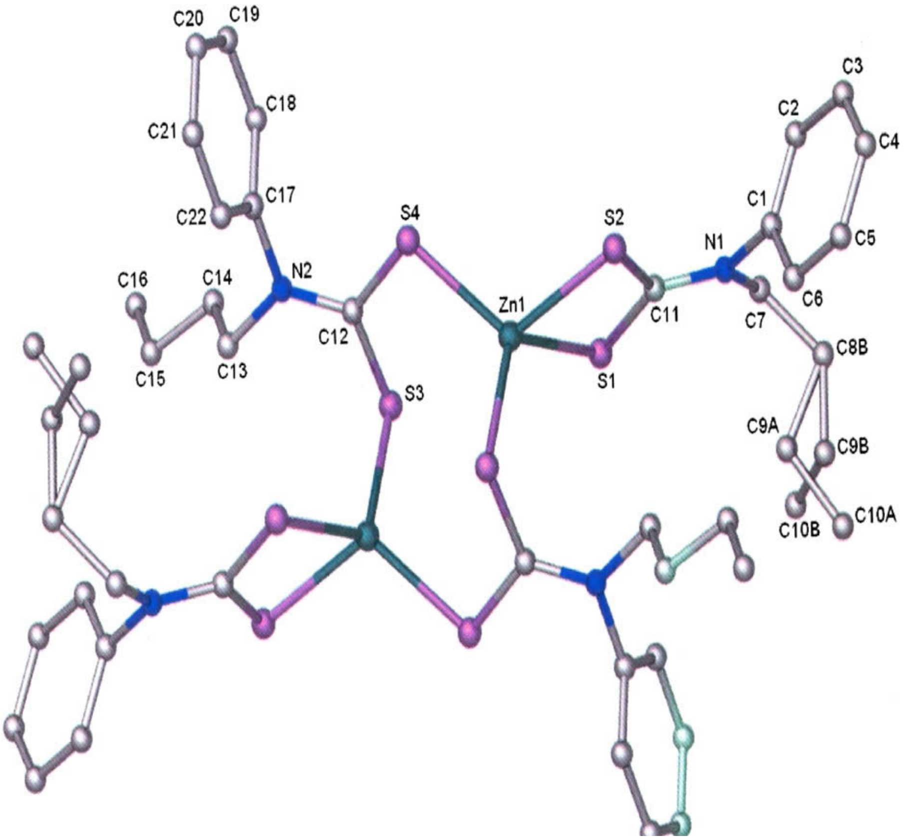

Fig. 3. Crystal structure of $[Zn_2(C_{11}H_{14}NS_2)_4]$.

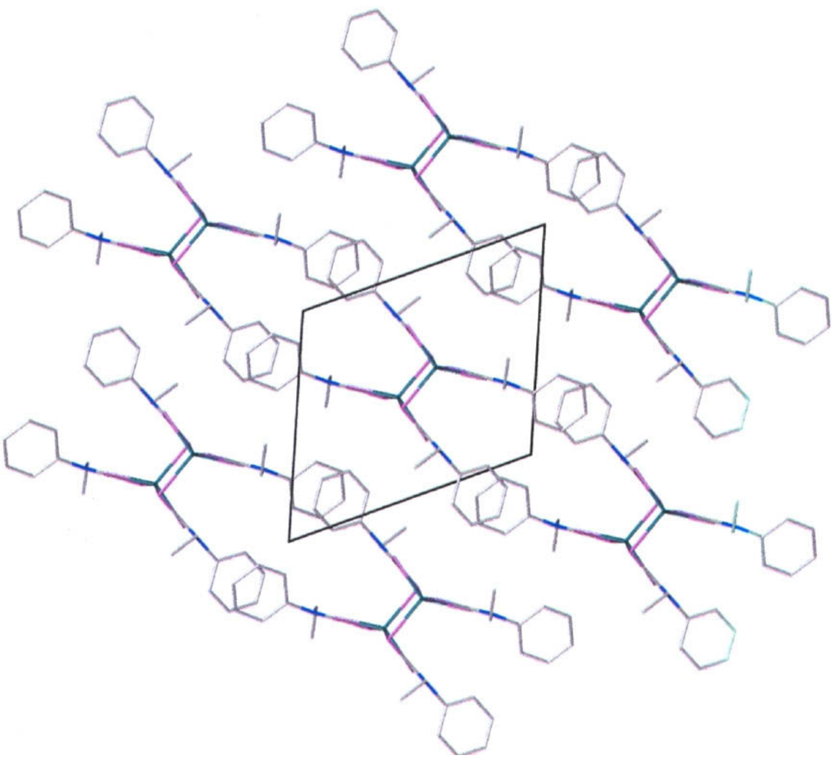

Fig. 4. Schematic drawing of the crystal packing of $[Zn_2(C_9H_{10}NS_2)_4]$.

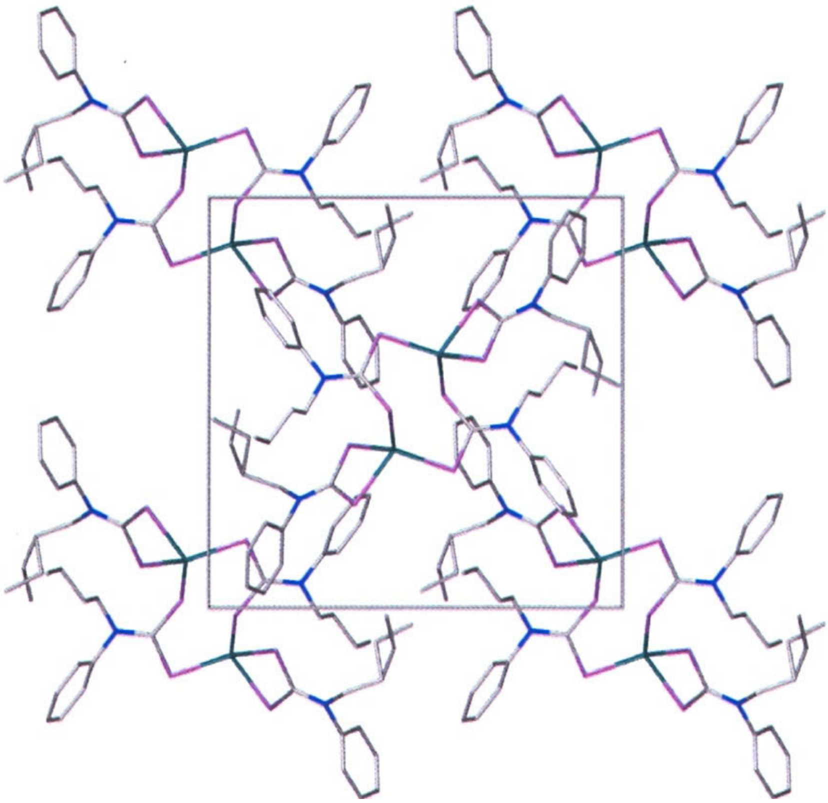

Fig. 5. Schematic drawing of the crystal packing of $[Zn_2(C_{11}H_{14}NS_2)_4]$.

4. Conclusion

Zn(II), Cd(II) and Hg(II) complexes of *N*-ethyl-*N*-phenyl dithiocarbamate and *N*-butyl-*N*-phenyl dithiocarbamate were prepared and characterized by elemental analyses, NMR and IR spectroscopy. Four coordinate geometry is proposed for the Cd(II) and Hg(II) complexes. X-ray crystal structures of the two zinc complexes revealed that one of the complexes has distorted trigonal bipyramidal geometry and the other is tetrahedrally coordinated. The potential of the complexes as single source precursors for semiconductor nanoparticles is being investigated.

Supplementary material

CCDC 725036 and 725037 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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