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Synthesis, spectral, thermal and BVS investigations on ZnS₄N^N/N coordination environment: Single crystal X-ray structures of bis(dibenzyldithiocarbamato)(N^N)Zinc(II) complexes (N^N = 1,10-phenanthroline, tetramethylethylenediamine and 4,4'-bipyridine)

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ABSTRACT

The current paper describes the synthesis and spectral investigations on the adducts of $[Zn(dbzdtc)_2](1)$ with 1,10-phen (2), tmed (3), 2,2'-bipy (4) and 4,4'-bipy (5) (where, dbzdtc = dibenzyldithiocarbamate anion, 1,10-phen = 1,10-phenanthroline, tmed = tetramethylethylenediamine, 2,2'-bipy = 2,2'-bipyridine, 4,4'-bipy = 4,4'-bipyridne) and single crystal X-ray structures of $[Zn(dbzdtc)_2(1,10-phen)]$ (2) and [Zn(dbzdtc)₂(tmed)] (3) and [Zn(dbzdtc)₂(4,4'-bipy)] (5). ¹H and ¹³C NMR spectra of 1,10-phen, tmed, 2,2'-bipy and 4,4'-bipy adducts were recorded. ¹H NMR spectra of the complexes show the drift of electrons from the nitrogen of the substituents forcing a high electron density towards sulfur via the thioureide π -system. In the ¹³C NMR spectra, the most important thioureide (N¹³CS₂) carbon signals are observed in the region: 206-210 ppm. Fluorescence spectra of complexes (2) and (4) show intense fluorescence due to the presence of rigid conjugate systems such as 1,10-phenanthroline and 2,2'-bipyridine. The observed fluorescence maxima for complexes with an MS₄N₂ chromophore in the visible region are assigned to the metal-to-ligand charge transfer (MLCT) processes. Single crystal X-ray structural analysis of (2) and (3) showed that the zinc atom is in a distorted octahedral environment. Bond Valence Sum was found to be equivalent to 1.865 for (2), 1.681 for (3) supporting the correctness of the determined structure. BVS of (3) deviates from the formal oxidation number of zinc due to the non-aromatic, sterically hindering tetramethyl bonding end of tmed. Thermal studies on the compounds show the formation of $Zn(NCS)_2$ as an intermediate during the decay.

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1. Introduction

Dithiocarbamates of zinc and cadmium have continued to attract attention in recent years on account of their industrial applications [1,2] and biological profiles [3,4]. A recent work has established that cadmium dithiocarbamates may be useful precursors to form CdS nanowires [5] with potential applications [6]. Various main group metal-dithiolates have been investigated as precursors in metal organic chemical vapor deposition (MOCVD) [7–9]. The affinity of Zn and Cd towards sulfur containing ligands leads to many structurally novel compounds, which is a well-documented phenomenon [10–12]. In our efforts to correlate structure and fluorescent properties of Group XII metal dithiocarbamates and their adducts, synthesis and spectral characterization of the

adducts of $[Zn(dbzdtc)_2]$ (1) with 1,10-phen (2), tmed (3), 2,2'-bipy (4) and 4,4'-bipy (5) (where, dbzdtc = dibenzyldithiocarbamate, 1,10-phen = 1,10-phenanthroline, tmed = tetramethylethylenediamine, 2,2'-bipy = 2,2'-bipyridine, 4,4'-bipy = 4,4'-bipyridne) along with the single crystal X-ray structures of $[Zn(dbzdtc)_2(1,10$ phen)] (2), $[Zn(dbzdtc)_2(tmed)]$ (3) and $[Zn(dbzdtc)_2$ (4,4'-bipy)] (5). are reported in this paper.

2. Experimental

All the regents and solvents employed were commercially available analytical grade materials and were used as supplied without further purification. IR spectra were recorded on an ABB Bomen MB 104 spectrometer (range 4000–500 cm⁻¹) as KBr pellets. The UV– Vis spectra were recorded in benzene on a HITACHI U-2001 spectrophotometer. Fluorescence spectra of the free ligands, parent complexes and adducts were recorded in benzene. To prevent any non-linearity of the fluorescent intensity, 400 nm was chosen

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as the excitation wavelength. Thermal analysis was carried out on a Perkin–Elmer-Pyris-Diamond instrument.

2.1. X-ray crystallography

Intensity data were collected at ambient temperature (295 K) using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker CCD diffractometer for (**2**) and (**5**), respectively. Data for (**3**) were collected on a Philips PW1100 diffractometer. Data for (**2**) and (**5**) were corrected for absorption using the sADABS program [13], while those for (**3**) were corrected using the Ψ -scan technique [14]. All non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed geometrically. The OR-TEP diagrams were drawn with the ORTEP-3 program [15].

2.2. Preparation of the complexes

2.2.1. Preparation of $[Zn(dbzdtc)_2]$ (1)

Dibenzylamine (2 mmol) and carbon disulfide (2 mmol) in ethanol (10 ml) were mixed under ice-cold condition (5 °C) to form a yellow solution of dithiocarbamic acid. An aqueous solution of zinc nitrate hexahydrate (1 mmol) was then added with continuous stirring. A pale yellow precipitate was obtained, which was washed with ethanol and was then dried in air. (Yield: 70%; dec. 170– 172 °C). Anal. Calc. for $C_{30}H_{28}N_2S_4Zn$: C, 59.05; H, 4.62; N, 4.59. Found: C, 59.01; H, 4.30; N, 4.26%.

2.2.2. Preparation of $[Zn(dbzdtc)_2(1,10-phen)]$ (2)

A mixture of Zn(dbzdtc)₂ (0.25 mmol, 0.152 g) and 1,10-phen (0.25 mmol, 0.049 g) in acetonitrile-methanol (2:1 v/v; 20 ml) was refluxed for about 2 h followed by concentration to 10 ml. After two days, a pure yellow solid separated out from the solution. The solid was filtered and was dried over anhydrous calcium chloride. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetonitrile, benzene and chloroform (1:1:1 v/v/v) solution. (Yield: 65%; dec. 254–256 °C). *Anal.* Calc. for C₄₂H₃₆N₄S₄Zn: C, 63.82; H, 4.59; N, 7.09. Found: C, 63.52; H, 4.29; N, 6.89%.

2.2.3. Preparation of [Zn(dbzdtc)₂(tmed)] (3)

A mixture of $Zn(dbzdtc)_2$ (0.25 mmol, 0.152 g) and tetramethylethylenediamine (0.25 mmol, 0.037 ml) in acetonitrile–methanol (2:1 v/v; 20 ml) was refluxed for about 2 h followed by concentration to 10 ml. After two days pale yellow solid separated out from the solution. The solid was filtered and was dried over anhydrous calcium chloride. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of an acetonitrile, benzene and chloroform (1:1:1 v/v/v) solution. (Yield: 65%; dec. 176-178°C). Anal. Calc. for C₃₆H₄₄N₄S₄Zn: C, 59.52; H, 6.11; N, 7.71. Found: C, 59.22; H, 5.85; N, 7.40%.

Table 1	
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Infrared spectral data (values in cm⁻¹) for the complexes.

2.2.4. Preparation of $[Zn(dbzdtc)_2(2,2-bipy)]$ (4)

A mixture of Zn(dbzdtc)₂ (0.25 mmol, 0.152 g) and 2,2'-bipyridine (0.25 mmol, 0.039 g) in acetonitrile–methanol (2:1 v/v; 20 ml) was refluxed for about 2 h followed by concentration to 10 ml. After two days a yellow solid separated out from the solution. The solid was filtered and was dried over anhydrous calcium chloride. (Yield: 70%; dec. 233–235 °C.). Anal. Calc. for C₄₀H₃₆N₄S₄Zn: C, 62.69; H, 4.73; N, 7.31. Found: C, 62.40; H, 4.44; N, 7.01%.

2.2.5. Preparation of [Zn(dbzdtc)₂(4,4-bipy)] (5)

A mixture of $Zn(dbzdtc)_2$ (0.25 mmol, 0.152 g) and 4,4'-bipyridine (0.25 mmol, 0.039 g) in acetonitrile–methanol (2:1 v/v; 20 ml) was refluxed for about 2 h followed by concentration to 10 ml. After two days a pale yellow solid separated out from the solution. The solid was filtered and was dried over anhydrous calcium chloride. (Yield: 85%; dec. 221–223 °C). *Anal.* Calc. for $C_{70}H_{64}N_6S_8Zn_2$: C, 61.07; H, 4.69; N, 6.10. Found: C, 60.77; H, 4.41; N, 5.92%.

3. Results and discussion

3.1. Infrared spectral studies

Infrared spectral data of the complexes are shown in Table 1. For the present set of compounds **1-5**, the v_{C-N} (thioureide) band appears in the region: 1470–1490 cm⁻¹. The v_{C-S} bands are observed around 1100 cm⁻¹ (**1-5**) without any splitting, supporting the bidentate coordination mode of the dithiocarbamate to the metal center, and the v_{C-H} bands are observed around 2900 and 2800 cm⁻¹. The characteristic bands due to 1,10-phenanthroline appear around 1650, 1600 cm⁻¹ in the adducts. In the case of 2,2'-bipyridine adduct a characteristic band appeared at 1598 cm⁻¹. Similarly, for 4,4'-bipyridine, a band appeared at 1608 cm⁻¹.

3.2. Thermogravimetric studies

 $Zn(dbzdtc)_2$ (1) starts to decompose above 60 °C, indicating the loss of water molecules of crystallization (experimentally observed loss: 2.8%; theoretically expected: 2.9%). Immediately after the loss of water molecules, a single decomposition step sets in and proceeds up to 360 °C corresponding to the stabilization of $Zn(NCS)_2$ (experimentally observed residue: 29.2%; theoretically expected 28.9%). At around 370 °C, another thermal decay is observed corresponding to the stabilization of ZnS (experimentally observed residue: 15.4; theoretically expected 15.5). All the three decompositions mentioned are endothermic in nature.

From the thermograms of the adducts, it is found that all the complexes show almost similar thermal behavior. $[Zn(dbzdtc)_2(1,10-phen)](2)$ shows the loss of 1,10-phenanthroline (385 °C; 21.8%) followed by the thermal decay of dithiocarbamate

Complex	v_{C-N} thioureide	v_{C-S}	v_{C-H}	1,10-phen, 2,2'-bipy/4,4'-bipy ring frequencies	Phenyl ring v_{C-H}
$[Zn(dbzdtc)_2]$ (1)	1482	1077	2920		635-754
			2852		
$[Zn(dbzdtc)_2(1,10-phen)]$ (2)	1493	1093	2917	1656	696-729
			2863	1600	
$[Zn(dbzdtc)_2(tmed)]$ (3)	1493	1077	2909		635-734
			2852		
$[Zn(dbzdtc)_2(2,2'-bipy)]$ (4)	1492	1075	2918	1598	697-762
			2854		
$[Zn(dbzdtc)_2(4,4'-bipy)]$ (5)	1470	1074	2922	1608	635-737
			2853		

up to 500 °C leading to formation of Zn(NCS)₂. Further increase in temperature indicates ZnS as the final residue. [Zn(dbzdtc)₂(tmed)] (3) shows the initial decomposition of the tmed (300 °C: 14.9%) followed by dithiocarbamate. The final residue stabilized around 610 °C conformed to ZnS. Thermal decay of [Zn(dbzdtc)₂(2,2'bipy)] (4) shows initial loss of 2,2'-bipy (20.0%; 350 °C). Subsequent loss led to the formation of Zn(NCS)₂ (24.3%; 500 °C) and ZnS as final residue. $[Zn(dbzdtc)_2(4,4'-bipy)](5)$ showed a single stage thermal decomposition starting at 310 °C. Loss of 4,4'-bipy and dithiocarbamate moieties concertedly decomposed in a single step. The final residue formed at 610 °C was found to be ZnS. Comparison of the thermal stabilities of the parent and its adducts clearly shows a higher thermal stability of the adducts during decomposition. Formation of Zn(NCS)₂ takes place at a relatively lower temperature for the parent compared to its adducts. However, the formation of ZnS for all the adducts is complete around 600 °C.

3.3. NMR spectral studies

NMR spectral data of all the synthesized compounds are given in Table 2 along with the splitting patterns.

3.3.1. ¹H NMR

Signals observed around 5.17 ppm for complexes (1), (2), (3), (4) and (5) are due to benzylic-CH₂ protons of the dithiocarbamate. The observed deshielding of the $-CH_2$ protons in all the compounds [16] is attributed to the shift of electron density towards the nitrogen of the NR₂ groups, forcing high electron density on the sulfur (or the metal) through the thioureide π -system. The phenyl ring

Table 2

¹H and ¹³C NMR spectral data of the complexes (chemical shifts in ppm).

protons undergo weak deshielding and appear in the range of 7.10–7.45 ppm in all the complexes. Apart from the aromatic signals due to the dibenzyl moiety, the ring protons of 1,10-phenan-throline in (**2**) appear above 7.45 ppm. Complexes (**4**) and (**5**) also show signals above 7.46 ppm due to 2,2'-bipyridine and 4,4'-bipyridine respectively. In all the adducts, (**2**), (**4**) and (**5**) which involve aromatic nitrogenous bases, the signal corresponding to the proton adjacent to the coordinated nitrogen is clearly shifted to higher field compared to the free base.

Methyl protons of tmed appear at 2.24 ppm and those of methylene group appear at 2.38 ppm in uncomplexed tmed. The two signals at 2.63 ppm and 2.59 ppm in complex (**3**) are ascribed to methylene and methyl protons of tmed on complexation. The N-CH₂ and N-CH₃ proton signals are clearly deshielded on complexation. All the adducts show slight downfield shift compared to free nitrogenous ligands due to the reduced electron density of 1,10phenanthroline, tmed, 2,2'-bipyridine and 4,4'-bipyridine groups.

3.3.2. ¹³C NMR

The signals observed around 206.2–210.3 ppm for the complexes (1), (2), (3), (4) and (5) are assigned to the thiouride carbon δ (N¹³CS₂). A down field shift of the α -carbon signals (to the thioureide π -system) in the case of complexes (2), and (3) is an indication of the important consequence of the complexation process, *viz.*, a significant thioureide contribution to the stability of the complexes and a resultant reduction in the electron density.

For the compounds (**2**), (**3**), (**4**) and (**5**) phenyl ring carbons resonate in the region of 127.4–141.4 ppm. The methylene and methyl carbons of tmed in (**3**) show signals at 56.6 and 46.3 ppm respectively. The assignment of the deshielded signal to the α -car-

Compound	NMR	Phenyl ring protons/carbons	Benzylic-CH ₂	N-CH ₃	N 13 C S ₂ (thioureide)	1,10-Phen ring/2,2'-bipy 4,4'-bipy ring/tmed $-CH_2-$ and $-CH_3$ protons and carbons
1	¹ H ¹³ C	7.28–7.45 134.5-ipso carbon 128.9 128.2 128.1	5.09 55.8		206.2	
2	1H	7.10–7.32	5.17			9.70 8.27-8.29 7.69-7.72 7.78
	¹³ C	141.4 136.3-ipso carbon 128.8	55.9		210.3	149.0 137.7 127.4 126.5 124.5
3	¹ H	7.23-7.35	5.17			2.63 -CH ₂ - 2.59 -CH ₃
	¹³ C	136.0-ipso carbon 128.6 127.8 127.4	55.8	46.3	209.8	56.6 -CH ₂ - 46.3 -CH ₃
4	¹ H	7.25-7.35	5.14			9.26 8.20-8.22 7.93-7.96 7.46-7.49
	¹³ C	138.6-ipso carbon 128.7 127.9 127.6	55.8		208.9	150.9 149.1 135.7 125.1 120.8
5	$^{1}\mathrm{H}$	7.287. 35–7 <i>44</i>	5.15			9.14-9.16
	¹³ C	135.1-ipso carbon 129.0 128.9 128.1	55.9		207.3	150.6 146.7 122.3

bon is accomplished by considering the pronounced electron withdrawing effect of the NCS₂ π -system and the closer proximity of the α -carbons to the metal center. The observed small differences in chemical shifts for the 1,10-phenanthroline, tmed,2,2'-bipyridine and 4,4'-bipyridine fragments in the adducts (2), (3), (4) and (5) compared to the free nitrogenous ligands signals can be attributed to charge delocalization, which prevents the movement of electron density from the adjacent carbons. Generally, the extent of deshielding for the thioureide N¹³CS₂ signal in main group metal dithiocarbamates is greater in magnitude than those of normal valence state transition metal dithiocarbamates, which is in line with the observed thioureide carbon chemical shifts of the synthesized compounds [17]. In the case of parent bisdithiocarbamate (1) the thioureide carbon appears at 206.2 ppm whereas all the adducts show the corresponding signals at higher values. The highest chemical shift for the thioureide carbon is observed for the1.10phenanthroline adduct (2), *viz...* 210.3 ppm.. The increasing trend in the chemical shifts of the thioureide carbon of adducts is a clear indication of the the reduced contribution of polar thioureide bond in the adducts compared to the parent dithiocarbamate.

3.4. Fluorescence spectral studies

 $M(dtc)_2$ (where M = Zn and Cd and dtc = general notation for the dithiocarbamate anion) complexes show less intense (or) no fluorescence in the visible region. It may be attributed to the absence of effective fluorophores in the parent complexes or a less effective charge transfer transition [18]. On excitation of complexes (2), (3), (4) and (5) which have MS₄N₂/MS₄N chromophores, fluorescence maxima are observed in the region of 400–420 nm. This is ascribed to a possible metal ligand charge transfer (MLCT) or the brief

masking of the lone pair of electrons of nitrogen through a photo-induced electron transfer (PET) [19]. Complex (**2**) shows fluorescence bands with comparatively high intensity compared to the other octahedral complexes due to the presence of rigid aromatic 1,10-phenanthroline in the metal chelate.

3.5. Structural analysis

Details of crystal data, data collection and refinement parameters for (2), (3) and (5) are summarized in Table 3. Selected bond distances and bond angles are given in Table 4, and a comparison of structural parameters for compounds (1), (2), (3) and (5) is given in Table 5. Crystal structure of (4) and (5) have been reported earlier and the structure of (5) showed the phenyl rings with disorder [20,21]. The crystal structure of (5) has been re-determined for comparison with better reliability index and fortunately there was no disorder.

 $[Zn(dbzdtc)_2(1,10-phen)]$ (2), $[Zn(dbzdtc)_2(tmed)]$ (3) and $[Zn(dbzdtc)_2(4,4'-bipy)]$ (5) are monomeric and discrete. ORTEP diagrams of (2), (3) and (5) are shown in Figs. 1–3 together with the atom-numbering scheme. Four formula units are present in the unit cell. In both complexes, the zinc metal center is six-coordinated by four sulfur atoms from the dithiocarbamte ligands and two nitrogen atoms from the chelating 1,10-phenanthroline and tmed.

The complex (**2**) has crystallographically imposed twofold symmetry, with Zn lying on a rotation axis. The short thioureide C–N distance of 1.341(2) Å indicates that the π electron density is delocalized over the S₂CN moiety and that this bond has some double bond character. Because of the small bite angle [S–Zn–S = 70.840(16)°] of the dithiocarbamte and the steric influence of

Table 3

Crystal data, data collection and refinement parameters for (2), (3) and (5).

-			
Complex	(2)	(3)	(5)
Empirical formula	$C_{42}H_{36}N_4S_4Zn$	$C_{36}H_{44}N_4S_4Zn$	$C_{70}H_{64}N_6S_8Zn_2$
Formula weight	790.4	726.4	1376.49
Crystal dimensions (mm)	$0.18 \times 0.18 \times 0.14$	$0.25\times0.17\times0.14$	$0.32 \times 0.20 \times 0.12$
Crystal system	monoclinic	monoclinic	triclinic
Color	colorless	colorless	pale yellow
Habit	block	block	block
Space group	C2/c	$P2_1/n$	ΡĪ
a (Å)	25.1103(17)	11.643(2)	10.775(2)
b (Å)	10.5234(17)	11.872(2)	12.793(2)
c (Å)	15.0366(10)	26.509(5)	13.497(3)
α (°)	90	90	94.290(3)
β (°)	108.9948(11)	92.646(7)	105.367(4)
γ (°)	90	90	107.255(3)
U (Å ³⁾	3757.0(4)	3660.3(11)	1689.3(6)
Ζ	4	4	1
D_{calc} (g cm ⁻³)	1.397	1.318	1.353
$\mu ({\rm cm}^{-1})$	0.913	0.930	1.003
F(0 0 0)	1640	1528	714
θ (°)	1.72-27.11	3.08-25.25	1.59-25.25
Diffractometer	Bruker APEXII CCD	Philips PW1100	Bruker SMART CCD
Scan type	ω scans	ω-2θ	ω scans
Index ranges	$-32 \leqslant h \leqslant 32; \ -13 \leqslant k \leqslant 13; \ -19 \leqslant l \leqslant 19$	$-13 \leqslant h \leqslant 13; \ 0 \leqslant k \leqslant 14; \ 0 \leqslant l \leqslant 31$	$-12 \le h \le 12; -15 \le k \le 15;$
Reflections collected	23 030	6463	16 340
Unique reflections	25 550 A155	6457	6008
Observed reflections	2264	4101	4729
$F_{\rm e} > A_{\rm eff}(F_{\rm e})$	5504	4101	4238
Weighting scheme	$w = 1/[\sigma^2(E^2) + (0.0534P)^2 + 0.5556P]$ where	$w = 1/[\sigma^2(E^2) + (0.0163P)^2]$ where	$w = 1/[\sigma^2(F^2) + (0.0114P)^2]$ where
weighting scheme	$P = (F_0^2 + 2F_c^2)/3$	$P = (F_0^2 + 2F_c^2)/3$	$P = (F_0^2 + 2F_c^2)/3$
Number of parameters refined	231	406	389
Final <i>R</i> , <i>Rw</i> (observed data)	0.0330, 0.0897	0.0370, 0.0537	0.0243, 0.0445
Goodness-of-fit (GOF) on F^2	1.073	0.984	0.992

Table 4
Selected bond distances (Å) and bond angles (°) for complexes (2), (3) and (5)

(2)		(3)		(5)	
Zn1-S1 Zn1-S2	2.5395(6) 2.5259(5)	Zn1-S1 Zn1-S2 Zn1-S3 Zn1-S4	2.6664(9) 2.4543(8) 2.6031(8) 2.4952(8)	Zn1-S1 Zn1-S2 Zn1-S3 Zn1-S4	2.3231(7) 2.6144(7) 2.3364(7) 2.6248(7)
Zn1-N2	2.1646(15)	Zn1–N3 Zn1–N4	2.261(2) 2.243(2)	Zn1-N3	2.0627(14)
S1-C1 S2-C1	1.7092(18) 1.7154(19)	S1-C1 S2-C1 S3-C16 S4-C16	1.711(2) 1.723(3) 1.704(3) 1.725(2)	S1-C1 S2-C1 S3-C16 S4-C16	1.7305(18) 1.7102(18) 1.7315(19) 1.7184(17)
N1-C1 N1-C2 N1-C9	1.341(2) 1.460(2) 1.463(2)	N1-C1 N1-C2 N1-C9 N2-C16 N2-C17 N2-C24	1.349(3) 1.477(3) 1.459(3) 1.350(3) 1.460(3) 1.462(3)	N1-C1 N1-C2 N2-C16 N2-C17 N2-C24	1.342(2) 1.466(2) 1.336(2) 1.4746(19) 1.482(2) 1.321(2)
N2-C16 N2-C20	1.320(3) 1.349(2)	N3-C33 N3-C34 N4-C32 N4-C35 N4-C35	1.475(3) 1.478(3) 1.477(3) 1.477(3) 1.477(3) 1.472(3)	N3-C35	1.324(2)
S1-Zn1-S2	70.840(16)	S1-Zn1-S2 S3-Zn1-S4	70.21(2) 70.69(3)	S1-Zn1-S2 S3-Zn1-S4	73.136(19) 72.866(18)
C1-S1-Zn1 C1-S2-Zn1	85.38(6) 85.69(6)	C1-S1-Zn1 C1-S2-Zn1 C16-S3-Zn1 C16-S4-Zn1	82.41(9) 88.92(8) 82.64(9) 85.62(9)	C1-S1-Zn1 C1-S2-Zn1 N3-Zn1-S1 N3-Zn1-S2	88.72(6) 80.03(6) 115.48(5) 95.54(4)
S1-C1-S2	118.02(11)	S1–C1–S2 S3–C16–S4	118.42(14) 118.72(16)	S1-C1-S2 N3-Zn1-S3	118.11(11) 115.14(4)
C1-N1-C2 C1-N1-C9 C2-N1-C9	122.73(16) 122.60(16) 114.62(16)	C1-N1-C2 C1-N1-C9 C2-N1-C9 C16-N2-C17 C16-N2-C24 C17-N2-C24	124.1(2) 121.2(2) 114.32(18) 121.8(2) 122.5(2) 115.3(2)	C1-N1-C2 N3-Zn1-S4 C2-N1-C9 S1-Zn1-S3 S2-Zn1-S4 S1-Zn1-S4	122.53(15) 93.65(4) 114.99(15) 129.20(2) 170.256(17) 99.92(2)

Table 5

Comparison of bond parameters (Å, °) of related complexes.

Complex	Zn–S	Zn–S	Zn-N	C _{dtc} -N	S-C-S
$[Zn(dbzdtc)_2]^a (1)$	2.3389(7)	2.3682(7)	2.1646(15)	1.335(3)	117.6(13)
[Zn(dbzdtc)_2(1,10-phen)] (2)	2.5395(6)	2.5259(5)		1.341(2)	118.02(11)
$[Zn(dbzdtc)_2(tmed)]$ (3)	2.6664(9)	2.4543(8)	2.261(2)	1.349(3)	118.42(14)
	2.6031(8)	2.4952(8)	2.243(2)	1.350(3)	118.72(16)
$\left[\text{Zn}(dbzdtc)_2(4,4'\text{-bipy})\right]^b(\textbf{5})$	2.3231(7) 2.3364(7)	2.6144(7) 2.6248(7)	2.0627(14)	1.342(2) 1.336(2)	118.11(11) 117.89(11)

^a Ref. [24].

^b Ref. [20].

1,10-phenanthroline, the metal atom is in a highly distorted octahedral coordination environment. The significant asymmetry in the Zn–S distances [2.5395(6) and 2.5259(5) Å] is due to the steric effect exerted by 1,10-phenanthroline, as observed in similar adducts. The C–S distances [mean value 1.7123(19 Å] are on the contrary not significantly different. The Zn–N distance is 2.1646(15) Å. The C–C and C–N bond distances associated with the benzyl groups are normal.

In complex (**3**), the values of the thioureide C–N distances [1.349(3) and 1.350(3) Å] and the bite angle of the dithiocarbamate $[70.21(2) \text{ and } 70.69(3)^\circ]$ are comparable with those observed in (**2**). The remarkable asymmetry in the Zn–S distances [mean values 2.6347(9) and 2.4747(8) Å] is due to the steric influence of neutral tmed ligand in the distorted octahedral geometry. The C-S distances within the same dbzdtc anion as well as the Zn–N bond

lengths (Table 4) are a little, but significantly different. The benzyl groups show normal bond parameters and the changes in the bond parameters of tmed are due to chelation with the metal ion. In complex (**5**), zinc is in a five coordinate environment with 4,4'-bipyridyl acting as a bridging ligand. The Zn–S distances are asymmetric due to adduct formation. The most important difference observed in the structural parameter of (**5**) is that the Zn–N distance is relatively very short (2.0627 (14) Å) compared to the bidentate nitrogenous adducts.

Comparison of the bond parameters of the parent bis(dithiocarbamato)zinc(II) and the adducts (Table 5) clearly shows the significant increase in the Zn–S distances due to the addition of a bulky 1,10-phenanthroline, 2,2'-bipyidine [20] tmed or 4,4'-bipyridyl ligands to zinc. Comparison of the thioureide C–N bond lengths clearly shows a significant elongation in the adducts which



Fig. 1. ORTEP diagram of $[Zn(dbzdtc)_2(1,10-phen)]$ (**2**) with displacement ellipsoids drawn at the 50% level. Symmetry code: i = -x, y, 1/2 - z.



Fig. 2. ORTEP diagram of $[Zn(dbzdtc)_2(tmed)]~(3)$ with displacement ellipsoids drawn at the 50% level.



Fig. 3. ORTEP diagram of [Zn(dbzdtc)₂(4,4'-bipy)] (**5**) with displacement ellipsoids drawn at the 50% level.

indicates a reduced electron density flow towards the metal ion from the dithiocarbamate moiety.

3.6. BVS analysis

Bond valence sum (BVS) analysis can be applied to estimate the bond lengths; vice versa the sum of the bond lengths should give information about the valence of the central metal ion. Hence BVS studies indirectly prove the correctness of the crystal structures determined. For complex (2), the BVS was calculated to be 1.8653 (OK/B) which is close to the expected formal oxidation state of 2 [22,23]. It has been already reported that in the case of the parent [Zn(dbzdtc)₂], the BVS value is 1.9 and generally the value is greater than those of the adducts. The decrease in BVS values in the case of adducts is due to the increase in Zn–S distances (which are longer than those observed in the parent bisdithiocarbamate.). For complex (**3**), the BVS is 1.6811 (OK/B), which is very low. The observation is supported by the fact that the Zn-S distances in tmed adduct are longer than those observed in 1,10-phenanthroline due to high steric hindrance. In complexes (2) and (3), the BVS values are approximately close to 2.0 irrespective of coordination number, confirming the formal valency of zinc in the complexes. The larger deviation of the BVS value of (3) from the formal oxidation number is due to the non-aromatic, sterically hindering tetramethyl bonding end of tmed as opposed to the aromatic, planar rigid phenanthroline.

4. Supplementary data

CCDC 724128, 724295 and 760692 contain the supplementary crystallographic data for (**2**), (**3**) and (**5**). 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 e-mail: deposit@ccdc.cam.ac.uk.

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