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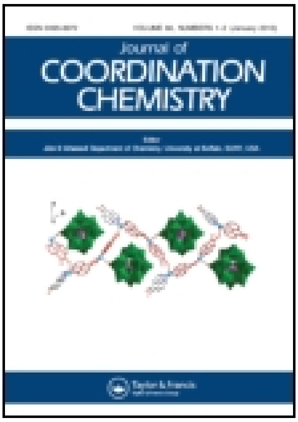

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Synthesis and characterization of group 12 complexes of N,N-methyl phenyl-N,N-butyl phenyl dithiocarbamate

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Synthesis and characterization of group 12 complexes of *N*,*N*-methyl phenyl-*N*,*N*-butyl phenyl dithiocarbamate

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Zn(II), Cd(II), and Hg(II) complexes of *N*-methyl-*N*-phenyl dithiocarbamate (L^1) and *N*-butyl-*N*-phenyl dithiocarbamate (L^2) formulated as ML^1L^2 have been synthesized and characterized by elemental analysis, FT–IR, ^{1}H- and ^{13}C-NMR spectroscopic techniques. Single-crystal X-ray structures of the Zn(II) and Hg(II) complexes are also reported. X-ray crystal structures revealed that in the zinc(II) complex, the dithiocarbamate is chelating and bridging, forming eight-member rings, while the Hg complex is monomeric with bidentate dithiocarbamate. In both complexes, the metals are in distorted tetrahedral geometry and the methyl and butyl groups of the dithiocarbamates exhibit compositional disorder between two positions.

Keywords: Crystal structure; Dithiocarbamates; Group 12 metals; Synthesis

1. Introduction

Dithiocarbamates constitute an interesting area of organosulfur chemistry. Dithiocarbamates are three-electron donors and can stabilize transition metals in high oxidation states [1–3]. Due to vacant dπ orbitals on sulfur, they can form multiple π-bonds and additional π-electrons can flow from nitrogen to sulfur *via* a planar delocalized π-orbital system, making dithiocarbamates strong electron donors [4]. Dithiocarbamates possess interesting electrochemical and optical properties [5, 6], existing in three different resonance forms (scheme 1), and thus acting as monodentate, bidentate chelating, or bidentate bridging. The binding properties determine the structural organization (scheme 2) of the metal complexes [7].

The chemistry of dithiocarbamates have received considerable attention due to its versatility and strong metal binding properties [8–10]. It can form chelates with virtually all transition elements and the bidentate anion could also bridge between two transition metal centers [11]. Metal complexes of dithiocarbamates are useful in rubber polymer and petrochemical industries [12, 13]. Some complexes which exhibit proteasome inhibitory properties have been explored as potential anticancer agents [14, 15]. Coordination compounds formed by dithiocarbamates and metal(II) ion with d^{10} electronic configuration ($Zn^{2+}, Cd^{2+}, Hg^{2+}$) have received attention for two main

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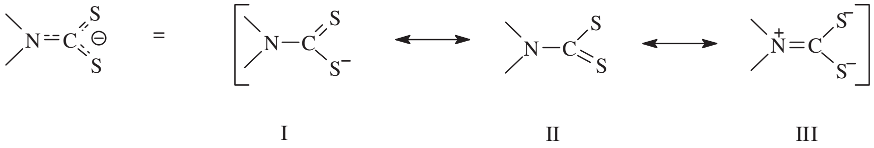
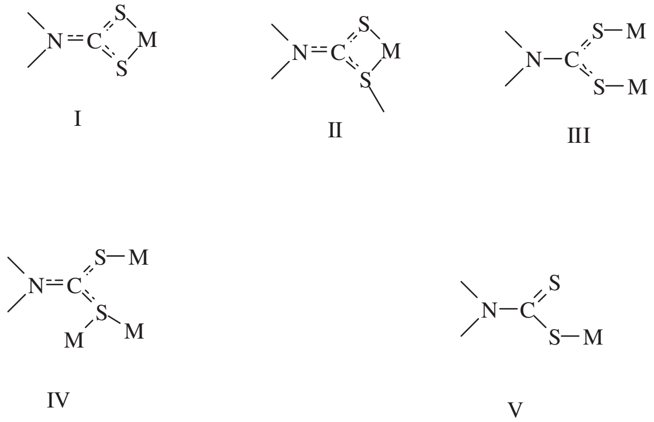


Scheme 1. Different resonant forms of dithiocarbamic moiety.



Scheme 2. Binding forms of dithiocarbamate metal complexes.

reasons: their non-linear optical properties and the convenient preparation of semiconducting materials based on metal sulfide through thermal decomposition of these complexes [16–19]. In continuation of our efforts [20–23] to develop dithiocarbamate complexes of group 12 metals as single-source precursors for the synthesis of metal sulfide semiconductor nanoparticles and thin films, we present the synthesis and characterization of Zn(II), Cd(II), and Hg(II) complexes of *N*-methyl-*N*-phenyldithiocarbamate and *N*-butyl-*N*-phenyldithiocarbamate.

2. Experimental

2.1. *Materials*

N-methyl aniline, *N*-butyl aniline, dichloromethane, chloroform, and hexane were purchased from Merck. $ZnCl_2$, $CdCl_2$, $HgCl_2$, and CS_2 were from Aldrich. All reagents were used as purchased without purification. Solvents were obtained from Aldrich and used without purification.

2.2. *Physical measurements*

All reagents and chemicals were used as obtained. Elemental analyses were performed on a Fisons elemental analyzer. FT–IR spectra were obtained as KBr discs on a Perkin

Elmer 2000 FT–IR spectrophotometer from 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.

2.3. *Synthesis of $C_6H_5N(CH_3)CS_2$, L^1*

The dithiocarbamate ligand ($C_6H_5N(CH_3)CS_2$) was prepared according to a literature procedure [3]. Typically, to a mixture of 10.88 mL (0.10 mol) of *N*-methyl aniline and concentrated aqueous ammonia (30 mL) in ice, 6.00 mL (0.10 mol) of ice cold carbon disulfide was added. After stirring the mixture for 6–7 h, the yellowish white solids which separated were filtered by suction and rinsed three times with cold ethanol (75 mL), giving yellowish ammonium *N*-methyl-*N*-phenyldithiocarbamate which is unstable and decomposes at room temperature. Yield: 11.60 g (58%). Selected IR, υ (cm^{-1}) $\mathbf{L^1}$: 1456 (C=N), 1261 (C_2–N), 982 (C=S), 3422 (N–H), and 1601 σ(N–H).

2.4. *Synthesis of $C_6H_5N(C_4H_9)CS_2$, L^2*

Synthesis of ammonium *N*-butyl-*N*-phenyldithiocarbamate follows the same procedure. A mixture of 16.40 mL (0.10 mol) *N*-butyl aniline and concentrated aqueous ammonia (30 mL) was allowed to attain ice temperature in a round bottom flask; 6.00 mL (0.10 mol) carbon disulfide was added to the mixture and stirred for 8 h. The solid product was filtered and rinsed three times with ice cold ethanol (75 mL). The yellowish white ammonium *N*-butyl-*N*-phenyldithiocarbamate obtained was temperature- and air-sensitive. Yield: 15.73 g (65%). Selected IR, υ (cm^{-1}) $\mathbf{L^2}$: 1456 (C=N), 1254 (C_2–N), 929 (C=S), 3423 (N–H), 1601 σ(N–H).

2.5. *Synthesis of the complexes*

All complexes were prepared by the following synthetic method: to a solution of freshly prepared ammonium *N*-methyl-*N*-phenyldithiocarbamate (0.25 g, 1.25 mmol) in 15 mL of distilled water, 20 mL solution of ammonium *N*-butyl-*N*-phenyldithiocarbamate (0.302 g, 1.25 mmol) was added. The solution was then stirred for 2 min. To this mixture, 1.25 mmol of a metal salt, 1.25 mmol of $ZnCl_2$ (0.170 g), $CdCl_2$ (0.230), and $HgCl_2$ (0.340) in 20 mL were added and stirred for 1 h. The solid product formed was rinsed thrice with 25 mL distilled water and dried over $CaCl_2$.

2.5.1. [$C_6H_5N(CH_3)CS_2ZnC_6H_5N(C_4H_9)CS_2$] (1). Yield: 0.55 g (94%). Anal. Calcd for $C_{19}H_{22}N_2S_4Zn$: C, 48.35; H, 4.70; N, 5.93; and S, 27.17. Found: C, 50.20; H, 4.67; N, 4.75; and S, 26.09%. IR (KBr disc, cm^{-1}) 1491 ν(C=N); 1283 ν(C_2=N); and 957 ν(C=S); ^{1}H-NMR ($CDCl_3$, ppm): δ_H (0.88 (CH_3-N(bu), t), 1.33 (γ-CH_2, m); 1.68 (β-CH_2, m); 3.72 (CH_3-(me), s); 4.10 (α-CH_2, t); 7.25–7.28 (C_6H_5-N(bu), m); and 7.30–7.44 (C_6H_5-N(me), m); ^{13}C-NMR ($CDCl_3$, ppm): δ_C 13.70 (CH_3-N(bu)); 19.83 (γ-CH_2); 29.21 (β-CH_2); 46.89 (CH_3-N(me)); 58.83 (α-CH_2); 126.64, 128.58, 129.19, 129.60 (C_6H_5-N(bu)); 144.30, 146.11 (C_6H_5-N (me)); and 206.71, 207.31 (CS_2).

2.5.2. [$C_6H_5N(CH_3)CS_2CdC_6H_5N(C_4H_9)CS_2$] (2). Yield: 0.55 g (94%). Anal. Calcd for $C_{19}H_{22}N_2S_4Cd$: C, 43.97; H, 4.27; N, 5.40; and S, 24.71. Found: C, 44.99; H, 4.51; N, 4.87; and S, 24.77%. IR (KBr disc, cm^{-1}) 1491 ν(C=N); 1276 $\nu(C_2{=}N)$; and 939 ν(C=S); ^{1}H-NMR ($CDCl_3$, ppm): δ_H (0.87 (CH_3-N(bu), t), 1.31 (γ-CH_2, m); 1.69 (β-CH_2, m); 3.77 (CH_3-(me), s); 4.16 (α-CH_2, t); 7.22–7.26 (C_6H_5-N(bu), t); and 7.30–7.39 (C_6H_5-N(me), m); ^{13}C-NMR ($CDCl_3$, ppm): δ_C 13.76 (CH_3-N(bu)); 19.92 (γ-CH_2); 29.22 (β-CH_2); 48.90 (CH_3-N(me)); 60.73 (α-CH_2); 126.61, 128.20, 129.37, 129.48 (C_6H_5-N(bu)); 146.07, 147.89 (C_6H_5-N (me)); and 207.21, 207.75 (CS_2).

2.5.3. [$C_6H_5N(CH_3)CS_2HgC_6H_5N(C_4H_9)CS_2$] (3). Yield: 0.71 g (93%). Anal. Calcd for $C_{19}H_{22}N_2S_4Hg$: C, 37.58; H, 3.65; N, 4.61; and S, 21.12. Found: C, 37.48; H, 3.56; N, 3.43; and S, 21.52%. IR (KBr disc, cm^{-1}) 1489 ν(C=N); 1278 $\nu(C_2{=}N)$; 948 ν(C=S); ^{1}H-NMR ($CDCl_3$, ppm): δ_H (0.85 (CH_3-N(bu), t),1.31 (γ-CH_2, m); 1.67 (β-CH_2, m); 3.69 (CH_3-(me), s); 4.06 (α-CH_2, t); 7.23–7.27 (C_6H_5-N(bu), t); and 7.32–7.41 (C_6H_5-N(me), m); ^{13}C-NMR ($CDCl_3$, ppm): δ_C 13.72 (CH_3-N(bu)); 19.86 (γ-CH_2); 29.11 (β-CH_2); 48.73 (CH_3-N(me)); 60.62 (α-CH_2); 126.40, 128.63, 129.53, 129.63 (C_6H_5-N(bu)); 145.58, 147.53 (C_6H_5-N (me)); and 206.68, 207.00 (CS_2).

2.6. *Crystal structure determination and structure refinement*

For **1**, a crystal with approximate dimensions 0.38 × 0.30 × 0.17 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam using a video camera. The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu-Kα ($\lambda = 1.54178$ Å) radiation and the diffractometer-to-crystal distance 4.03 cm. The initial cell constants were obtained from three series of scans at different starting angles. Each series consisted of 41 frames collected at intervals of 0.6° in a 25° range with an exposure time of 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 9690 strong reflections from the actual data collection. The data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.82 Å. A total of 34,762 data were harvested by collecting 15 sets of frames with 0.5° scans with an exposure time 20–40 s per frame.

For **3**, a yellow crystal with approximate dimensions 0.45 × 0.40 × 0.37 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam using a video camera. The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range with an exposure time of 10 s per frame. A total of 483 reflections were obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 9986 strong reflections from the actual data collection. The data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.71 Å. A total of 29,892 data were harvested by collecting three sets of frames with 0.36° scans and one set with 0.45° scans in φ with an exposure time 12 s per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [24].

For both complexes, systematic absences in the diffraction data were uniquely consistent for the space group *P2(1)/n* that yielded chemically reasonable and computationally stable results of refinement [25, 26]. A successful solution by direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps [27]. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless otherwise specified. All hydrogens were included in the structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

3. Results and discussion

3.1. *Synthesis*

Synthetic routes to transition metal dithiocarbamate complexes commonly involve direct ligand addition. This reaction often results in loss of a coordinated anionic ligand, and sometimes a second neutral ligand, depending on the coordination chemistry of the metal. These simple substitution reactions usually take place at ambient temperature. The complexes were prepared by reacting equimolar quantities of the metal chloride (MCl_2, M = Zn, Cd, and Hg) and the ligands. Mixed ligand complexes are more stable than simple complexes and are preferred over simple complexes [28], whenever the possibility of formation of these two complexes arises in a reaction medium. However, certain factors, such as the electronic structure of the metal and its coordination number, the donor nature of the ligands and the mutual effect of ligands in a mixed ligand complex, the structure of the complex and the coordination equilibria in solutions of mixed ligand complexes, have been studied for a large number of examples [29] and they play vital roles. Both ligands and complexes were prepared in good yields. The complexes were solids, soluble in chloroform, dichloromethane, and toluene, insoluble in polar solvents, and stable under ambient conditions. The yellow ammonium dithiocarbamate solids changed to liquid under prolonged contact with air at 298 K, possibly due to absorption of moisture.

3.2. *Molecular structure of the complexes*

3.2.1. Single crystal X-ray studies of the Zn(II) complex, [Zn_2(mpbpdtc)$_4$]. The molecular structure of **1** with atom numbering scheme is shown in figure 1. The crystal data and structure refinement are presented in table 1, and selected bond lengths and angles in table 2. The Zn(II) complex is dimeric and each Zn in the dimeric molecule is tetrahedrally coordinated to one dithiocarbamate as a chelating ligand and the other dithiocarbamate as bridging between Zn ions to give interconnected eight-member rings.

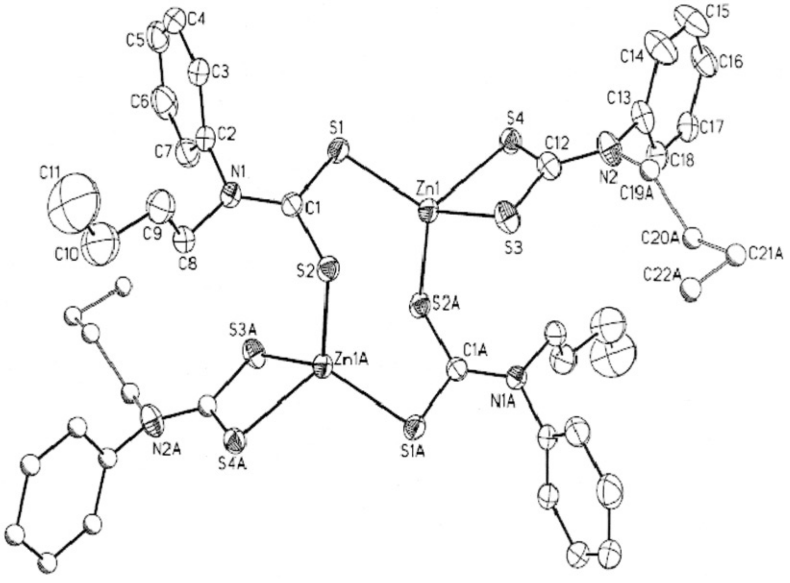


Figure 1. The molecular diagram with 50% probability ellipsoids of [Zn_2(mpbpdtc)$_4$]. All hydrogens and the minor components of the disordered carbons are omitted.

Table 1. Summary of crystal data and structure refinement for [Hg(mpbpdtc)$_2$] and [Zn_2(mpbpdtc)$_4$].

Compounds	[Hg(mpbpdtc)$_2$]	[Zn_2(mpbpdtc)$_4$]
Empirical formula	$C_{19}H_{22}N_2S_4Hg$	$C_{44}H_{56}N_4S_8Zn_2$
Formula weight	607.22	1028.15
Temperature (K)	100(2)	100(1)
Wavelength (Å)	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)/n*	*P2(1)/n*
Unit cell dimensions (Å, °)		
a	10.7074(11)	10.9795(4)
b	16.0014(16)	14.4972(b)
c	13.5035(13)	15.1120(5)
β	104.9070(10)	93.129(2)
γ		
Volume (Å^3), *Z*	2235.7(4), 4	2401.82(14), 2
Calculated density (Mg m^{-3})	1.804	1.422
Absorption coefficient (mm^{-1})	7.264	4.748
F(000)	1176	1072
Crystal size (mm^3)	0.45 × 0.40 × 0.37	0.38 × 0.30 × 0.17
θ range for data collection (°)	2.01–29.94	4.23–69.71
Reflections collected	29,892	34,762
Independent reflection	6074 [R(int) = 0.0314]	4407 [R(int) = 0.0275]
Completeness to $\theta = 25.00$ (%)	99.8	
Data/restraints/parameters	6074/9/236	4407/17/259
Goodness-of-fit on F^2	1.007	0.938
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $wR_2 = 0.1146$	$R_1 = 0.0363$, $wR_2 = 0.0984$
R indices (all data)	$R_1 = 0.0640$, $wR_2 = 0.1268$	$R_1 = 0.393$, $wR_2 = 0.1011$
Largest difference peak and hole (e Å^{-3})	2.186 and −1.279	0.567 and −0.547

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

Zn(1)–S(1)	2.3117(7)	S(1)–Zn(1)–S(3)	134.62(3)
Zn(1)–S(3)	2.3339(8)	S(1)–Zn(1)–S(2)	106.02(3)
Zn(1)–S(2)	1.3605(7)	S(3)–Zn(1)–S(2)	115.14(3)
Zn(1)–S(4)	2.4352(7)	S(1)–Zn(1)–S(4)	108.68(2)
S(1)–C(1)	1.721(2)	S(3)–Zn(1)–S(4)	76.56(2)
S(2)–C(1)	1.741(3)	S(2)–Zn(1)–S(4)	108.02(2)
S(2)–Zn(1)	1.3604(7)	C(1)–S(1)–Zn(1)	95.38(9)
S(3)–C(12)	1.735(3)	C(1)–S(2)–Zn(1)	1102.78(8)
S(4)–C(12)	1.719(3)	C(12)–S(3)–Zn(1)	84.18(9)
N(1)–C(1)	1.325(3)	C(12)–S(4)–Zn(1)	81.41(9)
N(1)–C(2)	1.452(3)	C(1)–N(1)–C(2)	120.1(2)
N(1)–C(8)	1.478(3)	C(1)–N(1)–C(8)	124.2(2)
N(2)–C(12)	1.327(3)	N(1)–C(1)–S(1)	119.01(19)
N(2)–C(12)	1.441(4)	N(1)–C(1)–S(2)	121.75(19)

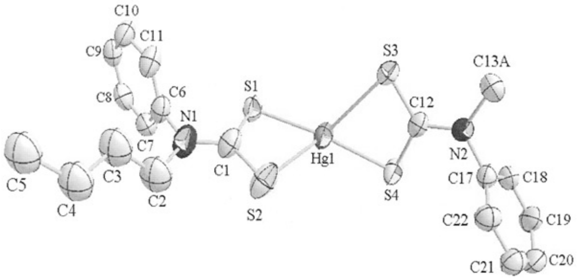


Figure 2. A molecular drawing of **3**. All hydrogens were omitted for clarity. Only the major components of the compositional and positional disorder are shown.

The eight-membered centrosymmetric dimeric Zn complex is similar to the complexes reported earlier [21, 30] with the same chain conformation but they differ in the alkyl substituents, giving rise to different disorder and site occupancy of the alkyl group in the mixed ligand complexes. Dithiocarbamates are considered as stereochemically rigid and sterically non-demanding [21, 31] because the planarity of MS_2CNC_2 determines the structures since all seven atoms approximately lie in a plane. In **1**, Zn occupies a crystallographic inversion center and the methyl group at C10 is disordered over two positions with the major component contributing 76.6(10)%. The entire tert–butyl group at N2 is disordered over two positions with the major component contribution of 63.4%. Zn–S bonds vary from 2.3117(7)–2.4352(7) Å and both the bridging and chelating dithiocarbamates consist of one short and one long Zn–S bonds. There are no significant differences in the Zn–S bond lengths compared to other dimeric Zn(II) dithiocarbamate complexes. Three of the C–N bonds, N(I)–C(1), N(1)–C(6), and N(2)–C(12), have bond lengths closer to a typical C–N double bond. The other three, N(1)–C(2) [1.496(10) Å], N(2)–C(13) [1.483(9) Å], and N(2)–C(17) [1.4557(2) Å], are closer to a typical C–N (1.47 Å) single bond. This is basically due to the compositional disorder observed at C(2) and C(13).

3.2.2. Single crystal X-ray studies of 3. The molecular structure of **3** with atom numbering scheme is shown in figure 2; crystal data and structure refinement are

Table 3. Selected bond lengths (Å) and angles (°) for **3**.

Hg(1)–S(1)	2.3824(15)	S(1)–Hg(1)–S(4)	172.77(6)
Hg(1)–S(4)	2.3926(15)	S(1)–Hg(1)–S(3)	118.25(5)
Hg(1)–S(3)	2.8483(17)	S(4)–Hg(1)–S(3)	68.89(5)
Hg(1)–S(2)	2.881(2)	S(1)–Hg(1)–S(2)	68.16(5)
S(1)–C(1)	1.736(7)	S(4)–Hg(1)–S(2)	111.52(6)
S(2)–C(1)	1.705(6)	S(3)–Hg(1)–S(2)	109.27(6)
S(3)–C(12)	1.705(6)	C(1)–S(1)–Hg(1)	93.6(2)
S(4)–C(12)	1.733(6)	C(1)–S(2)–Hg(1)	78.42(16)
N(1)–C(1)	1.328(8)	C(12)–S(3)–Hg(1)	77.9(2)
N(1)–C(6)	1.3432(9)	C(12)–S(4)–Hg(1)	91.79(19)
N(1)–C(2)	1.496(10)	C(1)–N(1)–C(6)	121.1(6)
N(2)–C(12)	1.330(7)	C(1)–N(1)–C(2)	122.7(7)
N(2)–C(17)	1.455(7)	N(1)–C(1)–C(2)	116.1(5)
N(2)–C(13)	1.483(9)	N(1)–C(1)–S(2)	122.9(5)
		N(1)–C(1)–S(1)	117.3(5)
		S(2)–C(1)–S(1)	119.9(4)
		C(3)–C(2)–N(1)	116.9(10)

presented in table 1 and selected bond lengths and angles in table 3. The molecular structure of **3** is monomeric with Hg tetrahedrally coordinated to two bidentate chelating dithiocarbamates. There is a compositional disorder at positions of C2 and C13 between a butyl and a methyl. The butyl is present 52.7% of the time at C2. Butyl cannot be present simultaneously at positions C2 and C13 due to steric limitations in the packing structures. When a butyl resides at C2, C5 exhibits postional disorder over two positions in a 32.3(13) : 20.5(13) ratio.

In the molecular structure of **3**, Hg(II) is four coordinate and can be described as distorted tetrahedral. This distortion is due to small bite angles of the chelating dithiocarbamates of about 68° which result in secondary deviations of the other perinuclear angles from ideal 109°. Bond angles in **3** are 118.25(5)–68.16(5)°. The Hg–S bond lengths are two short [2.3824(15) and 2.3926(15) Å] and two long [2.8483(17) and 2.881(2) Å] ones. The C–N bond varies between a typical single bond and a double bond, indicating that the Hg–S bond length has high covalent character [32].

3.3. *Spectroscopic analyses*

3.3.1. Infrared spectra. In infrared spectra of the mixed ligand complexes, two regions are vital in establishing structural and electronic characteristics. The thioureido band is at 1450–1490 cm^{-1}, masked by four unequal intensity bands around this region, characteristic of the aromatic ring of aniline. This band suggests the double bond character in the CN bond of $S_2C–NR_2$. It has been reported that mixed ligand complexes show uniformly greater υ(CN) absorption frequencies. This is attributed to increased flow of electron from nitrogen to sulfur, resulting in stronger metal–sulfur (M–S) bond and more stable chelates [33]. We compared υ(CN) of the three mixed ligand complexes with that of *N*-methyl-*N*-phenyl dithiocarbamate complexes (Zn, Cd, and Hg) and *N*-butyl-*N*-phenyldithiocarbamate complexes of the same metals and a shift of about 40 cm^{-1} to higher energy was observed. This supports the increased strength in the bond between the metal and the ligand. However, there is no significant influence on the position of the thioureide band by the nature of the metal.

Although basicity is expected to increase from methyl to butyl, the electron flow from nitrogen to carbon *via* hyperconjugation is prevented due to increased *N*-alkyl chain length (mass effect) [34]. The single and strong peaks at 955–960 $\mathrm{cm^{-1}}$ are attributed to C=S stretch of a symmetrically bound dithiocarbamate [35]. The position of these bands is about the same as those of the corresponding simple alkyl–aryl dithiocarbamate complexes. The observance of a single peak in this region indicates bidentate coordination of the dithio ligand; a doublet is expected for monodentate coordination [36–38]. In the free ligands, υ(CS) and υ(CN) are at 1055 $\mathrm{cm^{-1}}$ and 1460 $\mathrm{cm^{-1}}$, respectively, for both the *N*-methyl and *N*-butyl ligands.

Medium to strong bands (more intense in Zn and Cd) at 2957 $\mathrm{cm^{-1}}$ can be related to the asymmetric alkyl stretching vibration, while bands at 1380–1360 $\mathrm{cm^{-1}}$ are due to degenerate symmetric vibrations of alkyl [39]. Bands associated with υ(M–S) in dithiocarbamates are usually observed at 420–250 $\mathrm{cm^{-1}}$.

3.3.2. Electronic spectra. The electronic spectra of dithiocarbamates usually show high-intensity absorption due to NCS_2 [40]. Since the complexes are d^{10}, no absorption is expected in the visible region and only bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are expected. The $\pi \rightarrow \pi^*$ transition could appear as two bands ascribed to NCS and SCS. In the UV spectra of the ligands, two bands are observed at 234 and 374 nm for L^1, and 234 and 372 nm for L^2. Most literature reports [39, 41] have assigned these intense bands to intraligand $\pi \rightarrow \pi^*$ transition of the N–C–S group. The band due to $\pi \rightarrow \pi^*$ transition of S–C–S group, which usually appears as a shoulder on the NCS band, is obscured in spectra of both ligands and complexes. Bands at 372 and 374 nm for L^2 and L^1 are attributed to the $n \rightarrow \pi^*$ transition located on the sulfur [42]. On complexation these bands undergo bathochromic shift and appear at 325, 337, and 360 nm for the Zn(II), Cd(II), and Hg(II) complexes, respectively, probably due to ligand → d-orbital transition [43].

3.3.3. NMR. Signals observed at 4.10, 4.16, and 4.06 ppm in **1–3** are due to α-CH_2 of the butyl present in the dithiocarbamate. These peaks are triplets. In alkyl dithiocarbamates (NR_2, $R = CH_3$, $C_2H_5\ldots$), these signals are usually observed around 4.20 ppm. The variation could be ascribed to more deshielding of α–protons in (NR_2) compared to (NRPh) with more release of electrons on the nitrogen of the latter, forcing electron density toward the sulfur (or the metal) *via* the thioureide π-system [44]. The magnitude of this deshielding decreases with increase in distance of thioureide bond from the metal. Between 1.72 and 1.30 ppm are β-CH_2 and γ-CH_2 protons, each appearing as multiplets. Although variation of the metal is said not to affect the position of these signals since the interaction is mainly electrostatic [45], wide variation in the peak's position was observed between Cd and Hg complexes. The aromatic proton signals were at 7.44–7.22, 7.39–7.24, and 7.41–7.23 for Zn, Cd, and Hg complexes, respectively. In ^{13}C-NMR of the complexes, four groups of resonances can be assigned to ^{13}C sites: aromatic, methyl, methylene, and the thioureide carbons: C_6H_5–, CH_3–, –CH_2– and =NC(S)S–. The signals observed at 207 ppm for **1–3** are assigned to thioureide carbon $\partial(N^{13}CS_2)$. The aromatic carbons clearly reveal the magnetic unequivalence of the phenyl rings in the complexes. Two positions are evident in the spectra, peaks around 147.00 and 145.00 ppm which could be assigned to aromatic carbons of the *N*-methyl group. The second sets are signals between 129.60 and 125.30 ppm and appear as four peaks, assigned to aromatic carbons of the *N*-butyl group. The thioureide carbon signals occurred as two peaks with varying intensities at 207.00 ppm. The double resonance reflects the magnetic unequivalence of the ($N^{13}CS_2$). Signals around 60 ppm is assigned to the N-CH_2 (α-CH_2), attributed to the electronegativity of nitrogen and the fact that methylene (CH_2) carbons are less shielded than methyl [46]. The N–CH_3 carbons of the complexes resonate at 48.00 ppm, while the signal of the terminal CH_3 of the butyl group occurs at 13.70 ppm. The β and γ-CH_2 signals are at 29.20 and 19.80 ppm, respectively, due to the π-system.

4. Conclusions

Zn(II), Cd(II), and Hg(II) complexes of mixed dithiocarbamates, *N*-methyl-*N*-phenyl dithiocarbamate, and *N*-butyl-*N*-phenyl dithiocarbamate have been synthesized and characterized by elemental analyses, NMR, and IR spectroscopy. Single-crystal X-ray structures of the Zn(II) and Hg(II) complexes reveal distorted tetrahedral coordination geometries around the metals from dithiocarbamates with mixed alkyl substituents. The alkyl substituents are disordered over two positions with different site occupancies that affect the C–N bond length. The Zn(II) complex is dimeric with the dithiocarbamates acting as chelating and bridging ligands while the Hg complex is monomeric with bidentate chelating ligands; attempts to crystallize the cadmium complex were unsuccessful. The potential of the complexes as single-source precursors for semiconductor nanoparticles is being investigated.

Supplementary material

CCDC-737050 and 762810 contain the supplementary crystallographic data for this study. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: (+44)-1223-336-033 or Email: deposit@ccdc.cam.ac.uk.

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