

Spectral and thermal studies on mixed ligand complexes of zinc(II) and cadmium(II) with diethyldithiocarbamate and 2,2'-bipyridyl/1,10-phenanthroline

K HUSSAIN REDDY* and Y LINGAPPA†

Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003, India

† Department of Chemistry, SVU Post-Graduate Centre, Cuddapah 516 001, India

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Abstract. Mixed ligand complexes of zinc(II) and cadmium(II) with diethyldithiocarbamate (ddtc) as a primary ligand and pyridine (py), 4-picoline (4-pic), 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen) as secondary ligands have been prepared and characterized by elemental analysis, thermogravimetric (TG) studies, infrared and $^1\text{H-NMR}$ spectral data. The general formula of cadmium(II) complexes are $(\text{L})_2\text{Cd}(\text{ddtc})_2$ and $(\text{L-L})\text{Cd}(\text{ddtc})_2$ while corresponding zinc complexes have $(\text{L})\text{Zn}(\text{ddtc})_2$ and $(\text{L-L})\text{Zn}(\text{ddtc})_2$ (where, L = py, 4-pic; L-L = bpy, phen) as evidenced by their elemental analysis and thermogravimetric studies. Infrared spectral data reveal that ddtc acts as a bidentate ligand in all cadmium complexes. However, in $(\text{L})\text{Zn}(\text{ddtc})_2$ and $(\text{L-L})\text{Zn}(\text{ddtc})_2$ complexes ddtc acts as bi- and unidentate ligand respectively. Octahedral geometry is assigned for all cadmium(II) complexes. Although $(\text{py})\text{Zn}(\text{ddtc})_2$ and $(4\text{-pic})\text{Zn}(\text{ddtc})_2$ complexes are known to have pentacoordinate zinc, yet the other mixed ligand complexes of $\text{Zn}(\text{ddtc})_2$ with bpy and phen have tetracoordinate zinc as evidenced by their infrared spectra. High resolution (300 MHz) $^1\text{H-NMR}$ spectra support the characterization of all complexes. TG data indicate that cadmium complexes initiate decomposition at high temperature in comparison with their respective zinc complexes. Thermograms of all mixed ligand complexes have two decomposition regions, out of which the first one corresponds to the removal of secondary ligands.

Keywords. Mixed ligand complexes; zinc(II); cadmium(II); diethyldithiocarbamate; 2,2'-bipyridyl; 1,10-phenanthroline.

1. Introduction

Although some pyridine base adducts of $\text{Zn}(\text{ddtc})_2$ have been isolated and characterized (Gupta and Srivastava 1970), no report is available in the literature on spectral (IR and $^1\text{H-NMR}$) and thermal studies of mixed ligand complexes of zinc(II) and cadmium(II) using diethyldithiocarbamate (ddtc) and 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen). We therefore decided to synthesise zinc(II) and cadmium(II) derivatives of ddtc and of their adducts with pyridine (py), 4-picoline (4-pic), 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen). In contrast to the pentacoordinate zinc in the $(\text{py})\text{Zn}(\text{ddtc})_2$ complex, the corresponding $(\text{py})_2\text{Cd}(\text{ddtc})_2$ complex has hexacoordinate cadmium facilitated by the formation of 1:2 adducts.

* For correspondence

In (bpy)Zn(ddtc)₂ and (phen)Zn(ddtc)₂ complexes, the ddtc ligand acts formally as a unidentate ligand favoured by the inability of zinc to expand its coordination sphere and this leads to the formation of tetracoordinate zinc. The possible origins of the remarkable chemical and structural differences between these complexes of cadmium and zinc will be discussed here.

2. Experimental

All the chemicals and solvents used were of analytical reagent grade. ¹H-NMR spectra were recorded on a Varian XL-300 MHz high resolution NMR instrument in CDCl₃ solvent at room temperature. Infrared spectra were recorded in the range(s) 4000–400 cm⁻¹ (as KBr discs); 600–180 cm⁻¹ (as CsI discs) on a Perkin–Elmer 983G infrared spectrophotometer. Thermograms were recorded on General V2.2A DuPont 9900 thermal analysing system (TAS) with a heating rate of 6°C per min.

2.1 Synthesis of 2,2'-bipyridyl and 1,10-phenanthroline adducts

These adducts were produced under mild and simple reaction conditions. Metal dithiocarbamate [M(ddtc)₂, where M = Zn, Cd; 3 mmol] was placed in a Schlenk tube of 100-ml capacity and suspended in 25 ml of CH₂Cl₂. To this suspension suitable secondary ligand (bpy, phen) (15 mmol) was added to get a clear solution. After stirring this solution magnetically for 30 minutes and followed by the addition of *n*-hexane (25 ml) through the walls of the Schlenk tube, bright yellow-coloured crystalline compounds formed overnight. Adducts thus obtained were collected by filtration, washed with hot water and hexane and dried under vacuum over CaCl₂.

Zn(ddtc)₂ and Cd(ddtc)₂ and their pyridine and 4-picoline adducts were prepared as described earlier.

2.2 Synthesis of quinoline adducts

In contrast to the preparation of bpy and phen adducts described above, 8-hydroxyquinoline adducts were obtained under relatively wild reaction conditions. The melt method which has been used for obtaining mixed ligand complexes of dithiolenes (Schrauzer and Rabinowitz 1968; Miller and Dance 1973) was used for getting 8-hydroxyquinoline (Hquin) adducts of Zn-ddtc and Cd-ddtc. Zinc or cadmium dithiocarbamate (2.77 mmol) is mixed with 8-hydroxyquinoline (3 mmol) and the mixture is taken in a microsublimation apparatus. The solid mixture was heated at 110°C for 1 hour. The yellow solid residue is washed with hot water, 0.2 N acetic acid and hexane and dried under vacuum. The substance is taken in a dry test tube and dissolved in CH₂Cl₂. Hexane is then slowly added down the walls of the test tube for getting pure adducts.

3. Results and discussion

Colour, decomposition temperatures (°C) and analytical data for all mixed ligand complexes are presented in table 1. Thermal (table 2), infrared (table 3) and ¹H-NMR spectral (table 4) data are presented in the respective tables.

Table 1. Analytical data of mixed ligand complexes.

Complex	Colour	m.p.*(°C)	Percentage [†] of		
			Carbon	Hydrogen	Nitrogen
Zn(ddtc) ₂	Colourless	205–207	33.20 (32.73)	5.53 (5.60)	7.75 (8.10)
Zn(ddtc) ₂ bpy	Yellow	127–129	46.38 (46.67)	5.41 (5.35)	10.82 (11.10)
Zn(ddtc) ₂ phen	Yellow	205–207	46.45 (46.55)	5.11 (4.95)	10.23 (10.50)
Zn(ddtc)(quin)	Deep-yellow	132–135	47.00 (47.90)	4.47 (4.45)	7.83 (7.75)
Cd(ddtc) ₂	Colourless	228–229	29.85 (29.40)	4.60 (4.93)	6.75 (6.90)
Cd(ddtc) ₂ (py) ₂	Colourless	155–157	43.56 (43.16)	5.26 (5.39)	10.41 (10.07)
Cd(ddtc) ₂ (4-pic) ₂	Colourless	161–162	44.13 (44.41)	5.82 (5.72)	9.50 (9.42)
Cd(ddtc) ₂ bpy	Yellow	205–207	43.15 (42.52)	5.05 (4.96)	10.10 (9.92)
Cd(ddtc) ₂ phen	Yellow	280–281	45.00 (44.86)	4.80 (4.76)	9.90 (9.52)
Cd(ddtc)(quin)	Deep-yellow	125–127	42.55 (41.44)	4.00 (3.95)	6.60 (6.90)

* Decomposition occurs in the range indicated.

† Calculated values are given in parentheses.

Table 2. Thermogravimetric data of Zn(ddtc)₂, Cd(ddtc)₂ and their adducts.

Complex	Decomposition ranges (°C)	Loss corresponds to exp. (theor.) [†] (%)	Plateau region (°C)	Thermal product/residue exp. (theor.) [†] %
Zn(ddtc) ₂	205–325	ddtc –	325–475	11.5*
Zn(ddtc) ₂ bpy	135–215	bpy, 30.2(30.18)	215–220	Zn(ddtc) ₂ (69.9)(69, 82)
	220–325	ddtc –	325–450	20.0(18.8)**
Zn(ddtc) ₂ phen	225–275	phen, 34.0(33.24)	275–290	Zn(ddtc) ₂
	290–625	ddtc –	625–675	18.0(17.97)**
Zn(ddtc)(quin)	133–245	quin, 40.0(40.45)	245–275	–
	275–500	ddtc –	500–550	25.0(27.16)**
Cd(ddtc) ₂	230–380	ddtc –	380–500	24.2*
Cd(ddtc) ₂ bpy	205–285	bpy, 27.0(27.63)	285–320	Cd(ddtc) ₂ (73.5)(72.36)
	320–450	ddtc –	450–550	22.0*
Cd(ddtc) ₂ phen	240–275	phen, 29.0(30.59)	275–290	Cd(ddtc) ₂ (71.0)(69.40)
	290–600	ddtc –	600–650	25.0(24.48)**
Cd(ddtc)(quin)	135–220	– 28.5	220–340	–
	340–600	–	600–650	18.9*

*Do not correspond to metal sulphide; **correspond to metal sulphide; †calculated values are in parentheses.

Table 3. Important IR spectral bands of Zn(ddtc)₂, Cd(ddtc)₂ and their adducts (frequency in cm⁻¹).

Compound	Frequency (ν)				
	C=N (base)	C=N (ddtc)	C=S	M-N	M-S
Zn(ddtc) ₂	—	1498(s)	994(s)	—	326(m)
Zn(ddtc) ₂ py	1601(m)	1495(s)	992(s)	220(m)	327(m)
Zn(ddtc) ₂ 4-pic	1603(m)	1496(s)	992(s)	225(m)	330(m)
Zn(ddtc) ₂ bpy	1593(s)	1494(s)	992(s)	275(m)	349(m)
Zn(ddtc) ₂ phen	1621(m)	1491(s)	990(m)	282(m)	363(m)
Zn(ddtc)quin	1601(m)	1495(m)	994(s)	200(m)	400(m)
Cd(ddtc) ₂	—	1487(s)	990(s)	—	330(m)
Cd(ddtc) ₂ (py) ₂	1600(m)	1497(s)	993(s)	223(m)	325(m)
Cd(ddtc) ₂ (4-pic) ₂	1605(m)	1498(s)	992(s)	227(m)	330(m)
Cd(ddtc) ₂ bpy	1590(s)	1481(s)	987(s)	263(m)	354(m)
Cd(ddtc) ₂ phen	1610(s)	1483(s)	991(s)	270(m)	355(m)
Cd(ddtc)quin	1610(s)	1493(m)	988(s)	205(m)	398(m)

While zinc and cadmium adducts of pyridine and 4-picoline are colourless as expected, the mixed ligand complexes of bpy and phen and 8-hydroxyquinoline are yellow in the solid state and in solution, which is unusual for this class of zinc and cadmium complexes. Thermolysis studies were carried out for all mixed ligand complexes. Powdered samples (0.2 g each) of complexes were placed in microsublimation apparatus, which was heated to 250°C in an oil bath after evacuation by means of an oil diffusion pump. The sublimes of complexes are identified as secondary ligands (bases) by their melting points and their colour reactions with iron(II) solutions.

3.1 Thermogravimetric studies

Thermograms of some zinc and cadmium complexes are presented in figure 1. Thermogravimetric data (table 2) reveal that cadmium complexes initiate decomposition at higher temperatures in comparison with corresponding zinc complexes. High thermal stabilities of cadmium complexes may be due to their strong bonding and favourable configuration. Thermogravimetric data suggest that thermal stability of adducts largely depends on the electronic effects present in secondary ligands. For example, (bpy)Zn(ddtc)₂ and (bpy)Cd(ddtc)₂ adducts initiate decomposition at much lower temperatures than the corresponding 1,10-phenanthroline adducts. Phenanthroline adducts behave differently from the bipyridine adducts. Phenanthroline and quinoline adducts lose mass even around 600°C while bipyridine adducts do not lose mass beyond 450°C.

3.2 Infrared spectra

Relevant IR frequencies are listed in table 3. ν(C=N) (ring) of 2,2'-bipyridyl and 1,10-phenanthroline occurs at 1582 and 1558 cm⁻¹, respectively, and this band shifts to higher energies in all complexes. This positive shift occurs due to maintenance of

Table 4. ¹H-NMR spectral data of mixed ligand complexes.

Complex	Chemical shift (δ)	Multiplicity* (n)	Coupling constant J (Hz)	No. of protons	Assignment
Zn(ddtc) ₂ py	8.91	<i>d</i>	5.4	2 H	py H (2, 6)
	7.89	<i>t</i>	7.5	1 H	py H (4)
	7.50	<i>t</i>	6.9	2 H	py H (3, 5)
	3.89	<i>q</i>	7.9	8 H	methylene H
	1.29	<i>t</i>	7.9	12 H	methyl H
Zn(ddtc) ₂ 4-pic	8.85	<i>d</i>	6.0	2 H	pic H (2, 6)
	7.45	<i>d</i>	7.3	2 H	pic H (3, 5)
	3.85	<i>q</i>	7.9	8 H	methylene H
	2.38	<i>s</i>	—	3 H	pic methyl H
	1.29	<i>t</i>	7.9	12 H	methyl H
Zn(ddtc) ₂ bpy	8.90	<i>d</i>	5.4	2 H	bpy H (2, 9)
	8.31	<i>d</i>	9.0	2 H	bpy H (5, 6)
	7.87	<i>t</i>	8.6	2 H	bpy H (3, 8)
	7.40	<i>m</i>	5.4	2 H	bpy H (4, 7)
	3.88	<i>q</i>	7.9	8 H	methylene H
	1.30	<i>t</i>	7.9	12 H	methyl H
Zn(ddtc) ₂ phen	9.23	<i>d</i>	4.2	2 H	phen H (2, 9)
	8.52	<i>d</i>	8.8	2 H	phen H (3, 8)
	7.96	<i>s</i>	—	2 H	phen H (5, 6)
	7.89	<i>m</i>	5.2	2 H	phen H (4, 7)
	3.92	<i>q</i>	8.0	8 H	methylene H
	1.31	<i>t</i>	7.9	12 H	methyl H
Zn(ddtc)(quin)	8.82	<i>d</i>	4.7	1 H	quin H (2)
	7.48–7.15	<i>m</i>	—	4 H	quin H (3, 5, 6, 7)
	3.90	<i>q</i>	7.9	4 H	methylene H
	1.31	<i>t</i>	7.8	6 H	methyl H
Cd(ddtc) ₂ (py) ₂	8.83	<i>d</i>	5.5	4 H	py H (2, 6)
	7.80	<i>t</i>	7.5	2 H	py H (4)
	7.43	<i>t</i>	6.8	4 H	py H (3, 5)
	3.90	<i>q</i>	7.9	8 H	methylene H
	1.22	<i>t</i>	7.9	12 H	methyl H
Cd(ddtc) ₂ (4-pic) ₂	8.81	<i>d</i>	6.0	4 H	pic H (2, 6)
	7.39	<i>t</i>	7.2	4 H	pic H (3, 5)
	3.85	<i>q</i>	7.9	8 H	methylene H
	2.37	<i>s</i>	—	6 H	pic methyl
	1.22	<i>t</i>	7.9	12 H	methyl H
Cd(ddtc) ₂ bpy	8.86	<i>d</i>	6.6	2 H	bpy H (2, 9)
	8.25	<i>d</i>	10.0	2 H	bpy H (5, 6)
	7.87	<i>t</i>	6.7	2 H	bpy H (3, 8)
	7.39	<i>m</i>	4.3	2 H	bpy H (4, 7)
	3.91	<i>q</i>	7.9	8 H	methylene H
	1.23	<i>t</i>	7.9	12 H	methyl H
Cd(ddtc) ₂ phen	9.39	<i>d</i>	5.1	2 H	phen H (2, 9)
	8.37	<i>d</i>	9.0	2 H	phen H (3, 8)
	7.85	<i>s</i>	—	2 H	phen H (5, 6)
	7.77	<i>m</i>	5.1	2 H	phen H (4, 7)
	3.91	<i>q</i>	7.9	8 H	methylene H
	1.26	<i>t</i>	7.9	12 H	methyl H

**d* = doublet, *t* = triplet, *q* = quartet, *s* = singlet, *m* = multiplet.

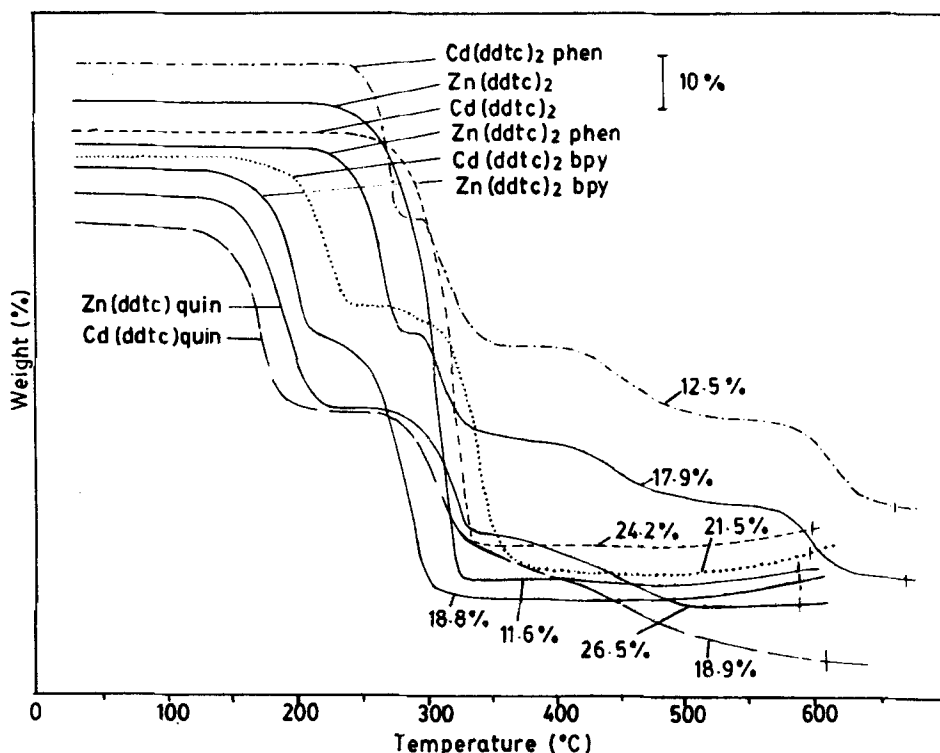


Figure 1. Thermograms of zinc and cadmium complexes.

a ring current arising out of electron delocalization in the chelate formation (Inskeep 1962). Attempts have been made (Bonati and Ugo 1967) to deduce the denticity of ddtc using $\nu\text{C-N}$ and $\nu\text{C-S}$ regions in the spectra. The $950\text{--}1050\text{ cm}^{-1}$ region has been shown to be reliable for determining whether the ligand is bidentate or unidentate. According to Bonati and Ugo (1967), the presence of only one strong band in the $950\text{--}1050\text{ cm}^{-1}$ region, which is associated with C-S stretching vibration, indicates complete symmetric bidentate bonding by dithiocarbamate ligand, while bonding is unidentate if a splitting of the peaks of $\approx 20\text{ cm}^{-1}$ is obtained. In IR spectra of $\text{Zn}(\text{ddtc})_2$, and its pyridine and 4-picoline adducts and in all cadmium complexes a strong absorption band (table 3) is observed around 990 cm^{-1} which indicates the bidentate nature of the ddtc ligand. In the infrared spectrum of $(\text{bpy})\text{Zn}(\text{ddtc})_2$ and $(\text{phen})\text{Zn}(\text{ddtc})_2$ this band is clearly split into two peaks. Since two peaks at $992, 990$ and $1016, 1020\text{ cm}^{-1}$ occur in the IR spectra of $(\text{bpy})\text{Zn}(\text{ddtc})_2$ and $(\text{phen})\text{Zn}(\text{ddtc})_2$, respectively, corresponding to $\nu\text{C-S}$ stretching vibration, which leads one to conclude safely (Brown *et al* 1976) that there is splitting of the required magnitude ($> 20\text{ cm}^{-1}$) which suggests the presence of formally unidentate ddtc ligand in $(\text{bpy})\text{Zn}(\text{ddtc})_2$ and $(\text{phen})\text{Zn}(\text{ddtc})_2$ complexes. The presence of unidentate ddtc in these complexes is in analogy with $\text{S}_2\text{CN.Me}_2$ present in $[\text{Zn}(\text{dtc})_3]^-$ anion-possessing zinc in distorted tetrahedral environment (Cotton and Wilkinson 1988).

3.3 $^1\text{H-NMR}$ spectra

All complexes are characterized by high resolution (300 MHz) $^1\text{H-NMR}$ spectra. This spectral data incorporating chemical shifts (δ), multiplicity (n), coupling constants (J) and the proton assignment are presented in table 4. Three signals with multiplicity of doublet, triplet and triplet are observed in low field strength regions of the spectra of py and 4-pic adducts. In the low field regions of the spectra, bpy adducts show four signals with multiplicity of doublet, doublet, triplet and multiplet in analogy with previous observation (Hussain Reddy *et al* 1991). As expected methyl and methylene protons of ddtc resonate at high field strength. Thus there is virtually no interference of proton signals that correspond to both ligands and the ratio of ddtc to secondary ligands (bases) can be easily evaluated. The ratios of ddtc to base are in good agreement with proposed formula of table 1 for all complexes. Typical $^1\text{H-NMR}$ spectra of a few complexes are given in figure 2.

In all mixed ligand complexes, cadmium has a clear preference for hexacoordination while in $(\text{bpy})\text{Zn}(\text{ddtc})_2$ $(\text{phen})\text{Zn}(\text{ddtc})_2$ complexes zinc adopts tetracoordination over hexacoordination though both Zn and Cd adopt pentacoordination in $\text{Zn}(\text{ddtc})_2$ and $\text{Cd}(\text{ddtc})_2$ complexes. Until recently, the thiolate chemistry of Cd(II) was believed to be characterized by tetrahedral coordination (Swenson *et al* 1978), and hexacoordinated structures were observed with special ligands such as dithiophosphates (Abrahams and Garner 1987). Our study shows that ddtc, the facultative mono-, and bidentate ligand in association with the present bases form hexacoordinated cadmium complexes under conditions where zinc reached only a maximum coordination number of five. The Cd atom is hexacoordinate in the present

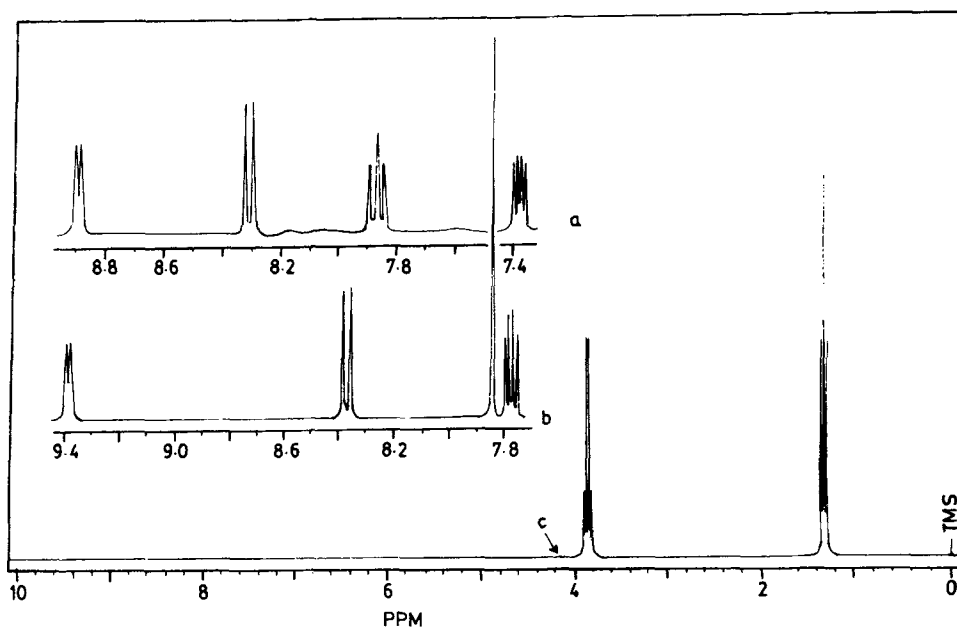
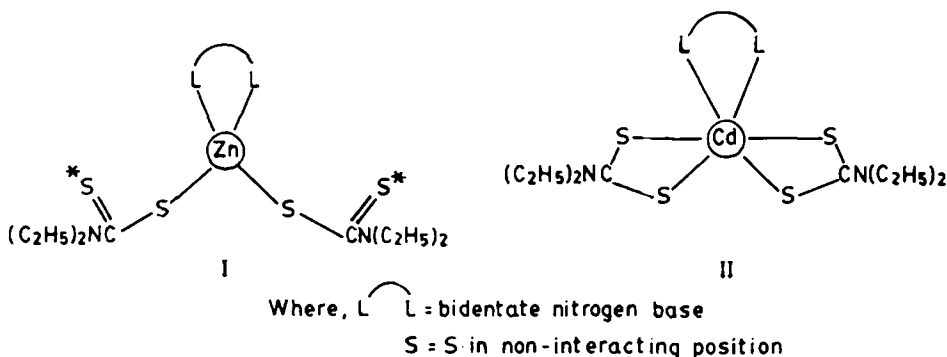


Figure 2. $^1\text{H-NMR}$ of (a) $(\text{bpy})\text{Zn}(\text{ddtc})_2$, (b) $(\text{phen})\text{Zn}(\text{ddtc})_2$ and (c) $\text{Zn}(\text{ddtc})_2$ complexes in CDCl_3 at room temperature.

complexes, although it was previously found to be tetracoordinate in other complexes (Corwin *et al* 1987) of S and N ligation.



Structures I & II.

Based on the results that we have presented so far, structures I and II are tentatively assigned for the $(\text{L-L})\text{Zn}(\text{ddtc})_2$ and $(\text{L-L})\text{Cd}(\text{ddtc})_2$ complexes respectively.

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