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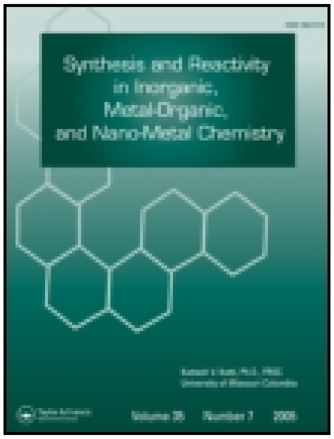

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Synthesis, Characterization and Thermal Studies of Bipyridine Metal Complexes Containing Different Substituted Dithiocarbamates

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Synthesis, Characterization and Thermal Studies of Bipyridine Metal Complexes Containing Different Substituted Dithiocarbamates

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Complexes of the type [Mpy$_2$(dedtc)$_2$], and [Mpy$_2$(dpdtc)$_2$], where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), py = pyridine, dedtc = diethyldithiocarbamate and dpdtc = diphenyldithiocarbamate, have been synthesized and characterized by elemental analyses, magnetic susceptibility, TGA/DSC and IR in the solid-state, and electronic spectroscopy and conductivity measurement studies in solution. The dithiocarbamato moiety has been found to be symmetrically bonded to the metal. The complexes are proposed to have a distorted-octahedral structure. The ligand field parameters 10 Dq, B and β have also been evaluated. The value of β indicates a considerable orbital overlap in the complexes. A two-stage decomposition pattern leading to the formation of respective metal sulfide as the end-product has been observed in all the complexes. Their molar conductance indicated them to be non-electrolyte in nitrobenzene.

Keywords diethyldithiocarbamate, diphenyldithiocarbamate, metal complexes

INTRODUCTION

Unidentate, as well as bidentate, nature of dithiocarbamate is well established (Kana et al., 2001; Law et al., 2003). Much attention has been devoted to the study of dialkyldithiocarbamates (Zhu et al., 2002; Jian et al., 1999) with special reference to Cu(II)dialkyldithiocarbamate because of its extensive use as single-source molecular precursors for the growth of semiconducting copper sulfide thin films (Ngo et al., 2003). In addition, Cu(II)dialkyldithiocarbamate is also employed in the preparation of single source MOVCD precursors for mixed metal sulfide thin films, like copper-indium sulfide or copper-doped cadmium sulfide (Ngo et al., 2003). Diethyldithiocarbamate has also been shown to inhibit Cu/Zn-superoxide dismutase (SOD) activity through the withdrawal of Cu from the protein both in vivo and in vitro systems (Cocco et al., 1981).

Beside this, dithiocarbamates have been clinically used and were shown to be safe and efficient in the treatment of HIV-infected patients (Nagano and Yoshimura, 2002).

One of the most striking properties of dithiocarbamate group is its high nucleophilicity, which leads to a large number of biologically active derivatives (Ileiv et al., 1984). In view of diverse application of dithiocarbamates (Chaurasia et al., 1981) and various biological aspects of pyridine (Gokhale et al., 2003) it is found worthwhile to study complexes containing both S and pyridine. Although the reports on metal dithiocarbamates are extensive, the studies on transition metal complexes containing both dithiocarbamate moiety and pyridine ligand are scarce (Ivanov et al., 1999; Yusuff et al., 1983). In this article, we are reporting the synthesis and characterization of mixed ligand complexes of the type [M(dedtc)$_2$(py)$_2$] and [M(dpdtc)$_2$(py)$_2$], where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), py = pyridine, dedtc = diethyldithiocarbamate and dpdtc = diphenyldithiocarbamate.

EXPERIMENTAL

General Consideration

Diethyl amine, diphenylamine, carbon disulphide, sodium hydroxide (Merck), pyridine (Ranbaxy) and hydrated metal chlorides (BDH) were used as received. Methanol was distilled before use. Elemental analyses (C, H, N and S) were carried out

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with a CE Instruments Flash EA 1112. IR spectra (4000–350 cm^{-1}) were recorded on a Perkin Elmer Spectrum BX as KBr discs. The conductivity measurements were carried out with CM-82T Elico conductivity bridge in nitrobenzene. The electronic spectra were recorded on a Cintra 5GBC spectrophotometer in nitrobenzene. Magnetic susceptibility measurements were done with a Sherwood Scientific MSB auto at room temperature. TGA/DSC was performed with a universal V3.5B TA SDT Q600 V3.8 built 51 thermal analyzer. The experiment was done under nitrogen atmosphere using alumina powder as the reference material. The weight of the sample was taken in between 6 to 16 mg, and the heating rate was maintained at 10°C/min.

Synthesis of Sodium Diethyl Dithiocarbamate (Nadedtc)

A solution of diethyl amine (50 mmol, 5.22 mL) in 50 mL of methanol was taken in a round bottom flask and cooled in an ice bath. Neat carbon disulphide (50 mmol, 3.02 mL) was added slowly with constant stirring to obtain a white precipitate. To this reaction mixture, NaOH (50 mmol, 2.0 g) dissolved in a minimum amount of water was added dropwise with stirring. The precipitate dissolved and the stirring was continued for four hours. The content was then allowed to stand overnight at room temperature to obtain needle shaped crystals of sodium salt of diethyl dithiocarbamate (dedtc), which was filtered, repeatedly washed with methanol and cold diethyl ether, and dried in vacuo.

Synthesis of Sodium Diphenyl Dithiocarbamate (Nadpdtc)

A methanolic solution (50 ml) of diphenylamine (50 mmol, 8.46 g) was taken in a round bottom flask and cooled in an ice bath. Neat carbon disulphide (50 mmol, 3.02 mL) was added dropwise with stirring to obtain an immediate white precipitation. To this, a solution of NaOH (50 mmol, 2.0 g) dissolved in minimum amount of water was slowly added with continuous stirring to obtain a yellow colored solution. The stirring was continued for four hours. The content was then allowed to stand overnight to obtain needle shaped crystals of sodium salt of diphenyl dithiocarbamate (dpdtc), which was filtered, repeatedly washed with methanol and cold diethyl ether, and dried in vacuo.

Synthesis of MCl_2py_2 Complexes

A methanolic solution of hydrated metal(II) chlorides (25 mL) was added to a methanolic solution of pyridine (15 mL) in 1 : 2 molar ratios with continuous stirring for about half an hour. The reaction mixture was left overnight at room temperature to obtain the required metal precipitate (Bailar et al., 1973), which was isolated by filtration, washed with methanol, and dried in vacuo.

Synthesis of the $Mpy_2(dedtc)_2$

A methanolic solution of MCl_2py_2 (25 mL) [where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)] was added to a methanolic solution (20 mL) of sodium salt of diethyl dithiocarbamate (dedtc) in 1 : 2 molar ratios with continuous stirring for about one hour. A solid compound in the form of precipitate was formed. It was left overnight at room temperature and the compound was isolated by filtration, washed with methanol and dried in vacuo (Figure 1).

$[Mn(py)_2(dedtc)_2]$ yield (54%); m. p. > 300°C; $\Lambda_M = 23$ $ohm^{-1}cm^2mol^{-1}$ Found (calcd. for $C_{20}H_{30}MnN_4S_4$) C, 46.96 (47.13), H, 5.8(5.93), N, 10.54(10.99), S, 25.45(25.16), Mn, 10.67(10.78). IR (KBr): ν_{max}/cm^{-1} 1497s (C…N), 1190 m (ring vib.), 397 m (Mn-S), 355 (Mn-N).

$[Fe(py)_2(dedtc)_2]$ yield (66%); m. p. 257°C; $\Lambda_M = 30$ $ohm^{-1}cm^2mol^{-1}$ Found (calcd. for $C_{20}H_{30}FeN_4S_4$) C, 46.88 (47.02), H, 5.57(5.92), N, 10.67(10.97), S, 25.27(25.11), Fe, 10.8(10.93). IR (KBr): ν_{max}/cm^{-1} 1494s (C…N), 1194 m (ring vib.), 397 m (Fe-S), 377 (Fe-N).

$[Co(py)_2(dedtc)_2]$ yield (60%); m. p. 297°C; $\Lambda_M = 39$ $ohm^{-1}cm^2mol^{-1}$ Found (calcd. for $C_{20}H_{30}CoN_4S_4$) C, 46.53 (46.77), H, 5.77(5.88), N, 10.72(10.91), S, 25.26(24.97), Co, 11.23(11.47). IR (KBr): ν_{max}/cm^{-1} 1486s (C…N), 1190 m (ring vib.), 403 m (Co-S), 371w (Co-N)

$[Ni(py)_2(dedtc)_2]$ yield (68%); m. p. 249°C; $\Lambda_M = 36$ $ohm^{-1}cm^2mol^{-1}$ Found (calcd. for $C_{20}H_{30}NiN_4S_4$) C, 46.59 (46.79), H, 5.74(5.89), N, 10.77(10.91), S, 25.18(24.98), Ni, 11.33(11.43). IR (KBr): ν_{max}/cm^{-1} 1504s (C…N), 1195 m (ring vib.), 417 m (Ni-S), 377w (Ni-N)

$[Cu(py)_2(dedtc)_2]$ yield (74%); m. p. 209°C; $\Lambda_M = 41$ $ohm^{-1}cm^2mol^{-1}$ Found (calcd. for $C_{20}H_{30}CuN_4S_4$) C, 46.28 (46.35), H, 5.69(5.83), N, 10.69(10.81), S, 24.91(24.75), Cu,

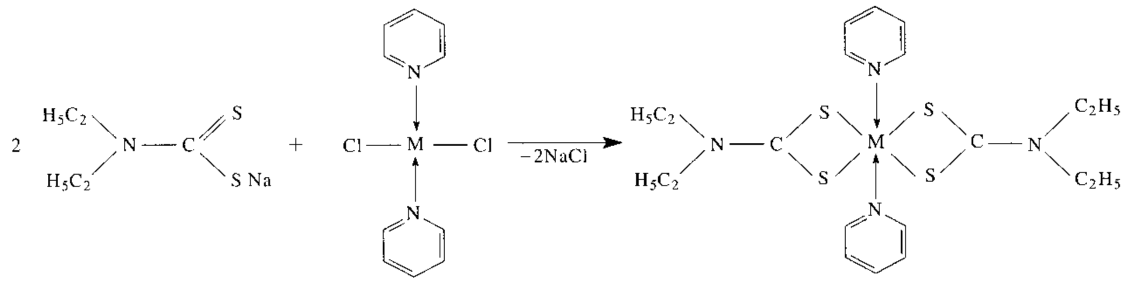

FIG. 1. Synthesis of the complexes $Mpy_2(dedtc)_2$, where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), py = C_5H_5N and dedtc = $S_2CN(C_2H_5)_2$.

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12.08(12.26). IR (KBr): ν_{max}/cm^{-1} 1504s (C…N), 1194 m (ring vib.), 393 m (Cu-S), 354w (Cu-N)

[Zn(py)$_2$(dedtc)$_2$] yield (70%); m. p. 208°C; $\Lambda_M = 42$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{20}H_{30}N_4S_4Zn$) C, 46.07 (46.16), H, 5.69(5.81), N, 10.68(10.77), S, 24.87(24.64), Zn, 12.49(12.62). IR (KBr): ν_{max}/cm^{-1} 1497s (C····N), 1193 m (ring vib.), 408 m (Zn-S) 362w (Zn-N)

Synthesis of the Mpy$_2$(dpdtc)$_2$

A methanolic solution of MCl$_2$py$_2$ (25 mL) [where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)] was added to a methanolic solution (20 mL) of sodium salt of diphenyl dithiocarbamate (dpdtc) in 1 : 2 molar ratios with continuous stirring for about two hours. A precipitate was formed, which was isolated by filtration, washed with methanol, and dried in vacuo (Figure 2).

[Mn(py)$_2$(dpdtc)$_2$] yield (40%); m. p. 225°C; $\Lambda_M = 28$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{36}H_{30}MnN_4S_4$) C, 61.49(61.61), H, 4.18(4.31), N, 7.69(7.98), S, 18.48(18.27), Mn, 7.69(7.83). IR (KBr): ν_{max}/cm^{-1} 1497s (C…N), 1195 m (ring vib.), 395 m (Mn-S), 370w (Mn-N).

[Fe(py)$_2$(dpdtc)$_2$] yield (60%); m. p. 162°C; $\Lambda_M = 39$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{36}H_{30}FeN_4S_4$) C, 61.29(61.53), H, 4.05(4.3), N, 7.66(7.97), S, 18.51(18.25), Fe, 8.06(7.95). IR (KBr): ν_{max}/cm^{-1} 1492s (C…N), 1190 m (ring vib.), 398 m (Fe-S), 375w (Fe-N).

[Co(py)$_2$(dpdtc)$_2$] yield (63%); m. p. 158°C; $\Lambda_M = 37$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{36}H_{30}CoN_4S_4$) C, 61.08(61.26), H, 4.11(4.28), N, 7.81(7.94), S, 17.98(18.17), Co, 8.52(8.35). IR (KBr): ν_{max}/cm^{-1} 1492s (C…N), 1194 m (ring vib.), 419 m (Co-S), 354w (Co-N).

[Ni(py)$_2$(dpdtc)$_2$] yield (70%); m. p. 212°C; $\Lambda_M = 43$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{36}H_{30}NiN_4S_4$) C, 61.15(61.28), H, 4.15(4.29), N, 7.66(7.94), S, 18.03(18.18), Ni, 8.44(8.31). IR (KBr): ν_{max}/cm^{-1} 1495s (C…N), 1190 m (ring vib.), 415 m (Ni-S), 360w (Ni-N).

[Cu(py)$_2$(dpdtc)$_2$] yield (70%); m. p. 254°C; $\Lambda_M = 39$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{36}H_{30}CuN_4S_4$) C, 60.59(60.86), H, 4.08(4.26), N, 7.59(7.89), S, 18.19(18.05), Cu, 9.08(8.94). IR (KBr): ν_{max}/cm^{-1} 1490s (C…N), 1190 m (ring vib.), 409 m (Cu-S), 363w (Cu-N).

[Zn(py)$_2$(dpdtc)$_2$] yield (73%); m. p. 225°C; $\Lambda_M = 17$ ohm^{-1}cm^{2}mol^{-1} Found (calcd. for $C_{36}H_{30}N_4S_4Zn$) C, 60.39(60.68), H, 4.05(4.24), N, 7.51(7.86), S, 18.06(17.99), Zn, 9.47(9.22). IR (KBr): ν_{max}/cm^{-1} 1497s (C…N), 1190 m (ring vib.), 413 m (Zn-S) and 372w cm^{-1} (Zn-N).

RESULTS AND DISCUSSION

The mixed ligand complexes of the type [M(py)$_2$(dedtc)$_2$], and [M(py)$_2$(dpdtc)$_2$], where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), py = pyridine, dedtc = diethyldithiocar bamate and dpdtc = diphenyldithiocarbamate, were readily obtained by the reaction of [M(py)$_2$Cl$_2$] with Nadedtc and Nadpdtc. The complexes are formed by the replacement of two chlorine atoms from [M(py)$_2$Cl$_2$] by dedtc and dpdtc (Figure 1). The metal complexes are stable to light and are amorphous powder.

$$M(py)_2Cl_2 + 2Nadedtc \rightarrow M(py)_2(dedtc)_2 + 2NaCl$$

$$M(py)_2Cl_2 + 2NadpdtcM(py)_2(dpdtc)_2 + 2NaCl$$

Conductance Measurements

The molar conductance value of 10^{-3} M solution of all the metal complexes measured in nitrobenzene fall well below those reported for univalent electrolyte at room temperature, indicating their non-electrolytic nature (Geary, 1971). The metal contents were determined by complexometric titration (Reilly et al., 1959).

IR Spectra

Literature survey reveals that almost all the dithiocarbamates studied to date, the region 950–1050 cm^{-1} is considered as highly diagnostic in deciding the nature of the coordination of the dithiocarbamato moiety (Bonati et al., 1967). According to the criterion laid by Brinkhoff and Grotens (1971) the presence of only one band in the 1000 ± 70 cm^{-1} region is characteristic of a bidentate nature for the dithiocarbamato moiety, while the splitting of the same band within a difference of 20 cm^{-1} in the same region is due to the monodentate binding of dithiocarbamate ligand. In the present study, a single sharp peak is observed in all the synthesized complexes in the 991–1023 cm^{-1}, confirming the symmetrical bonding of

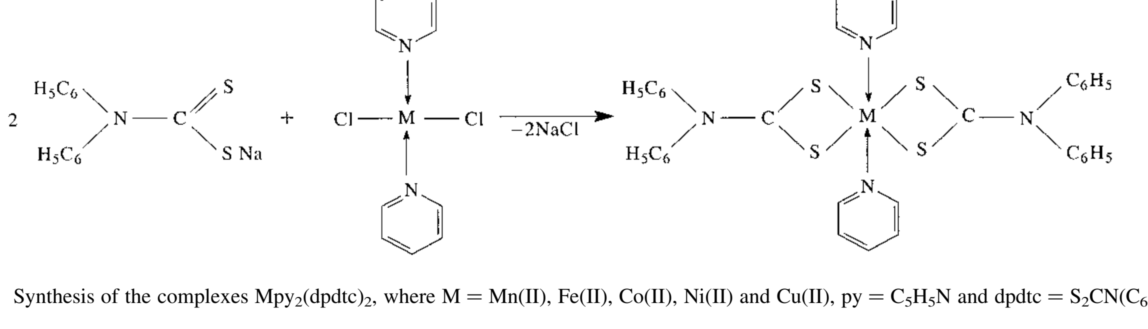

FIG. 2. Synthesis of the complexes Mpy$_2$(dpdtc)$_2$, where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II), py = C_5H_5N and dpdtc = $S_2CN(C_6H_5)_2$.

dithiocarbamato moiety in all the cases. The thioureide band ($S_2C\ldots NR_2$), which is another cardinal band of dithiocarbamato complexes, appears in the range 1486–1504 cm^{-1}, which is intermediate between a ν(C=N) band (1690–1640 cm^{-1}) and a ν(C–N) band (1360–1250 cm^{-1}), indicating a partial double bond character between carbon and nitrogen. Some new bands are also observed in the far IR region, which might be due to M-S stretching frequencies (Bradley and Gitlitz, 1969).

Electronic Absorption Spectra

The electronic spectral bands and the magnetic moments of the complexes are listed in Table 1. In and octahedral environment, Mn(II) complex gives spin forbidden as well as parity-forbidden bands (Cotton et al., 1999). In addition to the band due to n-π^* transition the electronic spectrum of Mn(II) complex in DMF exhibit three more bands in the region 31,104 to 30,350 cm^{-1}; 22,542 to 20,533 cm^{-1} and 17,513 to 16,890 cm^{-1}, which have been assigned to $^4T_1g(P) \leftarrow {}^6A_{1g}$;

TABLE 1
Magnetic susceptibility, electronic spectra and ligand field parameters of the complexes

Compounds	Magnetic moment (B.M.)	Electronic bands (cm^{-1})	Log ε ($mol^{-1}cm^2$)	Possible assignments	10Dq (cm^{-1})	B (cm^{-1})	β
$C_{20}H_{30}MnN_4S_4$	5.84	30,350	2.9	$^4T_{1g}(P) \leftarrow (^6A_{1g}$	17,760	427	0.83
$[Mn(py)_2(dedtc)_2]$		20,533	2.7	$^4T_{2g}(G) \leftarrow (^6A_{1g}$			
(509.68)		17,513	2.6	$^4T_{1g}(G) \leftarrow (^6A_{1g}$			
$C_{20}H_{30}FeN_4S_4$	5.30	15,772	2.8	$^5E_g \leftarrow {}^5T_{2g}$	15,722	—	—
$[Fe(py)_2(dedtc)_2]$							
(510.59)							
$C_{20}H_{30}CoN_4S_4$	4.18	20,790	2.7	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$	12,030	334	0.65
$[Co(py)_2(dedtc)_2]$		15,552	2.5	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
(513.67)		11,146	2.2	$^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
$C_{20}H_{30}NiN_4S_4$	3.21	22,371	2.6	$^3T_{1g}(P) \leftarrow (^3A_{2g}(F)$	11,760	392	0.62
$[Ni(py)_2(dedtc)_2]$		15,847	2.2	$^3T_{1g}(F) \leftarrow (^3A_{2g}(F)$			
(513.44)		11,764	1.8	$^3T_{2g}(F) \leftarrow (^3A_{2g}(F)$			
$C_{20}H_{30}CuN_4S_4$	1.93	17,452	2.7	$^2E_g \leftarrow {}^2B_{1g}$			
$[Cu(py)_2(dedtc)_2]$		11,824	2.7	$^2B_{2g} \leftarrow {}^2B_{1g}$	—	—	—
(518.29)							
$C_{20}H_{30}ZnN_4S_4$	Diamagnetic						
$[Mn(py)_2(dedtc)_2]$		—	—	—-	—	—	—
(520.44)							
$C_{36}H_{30}MnN_4S_4$	5.91	31,104	2.9	$^4T_{1g}(P) \leftarrow (^6A_{1g}$	16,885	439	0.85
$[Mn(py)_2(dpdtc)_2]$		22,542	2.7	$^4T_{2g}(G) \leftarrow (^6A_{1g}$			
(701.86)		16,890	2.4	$^4T_{1g}(G) \leftarrow (^6A_{1g}$			
$C_{36}H_{30}FeN_4S_4$	5.44				15,082	—	—
$[Fe(py)_2(dpdtc)_2]$		15,082	2.8	$^5E_g \leftarrow {}^5T_{2g}$			
(702.76)							
$C_{36}H_{30}CoN_4S_4$	4.21	22,321	2.5	$^4T_{1g}(P)\ (^4T_{1g}(F)$	12,080	402	0.78
$[Co(py)_2(dpdtc)_2]$		16,474	2.4	$^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$			
(705.85)		11,272	2.5	$^4T_{2g}(F) \leftarrow (^4T_{1g}(F)$			
$C_{36}H_{30}NiN_4S_4$	3.34	22,779	2.4	$^3T_{1g}(P) \leftarrow (^3A_{2g}(F)$	12,380	279	0.44
$[Ni(py)_2(dpdtc)_2]$		15,384	1.7	$^3T_{1g}(F) \leftarrow (^3A_{2g}(F)$			
(705.62)		12,544	1.4	$^3T_{2g}(F) \leftarrow (^3A_{2g}(F)$			
$C_{36}H_{30}CuN_4S_4$	1.98	18,248	2.8	$^2E_g \leftarrow {}^2B_{1g}$			
$[Cu(py)_2(dpdtc)_2]$		11,325	2.8	$^2B_{2g} \leftarrow {}^2B_{1g}$	—	—	—
(710.46)							
$C_{36}H_{30}ZnN_4S_4$							
$[Zn(py)_2(dpdtc)_2]$	Diamagnetic	—	—	—	—	—	—
(712.62)							

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$^4T_2g(G) \leftarrow {}^6A_{1g}$ and $^4T_1g(G) \leftarrow {}^6A_{1g}$ transitions, respectively. The high spin d^5 configuration gives an essentially spin-only magnetic moment of $\sim$ 5.9 B.M. and is temperature independent. The Mn(II) complex under consideration has the value of 5.84 B.M. and 5.91 B.M. for ethyl and phenyl dithiocarbamates, respectively, which are very close to the calculated value. Thus, the ligand field bands and magnetic moment value support a distorted octahedral geometry around the metal ion.

For the octahedral spin-free Fe(II) complexes, the magnetic moment values lies at about 5.5 B.M., and is nearly independent of temperature. In the present case, the magnetic moment values are found to be 5.30 and 5.44 B.M. for $Fepy_2(dedtc)_2$ and $Fepy_2(dpdtc)_2$ complexes, respectively. The slight deviation in magnetic moment value might be due to the deviation from the regular octahedral geometry (Cotton, 1964) (Table 1).

Octahedral cobalt(II) complexes have been widely studied. The spectra of $Copy_2(dedtc)_2$ and $Copy_2(dpdtc)_2$ have identical features, indicating similar stereochemistry around the Co(II) ion. They show absorptions at 20,790; 15,552 and 11,146 cm^{-1} in case of $Copy_2(dedtc)_2$ and 22,321; 16,474 and 11,272 cm^{-1} in case of $Copy_2(dpdtc)_2$. The low frequency band at around 11,000 cm^{-1} is characteristic of Co(II) in a distorted octahedral symmetry (Wang et al., 2003). The observed magnetic moment values for the $Copy_2(dedtc)_2$ and $Copy_2(dpdtc)_2$ are 4.18 and 4.21 B.M., respectively, which are within the predicted high-spin value for an octahedral Co(II) complex with considerable orbital contribution to the overall magnetic moment (Gebbink et al., 2002).

Octahedral Ni(II) complex is known to exhibit three spin allowed electronic transitions within the visible region (Lepetit and Che, 1996). In the present case of the $Nipy_2(dedtc)_2$, three absorption bands at 22,371 cm^{-1} (ν_1), 15,847 cm^{-1} (ν_2) and 11,764 cm^{-1} (ν_3) have been observed, while for the $Nipy_2(dpdtc)_2$ complex, these bands appear at 22,779 cm^{-1} (ν_1) 15,384 cm^{-1} (ν_2) and 12,544 cm^{-1} (ν_3) range. The ν_1 is due to one of the spin allowed electronic transitions in the visible region, and is assigned to $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$. The position of middle band (ν_2) has been attributed to $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition. The ligand field parameters, viz., 10Dq, B (Racah parameter), β (Nephelauxetic ratio) are almost identical for $Nipy_2(dedtc)_2$ and $Nipy_2(dpdtc)_2$. Values of ligand field parameters reflect that the M-L bond is sufficiently strong, which in turn suggest enough overlapping of metal orbitals with those of the ligand orbitals. The compounds are paramagnetic with a room temperature magnetic moment values ranging in between 3.21–3.34 B.M. One of the interesting features regarding the magnetic moments of octahedral Ni(II) complexes is their non-dependency in case of small departures from octahedral symmetry (Cotton, 1964).

Generally the octahedral Cu(II) complexes exhibit three transitions in the 18,000 to 12,000 cm^{-1} range with poorly separated bands. However, in the present study, a broad band maxima in the 11,905–11,765 cm^{-1} and 11,628–11,111 cm^{-1} range owing to the overlap of two bands corresponding to the $^2B_{2g} \leftarrow {}^2B_{1g}$ transition (Figgis, 1976) for $Cupy_2(dedtc)_2$ and $Cupy_2(dpdtc)_2$ complexes was observed. In addition to this, a shoulder at 17,452 cm^{-1} and 18,248 cm^{-1} for ethyl and phenyl analogue assigned to $^2B_{2g} \leftarrow {}^2B_{1g}$ transition was also observed and might be due to the distorted octahedral geometry around Cu(II) ion (Rana et al., 1982). It is difficult to predict the solution structure of the Cu(II) complexes from electronic spectroscopy alone because of a wide range of possible geometrical distortions and the typically poor resolution of absorption bands (Lever, 1984). The observed magnetic moment value lies in the range between 1.93–2.01 B.M., which further supports the above proposed geometry.

TGA/DSC

Thermogravimetric analysis is a useful technique for the determination of thermal stability and structural elucidation of various insoluble and infusible compounds (Bajpai and Tiwari, 2004), but to date, only a limited number of reports concerning thermal data and solution thermochemistry of metal dithiocarbamates have been appeared in the literature (Burkinshaw et al., 1983; Airoldi and Chagas, 1992; Szafranek and Szafranek, 1995; Lanjewar and Garg, 1992).

TABLE 2

Degradation of various fragments in the complex $M(py)_2(dedtc)_2$ (where M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II))

Fragments	Temperature range (°C)	$Mn(py)_2(dedtc)_2$	$Fe(py)_2(dedtc)_2$	$Co(py)_2(dedtc)_2$	$Ni(py)_2(dedtc)_2$	$Cu(py)_2(dedtc)_2$
Mass loss of the total organic moiety. found (calc.), %	85–500	75.91 (76.64)	75.73 (76.30)	76.44 (76.04)	75.90 (76.07)	81.50 (81.55)
Mass loss of the metal sulfide. found (Calc.), %	500–650	24.04 (23.35)	23.88 (23.49)	23.71 (23.95)	23.59 (23.92)	17.97 (18.44)

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In the present study, a two stage decomposition process is observed for $M(py)_2(dedtc)_2$, where $M = Mn(II)$, Fe(II), Co(II), Ni(II) and Cu(II) indicating similar structural features of the complexes. A literature survey reveals that the dithiocarbamate complexes either volatize leaving negligible amount of residue or decompose to yield respective metal sulfide (Bajpai and Tiwari, 2004). However, mixed ligand diethyldithiocarbamate complexes with different ligands were found to be nonvolatile with 17 to 55% residual weight (Lanjewar and Garg, 1992). In our study, the first thermolytic cleavage starts from 85 to 500°C with 76% loss of weight corresponding to whole organic moiety (found 75.5%) (Table 2). The second stage ranges between 500 to 650°C, after which a straight line is observed, indicating no change above this temperature range. The remaining weight loss corresponds to the respective metal sulfide (Bajpai and Tiwari, 2004).

In case of $Cu(py)_2(dedtc)_2$, the final product was heated under nitrogen atmosphere and CuS was detected quantitatively among the volatile products.

The DSC profile exhibits enthalpic changes from endothermal and exothermal bands and peaks. In the present case, the DSC peaks correlate well with the TGA data. A broad exothermic peak is obtained between 300–400°C due to the pyrolysis of the whole organic moiety. However, there is no well defined exotherm or endotherm corresponding to the last step of formation of metal sulfide.

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