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Research Article

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Preparation and characterization of the adducts of bis(piperidinedithiocarbamato)nickel(II) with substituted pyridines

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ABSTRACT

A series of new 1:1 and 1:2 adducts of Bis(piperidinedithiocarbamato) nickel(II) with substituted pyridines with general formula [Ni(pipedtc)$_2$ L] and [Ni(pipedtc)$_2$ L$_2$] respectively (where L= 2-ethylpyridine, 3-ethylpyridine, 4-ethylpridine, 2, 4, 6-collidine) have been synthesized. The addition complexes have been characterized by elemental analysis, conductivity measurements, and magnetic susceptibility measurements, infrared and electronic spectral studies. These studies suggest that 1:1 adducts are diamagnetic exhibiting magnetic moments around zero and may be assigned square pyramidal structure while 1:2 adducts are paramagnetic in nature and have a distorted octahedral structure. Antifungal activity of some adducts have been carried out against the fungal strain Sclerotium rolfsii.

Keywords: Piperidinedithiocarbamate; Ethylpyridine; Piperidine; Sclerotium rolfsii.

INTRODUCTION

Dithiocarbamates (DTC) are product of the reaction between a primary or secondary amine & carbon disulfide in basic media [1]. They found application as accelerators in vulcanization pesticides, fungicide and as bioactive compounds [2,3]. Most aliphatic and aromatic dithiocarbamate complexes synthesized until now have only the dithio group as ligand, so that they exhibit only uninegative bidentate possibility [4-6]. In addition, they are used as slimicides in pulp, paper and sugar production and they are also used in waste water treatment and as antifoulants for water cooling systems [7]. They play an important role as an adjuvant in the chemotherapy of human cancers; treat acquired immune depressive syndrome and drug resistant fungal infection [8-11].

EXPERIMENTAL SECTION

Preparation of sodium salt of piperidinedithiocarbamate

Piperidine (0.1 mol, 9.87 ml) and diethyl ether (150 ml) were taken in a round bottom flask and the contents were stirred for ten minutes. To this carbon disulfide (0.1 mol, 6ml) was added drop wise with continuous stirring. During the course of the reaction, dithiocarbamic acid was formed. To this, solution of sodium hydroxide (4g) prepared in 50 ml of water was added again with continuous stirring. As a result, two layers, an aqueous layer containing sodium salt of piperidine dithiocarbamate and a clear ethereal layer, were obtained. The aqueous layer was separated from the ethereal layer by using a separating funnel. The solution of sodium salt thus obtained was stored in a tightly stoppered flask.

Preparation of bis(piperidinedithiocarbamato)nickel(II) complex
The piperidinedithiocarbamate complex of Nickel (II) was prepared by adding an aqueous solution of sodium salt of piperidinedithiocarbamate (2.14g, 0.02 mol) to an aqueous solution of $NiCl_2.6H_2O$ (2.37g, 0.01 mol) with constant stirring. A pale green coloured complex precipitated out immediately which was washed repeatedly with cold distilled water and dried in vacuum over anhydrous calcium chloride. The composition of the complex was established to be [Ni $(S_2CNC_5H_{10})_2$] by elemental analysis.

Preparation of (1:1) adducts of bis(piperidinedithiocarbamato)nickel(II)
$Ni(pipedtc)_2$ (0.984g, 0.0026 mol) was dissolved in 100 ml of dimethylformamide by stirring. To the resulting solution was added substituted pyridines [2-ethylpyridine = 0.278616g, 3-ethylpridine = 0.2785g, 2,4,6-collidine = 0.3150g; (0.0026 mol)]. The mixture was refluxed for about one hour and the contents were kept undisturbed overnight. Light green coloured needle like structures of the adduct were obtained which were filtered and dried in a vacuum desiccator over anhydrous calcium chloride.

Preparation of (1:2) adducts of bis(piperidinedithiocarbamato)nickel(II)
$Ni(pipedtc)_2$ (0.984g, 0.0026 mol) was dissolved in 100ml of dimethylformamide by stirring. To the resulting solution was added substituted pyridines [2-ehtylpyridine = 0.557232g, 3-ethylpyridine = 0.557232g, 4-ethylpyridine = 0.55718g, 2, 4, 6-collidine = 0.630136g; (0.0052 mol)]. The mixture was refluxed for about one hour and the contents were kept undisturbed overnight. Light green coloured needle like structures of the adduct were obtained which were filtered and dried in a vacuum desiccator over anhydrous calcium chloride.

METHOD
Piperidine and substituted pyridines were used as such. Metal analysis was done by the reported methods [12]. Carbon, Hydrogen and Nitrogen analysis were performed by microanalytical methods. Molar conductivity in chloroform and DMF (10^{-3}M) at room temperature was measured using a digital conductivity meter "Century CC 601" and a conductivity cell with a cell constant 1. Magnetic susceptibility of the complexes was recorded at room temperature by VSM technique. IR spectra of the complexes over the region 4000-400 cm^{-1} were recorded on Perkin Elemer FTIR spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded in the range 12500-40000 cm^{-1} on Systronics 119 UV-visible spectrophotometer. Thermogravimetric analysis (TGA/DTA) of the complexes was recorded on EXSTAR TGA/DTA 6300 thermoanalyzer at the heating rate of 10^0C/min. The antifungal activity of the complexes was tested by poisoned food technique against the pathogenic fungus, Sclerotium rolfsii. All the experiments were carried out at room temperature.

RESULTS AND DISCUSSION

The complexes were analysed by various analytical and physicochemical techniques and the results show that $[Ni(pipedtc)_2]$ forms 1:1 and 1:2 adducts with general formula $[Ni(pipedtc)_2 L]$ and $[Ni(pipedtc)_2 L_2]$ respectively. All the complexes are coloured and stable in air. Conductance measurements were done to ascertain the electrolytic / non-electrolytic nature of metal complexes. The molar conductivity values were measured in 10^{-3}M chloroform solution is found to be in the range of 7-27 ohm^{-1} cm^2 mol^{-1}. **(Table 2)** .These values suggest non-electrolytic nature of these adducts.

PRELIMINARY INVESTIGATIONS
The adducts of bis(piperidinedithiocarbamato)nickel(II) with various nitrogen donors are microcrystalline solids and are shining dark green to light green in colour. 1:1 Adducts are somewhat light green in colour while 1:2 adducts are found to be dark green in colour. All the adducts are stable in air. They are insoluble in water, methanol, ethanol, acetone etc., partially soluble in chloroform, DMF and DMSO. The elemental analysis reveals that $Ni(pipedtc)_2$ forms both 1:1 and 1:2 adducts with substituted pyridines. The 1:1 addition complexes of bis(piperidinedithiocarbamato)nickel(II) have been assigned the general formulae $Ni[(S_2CNC_5H_{10})_2L]$ whereas the 1:2 adducts have been assigned the formulae $Ni[(S_2CNC_5H_{10})_2L_2]$ (**Table 1)**

MAGNETIC MEASUREMENTS:
The magnetic moments of all the complexes were measured at room temperature and presented in (**Table 2)**. The 1:1 adducts of bis(piperidinedithiocarbamato)nickel(II) with nitrogen donors exhibit the magnetic moment around zero reflecting that these adducts are diamagnectic and may be having five coordinate square pyramidal structures as observed in many low spin square pyramidal complexes of Nickel(II). While the magnetic moment values for 1:2

adducts come in the range of 2.86-3.19. Thus these adducts are paramagnetic having two unpaired electrons and may be assigned 6-coordinated octahedral structure.

INFRARED SPECTRA

The infrared spectra of 1:1 and 1:2 adducts of bis(morpholine dithiocarbamato)nickel(II) with primary and secondary amines prepared in the present work were recorded using KBr pellets in the range 4000-400 cm^{-1}. The IR bands of the free dithiocarbamate ligands on coordination with nickel(II) show a shift towards higher wave numbers. In these complexes a strong band observed in the region 1499-1490 cm^{-1} is attributed to υ(C—N) stretching vibration which lies intermediate between υ(C—N) and υ(C═N) indicating a partial double bond character of the C—N bond.[13,14]**.** It shows a positive shift of 35-40 cm^{-1} in comparison to the corresponding band in the free ligands. A single band of strong intensity was observed in the range 1025-1011 cm^{-1} which may be due to υ(CSS) vibration. There is a positive shift of 10-35 cm^{-1} in comparison to the corresponding band in the free ligands which indicates that the dithiocarbamate ligand coordinates with metal through sulfur atoms. A single absorption in the range 1025-1011 cm^{-1} is indicative of bidentate nature of the dithiocarbamate ligand which is due to equivalent C—S stretching vibrations[15-18] .A band of medium to strong intensity, observed in the region 420-416 cm^{-1}, may be assigned to υ(Ni—S) stretching mode.[19-22] **.(Table 3)**

ELECTRONIC SPECTRA

The electronic spectra of 1:1 and 1:2 adducts of $Ni(pipedtc)_2$ were recorded in chloroform. 1:1 adducts show a broad slightly asymmetric band appearing in the range 24086-24995 cm^{-1}. This transition of very high intensity can be assigned to $^1A_1 \rightarrow {}^1E$ (υ_2) transition. The shoulder around 17000 cm^{-1} can be assigned to spin allowed orbitally forbidden transition (υ_1) i.e., $^1A_1 \rightarrow {}^1B_1$ ($d_z^2 \rightarrow d_{x^2-y^2}$).[23] The appearance of strong, asymmetric absorption band of very high intensity suggests that square pyramidal geometry can be preferred over trigonal bipyramidal geometry for these adducts. In addition absorption bands observed in the region 33000-41000 cm^{-1} can be assigned to M→L charge transfer transitions.[24]The electronic spectra of 1:2 adducts of $Ni(pipedtc)_2$ on the other hand show three broad absorption bands υ_1, υ_2 and υ_3. The band υ_1 appears in the range 11242-11325 cm^{-1} and is assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition. The second band υ_2 is observed in the range 17242-17994 cm^{-1} and is attributed to $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition. The third band, υ_3, seen around 26990-28770 cm^{-1} corresponds to $^3A_{2g}(F) \rightarrow {}^3T_1g$ transition. The appearance of these three broad bands along with shoulders show that the adducts formed have trans distorted octahedral geometry around Ni(II) metal ion. In addition to these low intensity bands, M→L charge transfer transitions are also observed as intense bands above 30000 cm^{-1}.[25-27]. The electronic spectra of 1:1 and 1:2 adducts of $Ni(pipedtc)_2$ with substituted pyridine are shown in **(Table 3)**

Table 1:- Analytical data of 1:1 and 1:2 adducts of bis(piperidinedithiocarbamato)nickel(II) with substituted pyridines

S.No.	Name of the adducts	Formula	%age (Found)				%age (Calculated)			
			C	H	N	S	C	H	N	S
1.	Bis(piperidinedithiocarbamato) (2-ethylpyridine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)$	45.75	5.65	7.45	25.44	46.94	5.97	8.64	26.35
2.	Bis(piperidinedithiocarbamato) (3-ethylpyridine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)$	45.98	5.11	7.30	25.89	46.94	5.97	8.64	26.35
3.	Bis(piperidinedithiocarbamato) (4-ethylpyridine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)$	45.78	5.19	7.40	25.74	46.94	5.97	8.64	26.35
4.	Bis(piperidinedithiocarbamato) (2,4,6-collidine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_8H_{11}N)$	47.01	5.61	7.58	25.01	48.02	6.20	8.40	25.61
5.	Bis(piperidinedithiocarbamato)bis (2-ethylpyridine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)_2$	51.11	5.38	9.05	20.12	52.64	6.41	9.44	21.59
6.	Bis(piperidinedithiocarbamato)bis (3-ethylpyridine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)_2$	51.99	5.81	8.90	20.88	52.64	6.41	9.44	21.59
7.	Bis(piperidinedithiocarbamato)bis (4-ethylpyridine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)_2$	51.89	6.01	8.87	20.34	52.64	6.41	9.44	21.59
8.	Bis(piperidinedithiocarbamato)bis (2,4,6-collidine)nickel(II)	$Ni(S_2CNC_5H_{10})_2(C_7H_9N)_2$	53.78	6.12	8.90	19.81	54.13	6.76	9.02	20.62

Table 2:- Molar conductance and magnetic data of 1:2 adducts of bis(piperidinedithiocarbamato)nickel(II) with substituted pyridines

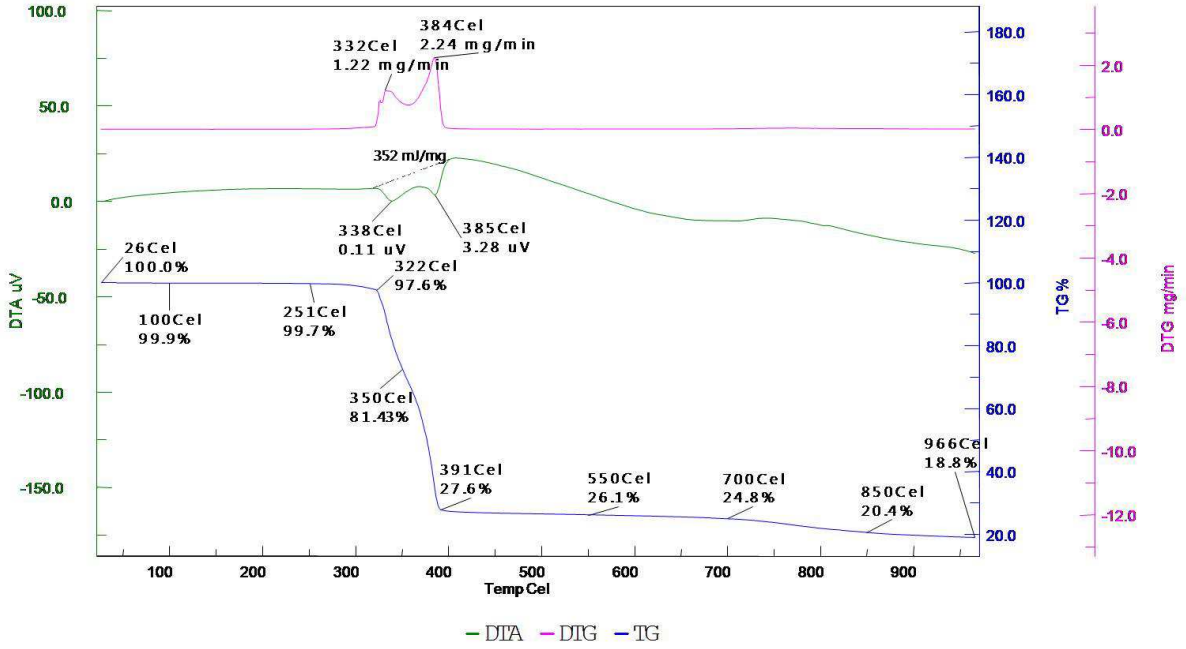
S.No	NAME OF THE ADDUCT	MOLAR CONDUCTANCE (Ohm^{-1} mol^{-1} cm^2)	MAGNETIC DATA	
			μ_{eff}(B.M)	TEMPERATURE(K)
1	Bis(piperidinedithiocarbamato) (2-ethylpyridine)nickel(II)	24	3.02	300
2	Bis(piperidinedithiocarbamato)(3-ethylpyridine)nickel(II)	16	3.04	300
3	Bis(piperidinedithiocarbamato)(4-ethylpyridine)nickel(II)	15	3.16	300
4	Bis(piperidinedithiocarbamato)(2,4,6-collidine)nickel(II)	15	3.09	300
5	Bis(piperidinedithiocarbamato)bis(2-ethylpyridine)nickel(II)	22	3.24	300
6	Bis(piperidinedithiocarbamato)bis(3-ethylpyridine)nickel(II)	15	2.99	300
7	Bis(piperidinedithiocarbamato)bis(4-ethylpyridine)nickel(II)	21	2.98	300
8.	Bis(piperidinedithiocarbamato) bis(2,4,6-collidine)nickel(II)	25	3.11	300

Table3:-Important IR bands and electronic spectral data of 1:1 and 1:2 of adducts of Bis(piperidinedithiocarbamato)nickel(II) with substituted pyridines

S.No.	Name of the adduct	Electronic spectral data in cm^{-1}		Vibrational spectral data in cm^{-1}			
		v1	v2	ν (N-H)	ν (C-N)	ν (CSS)	ν (Ni-S)
1	Bis(piperidinedithiocarbamato)(2-ethylpyridine)nickel(II)	16885	24380	3329	1497	1025	420
2	Bis(piperidinedithiocarbamato)(3-ethylpyridine)nickel(II)	16729	24882	3266	1495	1011	419
3	Bis(piperidinedithiocarbamato)(4-ethylpyridine)nickel(II)	16826	24865	3250	1497	1013	420
4	Bis(piperidinedithiocarbamato)(2,4,6-collidine)nickel(II)	16798	24993	3245	1495	1025	418
5	Bis(piperidinedithiocarbamato)bis(2-ethylpyridine)nickel(II)	16896	24892	3310	1491	1013	416
6	Bis(piperidinedithiocarbamato)bis(3-ethylpyridine)nickel(II)	16749	24086	3305	1492	1011	420
7.	Bis(piperidinedithiocarbamato)bis(4-ethylpyridine)nickel(II)	16843	24995	3335	1496	1011	418
8.	Bis(piperidinedithiocarbamato)bis(2,4,6-collidine)nickel(II)	16773	24899	3345	1487	1004	417

THERMOGRAVIMETRIC ANALYSIS

The adducts were subjected to TG analysis from 25°C to 1000°C in nitrogen atmosphere and the results of the novel investigated adducts is as given below. The TG curve of the adduct show a continuous weight loss and a stable sulfide, NiS, is formed as an end product. An initial weight loss of 35.14% is observed at around 350°C due to the loss of two ethylpyridine molecules (calculated weight loss = 36.14%). Then a continuous weight loss of 83.7% is observed, which may be due to the loss of $C_{12}H_{20}N_2S_3$ moiety (calculated weight loss = 84.7%), till a stable sulfide NiS is formed. **(Figure1).**



Biological studies:
The antifungal activity of the adducts was tested by **Poisoned food technique** against the pathogenic fungus *Sclerotium rolfsii*. The linear growth of the fungus in controlled manner was recorded at different concentration of the adducts. The growth inhibition of Sclerotium rolfsii over control was calculated **(Table 4).** It is found that on increasing the concentration of the adducts,the colony diameter of the fungus decreases and hence percent inhibition increases**(Figure 2)**. The growth inhibition of Fungus over control was calculated as:

% inhibition (I) = C-T/C×100

Where I = percent inhibition,C = mean growth of fungus(in mm) in control and T = mean growth of fungus(in mm) in treatment.

Table 4:-Invitro evaluation against *Sclerotium Rolfsii*, Mean Colony Diameter =90 mm

S.No.	Name of the adduct	concentration, ppm	Colony diameter, mm	% inhibition (I) = [(C-T)/C]×100
1	Bis(piperidinedithiocarbamato)(2-ethylpyridine)nickel(II)	50	60.5	31
		100	24.7	75
		150	6	93
		200	1.5	98
2	Bis(piperidinedithiocarbamato)bis(2,4,6-collidine)nickel(II)	50	37.5	58
		100	18.5	79
		150	9.5	89
		200	2	98

(a) **(b)**

Figure 2:- Antifungal activity of the adducts
(a) Bis(piperidinedithiocarbamato)(2-ethylpyridine)nickel(II)
(b) Bis(piperidinedithiocarbamato)bis(2,4,6-collidine)nickel(II)

CONCLUSION

On the basis of above studies it is found that 1:1 and 1:2 adducts of bis(piperidinedithiocarbamato)nickel(II) are diamagnetic and paramagnetic in nature having square paramidal and distorted octahedral geometry respectively. The complexes also show considerable antifungal activity.

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