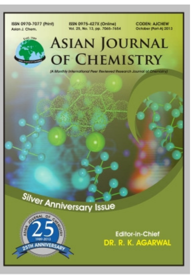
Asian Journal of Chemistry; Vol. 25, No. 18 (2013), 10057-10061

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15135



Synthesis, Characterization and Thermal Study of Phenanthroline Adducts of Zn(II) and Cd(II) Complexes of *bis*-N-Alkyl-N-phenyl dithiocarbamates

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(*Received*: 14 January 2013; *Accepted*: 5 November 2013) AJC-14334

Phenanthroline adducts of Zn(II) and Cd(II) complexes of N-alkyl-N-phenyl dithiocarbamate has been synthesized and characterized. The compounds formulated as [Zn(Rpdtc)$_2$phen] and [Cd(Rpdtc)$_2$phen], (where R = methyl, ethyl, butyl; p = phenyl; phen = 1,10-phenanthroline) were characterized by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy. The octahedral geometry around the metal ions consists of two molecules of chelating dithiocarbamate and one molecule of phenanthroline ligands. Thermogravimetric studies show that the Zn(II) adducts undergo similar decomposition profile *via* the isothiocyanate to the ZnS whereas the Cd(II) adducts undergo a complex and different decomposition pattern.

Key Words: Zinc(II), Cadmium(II), Dithiocarbamates, 1,10-Phenanthroline, Adducts, Thermal studies, Synthesis.

INTRODUCTION

Dithiocarbamate derived from secondary amines are widely studied because they possess interesting electrochemical and optical properties[1,2]. They exist in three different resonance forms and their binding properties determine the structural organization of their respective metal complexes[3-5]. Group 12 metal complexes of dithiocarbamates constrained to the +2 oxidation state are disposed toward a four coordinate geometry (MS$_4$) in which the metal ions are coordinated to two molecules of chelating ligands. The MS$_4$ forms of dithiocarbamates are coordinately unsaturated. Their large ionic size and small bite angle make it easy for them to form higher coordination number by the addition of two molecules of a Lewis base or by polymerization[6,7]. Much attention has been focused on studying their interaction with different types of nitrogenous Lewis bases[8,9] and the fascinating structural conformations which result as the base occupies a higher coordination position. The bidentate ligands: 2,2'-bipyridine and 1,10-phenanthroline, with two nitrogen donor atoms form compounds having MS$_4$N$_2$ chromophore with dithiocarbamate complexes and play major role in directing the framework topology[10-12].

Dithiocarbamate adducts are of importance due to their application in material chemistry as precursors in the preparations of metal sulphide thin films[13-16]. Recently, we reported the bipyridyl adducts of some N-alkyl-N-phenyl dithiocarbamates[17]. The decomposition of adducts of dithiocarbamate complexes of Zn(II) and Cd(II) with N-donor ligands are usually initiated by the loss of the neutral ligand[17-19]. The decomposition of the Cd(II) adducts of 1,10-phenanthroline has been observed to undergo a more complex decomposition[19]. In the present study, we report the synthesis, characterization and thermal study of 1,10-phenanthroline adducts of Zn(II) and Cd(II) complexes of N-alkyl-N-phenyl dithiocarbamates.

EXPERIMENTAL

All reagents and metal salts were used as obtained from Aldrich. Infrared spectra were recorded on Perkin-Elmer paragon 2000 FT-IR spectrometer in the range 3600-370 cm^{-1} as KBr disc. NMR spectra were obtained on a Bruker NMR spectrometer. Proton chemical shifts (δ) are reported in ppm relative to Me$_4$Si. Elemental analyses were performed by using a Fissions elemental analyzer. Thermogravimetric analysis was performed on a Perkin-Elmer thermogravimetric analyzer (TGA 7) fitted with a thermal analysis controller (TAC 7/ DX). A flow of N$_2$ was maintained with a heating rate of 10 °C/min between ambient temperature and 750 °C. 10-12 mg of the sample was loaded into an alumina cup and weight changes were recorded as a function of temperature. The dithiocarbamates complexes were prepared following a literature procedure[20].

Synthesis of 1,10-phenanthroline adducts: The adducts were prepared by adding a 20 mL hot chloroform solution of 1,10-phenanthroline (0.50 mmol, 0.099 g) into a hot 20 mL solution of 2 mmol of the respectively precursor complex in the same solvent. The resulting solution was refluxed for 0.5 h, filtered and then concentrated to about 10 mL 25 mL petroleum ether (boiling range 40-60 °C) was added to the solution. The precipitates that separated out from the solution were filtered, rinsed with ethanol and dried over anhydrous calcium chloride.

[Zn(mpdtc)₂phen]: (Yield: 0.220 g, 76 %; m.p. >250 °C). IR, (KBr, ν_{max}, cm^{-1}): 1422 (C=N), 1262 (C_2-N), 967 (C=S). ^{1}H NMR ($CDCl_3$): (N-C_6H_5) δ = 7.22 - 7.34 (m); [C_6H_5(phen)] δ = 7.76 - 7.80 (q), 7.78 (s), 8.37, 8.39 (d), 9.57 (s); (N-CH_3): δ = 3.74. ^{13}C NMR ($CDCl_3$): (C_6H_5) d = 126.17, 126.48, 129.09; C_6H_4(phen) δ = 149.19, 146.50, 142.35, 137.50; (N-CH_3): δ = 47.14

[Zn(epdtc)₂phen]: (Yield: 0.289 g, 88 %; m.p. 206-208 °C). IR (KBr, ν_{max}, cm^{-1}): 1423 (C=N), 1264 (C_2-N), 976 (C=S). ^{1}H NMR ($CDCl_3$): (N-C_6H_5) δ = 7.20-7.33 (m); [C_6H_5(phen)] δ = 7.73, 7.744, 7.751, 7.763 (q); 7.84 (s); 8.36, 8.34 (d), 9.53 (s); (α-CH_2) δ = 4.28, 4.26, 4.225, 4.23 (q); (CH_3) δ = 1.20, 1.22,1.24 (t). ^{13}C NMR ($CDCl_3$): (C_6H_5) δ = 124.30, 126.46, 127.36, 128.59 129.03; C_6H_5 (phen) δ = 137.35, 146.12, 149.25; (N-CH_2) δ = 53.66; (CH_3) δ = 12.67

[Zn(bpdtc)₂phen]: (Yield: 0.313 g, 87 %; m.p. 200-203 °C). IR (KBr, ν_{max}, cm^{-1}): 1426 (C=N), 1267 (C_2-N), 982 (C=S). ^{1}H NMR ($CDCl_3$): (N-C_6H_5) δ = 7.20-7.38 (m); [C_6H_5 (phen)] δ = 7.70, 7.72, 7.74, 7.75 (q); 7.82 (s); 8.34, 8.32 (d), 9.51 (s); (α-CH_2) δ = 4.26, 4.24, 4.23, 4.21 (q); (β-CH_2) δ = 1.74, 1.72, 1.71, 1.69 (q); (γ-CH_2) δ = 1.96, 1.94, 192, 1.88 (q), (CH_3) δ = 0.82 (t). ^{13}C NMR ($CDCl_3$): (C_6H_5) δ = 122.50, 124.18, 125.14, 126.55, 127.16; C_6H_4 (phen) δ = 146.55, 144.68, 139.25; (α-CH_2) δ = 57.83; (β-CH_3) δ = 40.45; (γ-CH_2) δ = 24.63; (?-CH_3) δ = 9.22

[Cd(mpdtc)₂phen]: 0.286 g, 85 %; m.p. > 250 °C). IR (KBr, ν_{max}, cm^{-1}): 1423 (C=N), 1263 (C_2-N), 971 (C=S). ^{1}H NMR ($CDCl_3$): (N-C_6H_5) δ = 7.22-7.34 (m); [C_6H_5(phen)] δ = 7.75, 7.76, 7.77, 7.78 (q), 7.87 (s), 8.36, 8.37, 8.38, 8.39 (q), 9.33, 9.34 (d); (N-CH_3): δ = 3.74. ^{13}C NMR ($CDCl_3$): (C_6H_5) δ = 124.59, 126.00, 127.32, 128.85, 129.11; C_6H_4 (phen) δ = 137.74, 141.63, 148.89, 149.74; (N-CH_3): δ = 48.28

[Cd(epdtc)₂phen]: (Yield: 0.302 g, 85 %; m.p. > 250 °C). IR (KBr, ν_{max}, cm^{-1}): 1446 (C=N), 1273 (C_2-N), 993 (C=S). ^{1}H NMR ($CDCl_3$): (N-C_6H_5) δ = 7.20-7.35 (m); [C_6H_5 (phen)] δ = 7.36, 7.40, 7.42, 7.43 (q); 7.87, 7.89, 7.91, (t); 8.1.0, 8.12 (d), 8.92, 8.93 (d); (α-CH_2) δ = 4.26, 4.25, 4.23, 4.21 (q); (CH_3) δ = 1.20, 1.23, 1.25 (t). ^{13}C NMR ($CDCl_3$): (C_6H_5) δ = 121.054, 125.311, 127.06, 127.53, 129.10; C_6H_4 (phen) δ = 138.57, 146.64, 149.75; (N-CH_2) δ = 55.03; (CH_3) δ = 12.53.

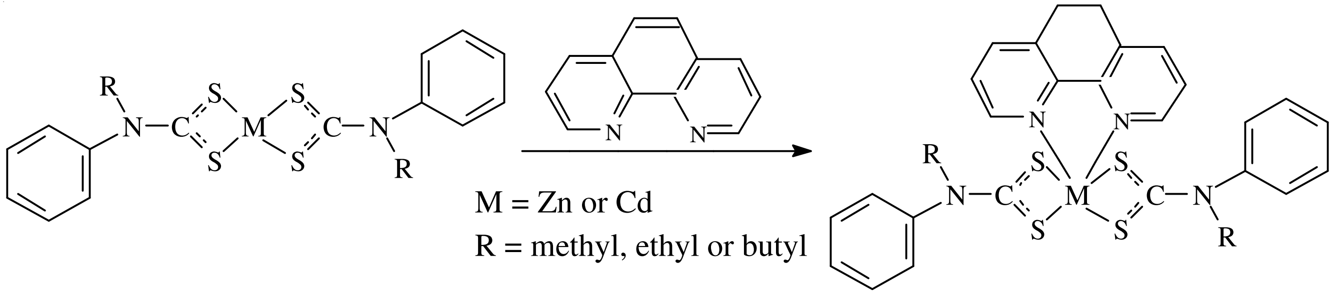
[Zn(bpdtc)₂phen]: (Yield: 0.332 g, 88 %; m.p. > 250 °C). IR (KBr, ν_{max}, cm^{-1}): 1448 (C=N), 1276 (C_2-N), 996 (C=S). ^{1}H NMR ($CDCl_3$): (N-C_6H_5) δ = 7.20-7.34 (m); [C_6H_5 (phen)] δ = 7.73 (s); 7.85 (s); 8.33, 8.35 (d), 9.29 (s); (α-CH_2) δ = 4.17, 4.15, 4.13, 4.10 (q); (β-CH_2) δ = 1.67, 1.65, 1.55 (q); (γ-CH_2) δ = 1.29, 1.27, 1.25, 1.23 (q), (CH_3) δ = 0.87, 0.85, 0.83 (t). ^{13}C NMR ($CDCl_3$): (C_6H_5) δ = 122.50, 124.18, 125.14, 126.55, 127.16; C_6H_4 (phen) δ = 146.00, 142.00; (α-CH_2) δ = 58.07; (β-CH_3) δ = 29.30; (γ-CH_2) δ = 19.98; (CH_3) δ = 13.76.

RESULTS AND DISCUSSION

The Zn(II) and Cd(II) complexes of N-alkyl-N-phenyl dithiocarbamate were refluxed in chloroform in the presence of 1,10-phenanthroline in 1:1 mole ratio to give the respective adducts. Attempts to synthesize the Hg(II) adducts of both Lewis bases were unsuccessful. This follows the fact that unlike Cd, Hg does not readily form compounds of higher coordination number. The ease of formation of group 12 adducts could be said to follow the trends Cd(II) > Zn(II) > Hg(II). It was observed that the 2,2'-bipyridine adducts[17,21] readily crystallized out of solution compared to the 1,10-phenanthroline analogue and could be ascribed to the effect of the rigidity due to the extended conjugation of the 1,10-phenanthroline. They are soluble in common organic solvents, such as dichloromethane and chloroform. The analytical data of the adducts are given in Table-1 and their formation in **Scheme-I**.

TABLE 1
ANALYTICAL DATA FOR 1,10-PHENANTHROLINE ADDUCTS OF Zn AND Cd COMPLEXES

Complexes	f.w.	Elemental analysis (%): Calcd. (Found)			
		C	H	N	S
[Zn(mpdtc)₂phen]	610.15	55.12 (55.11)	3.96 (3.89)	9.18 (9.21)	21.02 (21.02)
[Zn(epdtc)₂phen]	624.17	56.64 (56.65)	4.12 (4.13)	8.81 (8.82)	20.16 (20.18)
[Zn(bpdtc)₂phen]	652.23	37.29 (37.67)	3.68 (3.98)	4.96 (4.58)	22.48 (22.78)
[Cd(mpdtc)₂phen]	657.18	51.17 (51.20)	3.68 (4.00)	8.53 (8.50)	19.51 (19.45)
[Cd(epdtc)₂phen]	671.20	51.89 (51.80)	3.90 (3.88)	8.35 (8.36)	19.11 (19.20)
[Cd(bpdtc)₂phen]	699.26	53.25 (53.50)	4.32 (4.30)	8.01 (8.00)	18.34 (18.32)



Scheme-I: Formation of the compounds

Infrared spectra studies of the adducts: The infrared spectra of the adducts and their precursor complexes were compared and assigned on careful comparison. The thioureide band ν(C-N) for the adducts show a vibrational peak which are considerably lower than the ν(C-N) values of their respective parent complexes and can be ascribed to the change in the coordination geometry from tetrahedral to octahedral[21]. It is also an indication of the transfer of electrons from the nitrogen of the Lewis base (1,10-phenanthroline) to the metal ion causing an increase in electron density upon formation of the adduct[22]. Comparing the position of the ν(C-N) in the different adducts with respect to the alkyl group, lower vibrational frequencies were observed in the ν(C-N) of the zinc(II) bipyridine adducts which has the butyl substituent[17]. This may be due to the lengthening of the alkyl chain which has been found to be accompanied by a decrease in ν(C-N)[23]. However, in the 1,10-phenanthroline adducts of both metals and in the bipyridine adducts of cadmium[21], an increasing sequence in the vibrational peak of ν(C =N), ν(C_2-N) and ν(C=S) was observed in the order [M(mpdtc)$_2$bpy] < [M(epdtc)$_2$bpy] < [M(bpdtc)$_2$bpy] and [M(mpdtc)$_2$phen] < [M(epdtc)$_2$phen] < [M(bpdtc)$_2$phen] (where, m = methyl, e = ethyl and b = butyl; M = Zn and Cd) and may be ascribed to the increasing electron donating effect of the alkyl group with carbon chain.

The spectra of all the compounds show a single peak at the region (1000 ± 70 cm^{-1}), indicating that the dithiocarbamate ligands are bidentately coordinated to the metal ions[24-26]. The C-H stretching for the methyl, ethyl and butyl groups showed in the region 2930-2928 cm^{-1}. The C-H bending modes appear as medium intensity band between 1340-1338 cm^{-1} while the C-H bending of the aromatic rings were observed in the range 1370-1360 cm^{-1}, as a high intensity band. The =C-H stretch of the aromatic ring show bands between 3090-3038 cm^{-1}. The increase in the vibrational frequency has been ascribed to the effect of the increased electronegativity of sp^2 hybridised carbon as compared to sp^3 hybridized[27].

NMR spectral studies of the adducts: The ^{1}H and ^{13}C NMR spectra of the adducts in chloroform confirmed the presence of 1,10-phenanthroline in the molecular structure of the compounds. ^{1}H NMR spectra show signals for the hydrogen of the methyl, integrated as six protons, in three distinctly separate positions, at δ = 3.74 (6H, s), 1.22 (6H, t) and 0.82 (6H, t) for the Zn(II); 3.74 (6H, s), 1.23 (6H, t) and 0.85 (6H, t) for the Cd(II). The positions of these resonant peaks reflect the reduction in the deshielding effect of the electronegative N-atom as the distance between the nitrogen and the carbon bearing the protons increases. The compounds [Zn(epdtc)$_2$phen], [Zn(bpdtc)$_2$phen], [Cd(epdtc)$_2$phen] and [Cd(bpdtc)$_2$phen] show signals around δ = 4.20 ppm (4H, q), which correspond to the -CH_2 protons on a highly deshielding/electronegative atom (nitrogen). It is observed that these peaks appear at a slightly lower field region in the zinc compounds compared with the cadmium.

The peaks due to the methylene protons of the butyl group appear as four hydrogen triplet at about δ = 1.30 and 1.70 ppm. The peaks in the region δ = 7.22-7.30 ppm in the compounds are ascribed to the phenyl ring protons. The relative weak deshielding observed could be attributed to the shift of electron density towards the nitrogen of the NRR' (R = alkyl; R' = phenyl) thereby enhancing the electron density on the sulphur *via* the thioureide π-system[28]. The peaks around δ = 7.70, 7.80, 8.30 and 9.50 ppm in the compounds are due to the ring protons of the 1,10-phenanthroline[29].

The ^{13}C NMR spectra of the compounds show five signals in the region δ = 124-129 ppm which correspond to the aromatic carbons from the phenyl substituent of the dithiocarbamate ligand. The resonant peaks due to 1,10-phenanthroline carbons appeared around δ = 137-149 ppm. In the adducts, it is observed that the resonances for the carbons of the (2, 9), (3, 8) and (5, 6) positions display a downfield coordination shifts (0.2-1.2 ppm) with respect to that in free 1,10-phenanthroline. These shifts are characteristic of coordinated 1,10-phenanthroline[30].

The signals for the carbon of the methylene bound to nitrogen in the dithiocarbamate were observed between 53-58 ppm in the zinc compounds and between 54-60 ppm in the cadmium compounds. The higher downfield shift observed in N-butyl-N-phenyl derivatives as compared to the other alkyl substituents (ethyl and methyl) may be due to the high inductive effect of the butyl substituent compared to the ethyl and methyl group. The resonant peak for the nitrogen bound methyl group appeared around 47-48 ppm in all compounds. The δ- and γ-methylene carbons of the butyl group appeared around 29 and 20 ppm, respectively. The signals due to the carbon of the -NCS_2 are usually observed between 208-209 ppm in the Lewis base adducts of N-alkyl-N-phenyl dithiocarbamates.

Thermal studies: The thermogravimetric analysis (TG) of the adducts, carried out under nitrogen environment. It should be noted here that the weight loss trend as a function of temperature followed similar trends in all the zinc(II) adduct but different pattern in the cadmium(II) adducts. Weight loss is in two distinct steps: (i) in the range of 226-330 °C, (ii) 209-345 °C and (iii) at 196-335 °C, for [Zn(mpdtc)$_2$phen], [Zn(epdtc)$_2$phen], and [Zn(bpdtc)$_2$phen] respectively. The corresponding weight losses are 70.97, 71.52 and 74.22 %; which approximately correspond to concerted loss of a molecule of phenanthroline and the destruction of the dithiocarbamate moiety (theoretical loss is (i) 70.42, (ii) 70.94 and (iii) 72.17 % respectively) resulting in the formation of the corresponding isothiocyanate. The estimated mass of the residues agrees well with the TGA values. Above this temperature, the complexes maintained its weight for a stretch of approximately 200 °C after which the second decomposition step sets in. The second step on the TGA curve is attributed to the thermal decomposition of the isothiocyanate. The mass remaining after the second step which resumed around 560, 528, 540 °C and terminated at 651, 749 and 667 °C for [Zn(mpdtc)$_2$phen], [Zn(epdtc)$_2$phen] and [Zn(bpdtc)$_2$phen] respectively roughly corresponds to the mass of zinc(II) sulphide (Table-2) as the final white-creamy, fine-powdered product. The decomposition of the 1,10-phenanthroline adducts of the cadmium(II), unlike the zinc(II) adducts, do not follow similar pathways because the cadmium(II) adducts are less thermally stable than the zinc(II) analogue. The thermograms of the zinc(II) adducts indicated a well defined step, whereas the corresponding cadmium(II) analogues showed an undefined decomposition pattern.

The decomposition of [Cd(mpdtc)$_2$phen] involves the break-off of the 1,10-phenanthroline molecule to form an unstable four coordinate complex [Cd(mpdtc)$_2$], the formation of isothiocyanate, Cd(NCS)$_2$ and the decomposition of the isothiocyanate to form CdS residue. These steps are peculiar with adducts of N, N donor ligands with Zn and Cd dithiocarbamate complexes[17,18,31]. The loss in weight is corresponding to the decomposition of the four coordinate complex started around 288 °C and continued to about 348 °C with a peak temperature at 317 °C. The weight loss of 2.66 mg observed fairly agrees with the calculated weight of 2.90 mg which corresponds to a weight decomposition of 68 %. The short plateau observed afterward indicates a little stability and the third stage of decomposition commenced at 436 °C up to 610 °C, leaving a 1.78 mg of residue which is believed to be CdS (calculated as 1.83 mg). The total mass loss up to this decomposition point was found to be 79 %. Beyond 610 °C, the observed little peak in the DTG curve could be ascribed to the oxidation of the CdS residue.

The thermogram of [Cd(epdtc)$_2$phen], consist of three stages decomposition pattern.. The weight loss between 66 °C and 156 °C is about 25 % and corresponds to the release of the 1,10-phenanthroline molecule. The second stage (II) of decomposition started at 190 °C and progressed till 358 °C with a mass loss of 41 %. The mass of the residue (4.57 mg) obtained agrees favourably with the calculated (4.12 mg). The third stage of mass loss followed the second stage abruptly and occurred in the range 361-733 °C, given a 12 % weight loss with a residual mass of 1.35 mg. This could be attributed to the formation of CdS by the decomposition of Cd(SCN)$_2$. The theoretical value of 1.40 mg agrees well with the experimental data.

The decomposition profile of [Cd(epdtc)$_2$phen] showed mass loss corresponding to three major decomposition stages. The decomposition peak temperatures of the different stages are 102 °C (stage I), 297 °C (stage II) and 536 °C (stage III). The first decomposition step shows an initial mass loss of 9.2 % in the temperature range 56-141 °C. The initiating temperature of this decomposition step is too low to be ascribed to the breaking of Cd–N bond and the weight expunged (0.97 mg) did not correspond to the stoichiometric weight of the 1,10-phenanthroline (2.97 mg). The second stage of decomposition sets in immediately at 141 °C and progressed up to 338 °C with a weight loss of about 70 %. The weight of the residue obtained is 7.40 mg and it agrees with the weight of CdS (calculated 7.33 mg). The plateau which is observed over a temperature stretch of 118 °C indicates some degree of stability in the obtained residue. The third stage of decomposition began at 458 °C and ended at 702 °C. At this point, a total of 92 % decomposition has occurred and results in the residual weight of 1.36 mg. The obtained product in this final stage of decomposition is undefined.

For adducts of zinc and cadmium of similar alkyl substituents, it could be observed that the decomposition peak temperature leading to the formation of their respective metal isothiocyanate is higher in the cadmium(II) than in the zinc(II) adducts; while in the decomposition peak temperature leading to the formation of the metal sulphide a higher temperature value is observed in the zinc(II) than in the cadmium(II) adducts (Tables 2 and 3). It is possible that cadmium, with larger ion, is able to accommodate the phenanthroline group making the interaction ideal; whereas for the zinc the interaction is less favourable, so the structure breaks down at lower temperatures and accompanied with the expulsion of the phenanthroline molecule.

Conclusion

Six 1,10-phenanthroline adducts of Zn(II) and Cd(II) N-alkyl-N-phenyl dithiocarbamate formulated as [M(Rpdtc)$_2$bpy] and [M(Rpdtc)$_2$phen] [R = CH_3, C_2H_5, C_4H_9 and M = Zn, Cd] was synthesized and characterized by elemental analysis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopy and TGA. In the complexes, the metal ions are coordinated to two molecules of dithiocarbamate and one molecule of 1,10-phenanthroline

TABLE-2
THERMAL DECOMPOSITION DATA FOR THE Zn(II) ADDUCTS

Compounds	Decomposition range (°C)	Peak temperature (°C)	Total mass loss (%)	Product obtained	Mass obtained	
					Exp.	Theor.
Zn(mpdtc)$_2$phen	226-330	290	70.97	Zn(NCS)$_2$	3.17	3.23
	560-651	605	86.32	ZnS	1.41	1.73
Zn(epdtc)$_2$phen	209-345	295	71.52	Zn(NCS)$_2$	2.95	3.01
	528-749	623	86.77	ZnS	1.37	1.60
Zn(bpdtc)$_2$phen	196-335	271	67.22	Zn(NCS)$_2$	3.77	3.20
	540-667	610	84.69	ZnS	1.76	1.71

TABLE-3
THERMAL DECOMPOSITION DATA FOR THE Cd(II) ADDUCTS

Compounds	Decomposition range (°C)	Peak temperature (°C)	Total mass loss (%)	Product obtained	Mass TG	Obtained theory
[Cd(mpdtc)$_2$phen]	120-288	277	13	Undefined	–	–
	288-348	317	68	[Cd(NCS)$_2$]	2.90	2.66
	436-610	475	79	CdS	1.83	1.78
[Cd(epdtc)$_2$phen]	66-156	124	25	[Cd(epdtc)]	3.28	2.81
	190- 358	322	66	[Cd(NCS)$_2$]	4.12	4.57
	361-733	563	78	CdS	1.40	1.35
[Cd(bpdtc)$_2$phen]	56-141	102	9	[Cd(bpdtc)$_2$phen]	–	–
	141-338	297	79	CdS	7.33	7.40
	459-702	536	92	Undefined	–	–

to form six coordinate octahedral complexes. Thermal gravimetric analysis of the compounds showed that all the zinc(II) adducts undergo similar and simple decomposition pattern while the cadmium(II) adducts showed different and complex pattern of decomposition.

ACKNOWLEDGEMENTS

The authors are grateful to Govan Mbeki Research and Development Centre, University of Fort Hare for financial support.

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