



Synthesis, TGA, Luminescent and Antifungal Activity Studies of Nickel(II) Complexes of 1,1-Dithiolate

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Mixed ligand complexes of nickel(II) with 1,8-diaminonaphthalene (dan) and 1,1-dicyanoethylene-2,2-dithiolate (i-MNT²⁻) of the composition, Ni(dan)_x(i-MNT)·yH₂O [x = 1, y = 2; x = 2, 3, y = 0] and Ni(dan)(i-MNT)L₂·zH₂O [L = α-picoline (α-pic), β-picoline (β-pic), z = 0; L = γ-picoline (γ-pic), z = 2] have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurement, TGA, infrared, fluorescence and UV-visible spectral studies. The antifungal property of these complexes have also been studied using different fungi. IR spectral study suggest bidentate chelating behaviour of 1,8-diaminonaphthalene and 1,1-dicyanoethylene-2,2-dithiolate ion. The electronic spectral study suggests distorted octahedral stereochemistry around nickel(II) ion in these complexes.

Keywords: 1,8-Diaminonaphthalene, 1,1-Dicyanoethylene-2,2-dithiolate, Mixed ligand complexes, Nickel(II), TGA, Luminescent, Antifungal.

INTRODUCTION

Aromatic diamines have been area of interest for coordination chemists as aromatic diamines have been used as ligand in synthesis of transition as well as non-transition metal complexes. 1,8-Diaminonaphthalene played a vital role in synthesis of transition metal complexes [1-4]. 1,8-Diaminonaphthalene has also been of interest in synthesizing Schiff bases after condensation with aldehydes and ketones which have been used for complexation with transition metal ions [5-13]. The complexes have found many application in polymerization [6], as antioxidant [11] and as antimicrobial agents [13]. A 1,8-diaminonaphthalene copper complex appended conducting polymer have been reported for the electro catalytic reduction of oxygen [14]. The nickel(II) complexes of 1,8-diaminonaphthalene and other diamines have been used in hydrogenation of acetophenone in place of complexes of precious metals such as Ru, Rh and Ir [15]. Poly(1,8-diaminonaphthalene) and poly(metal-1,8-diaminonaphthalene) films have also been synthesized and used in electro catalytic reduction of molecular oxygen [16,17].

On the other hand, dithiolates have been area of interest for coordination chemists for a long period [18,19]. The dithio ligands have been used in designing electrically conducting molecular solids [20-23] and metal dithiolates have found

industrial and biological application [19,24]. 1,1-Dicyanoethylene-2,2-dithiolate shows chelating and bridging behaviours in its binary, ternary and hetero-bimetallic complexes [19,25-27].

Mixed ligand complexes of transition metal ions with nitrogen donors and 1,1-dithiolates have been reported [28]. But there is no report on mixed ligand complexes of nickel(II) with 1,8-diaminonaphthalene (dan) and 1,1-dicyanoethylene-2,2-dithiolate (i-MNT²⁻). Thus, we undertake the synthesis and structural characterization of mixed ligand complexes of nickel(II) with 1,8-diaminonaphthalene and 1,1-dicyanoethylene-2,2-dithiolate and their reactivity study towards heterocyclic nitrogen donors [pyridine(py), α-picoline(α-pic), β-picoline(β-pic) or γ-picoline (γ-pic)]. The photo-physical and antifungal activities of synthesized complexes have also been carried out.

EXPERIMENTAL

All chemicals used in this study were obtained from E. Merck of GR grade or equivalent quantity; α-, β- and γ-picoline were obtained from Aldrich chemical company. 1,8-Diaminonaphthalene was also purchased from Aldrich chemical company and was used after recrystallization. K₂ i-MNT·H₂O was synthesized by literature method [29].

[Ni(dan)₃](i-MNT) (1): A 15 mL ethanolic solution of 1,8-diaminonaphthalene (0.4746 g, 3 mM) was added with constant stirring to a 20 mL aqueous solution containing hydrated nickel nitrate (0.291 g, 1 mM) yielding purple coloured precipitate, changing instantaneously to buff colour. The precipitate was stirred for 1 h and suction filtered, washed with water, alcohol and ether. The precipitate thus obtained was dissolved in 30 mL hot water and filtered. To this filtrate, 20 mL aqueous solution of K₂i-MNT·H₂O (0.236 g, 1 mM) was added with stirring giving bright yellow precipitate which changed instantaneously into buff colour. The mixture was stirred for 1 h and suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused CaCl₂.

[Ni(dan)₂](i-MNT) (2): A 10 mL ethanolic solution of 1,8-diaminonaphthalene (0.3164 g, 2 mM) was added with constant stirring to a 20 mL aqueous solution containing hydrated nickel nitrate (0.291 g, 1 mM) yielding purple coloured precipitate, changing instantaneously to deep brand colour. The precipitate was stirred for 2 h and suction filtered, washed with water, alcohol and ether. The precipitate thus obtained was dissolved in 30 mL hot water and filtered. To this filtrate, 20 mL aqueous solution of K₂i-MNT·H₂O (0.236 g, 1 mM) was added with which resulted yellow precipitate. The mixture was stirred for 3 h and suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused CaCl₂.

[Ni(dan)(i-MNT)·2H₂O] (3): A 10 mL ethanolic solution of 1,8-diaminonaphthalene (0.1582 g, 1 mM) was added with constant stirring to a 20 mL aqueous solution containing hydrated nickel nitrate (0.291 g, 1 mM) which resulted dark brown solution with very small precipitate. The mixture was filtered and rejected the little black precipitate. To this filtrate, 20 mL aqueous solution of K₂i-MNT·H₂O (0.236 g, 1 mM) was added with stirring which yielded golden yellow precipitate. The mixture was stirred for 2.5 h and suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused CaCl₂.

[Ni(dan)(i-MNT)(α-pic)₂] (4): [Ni(dan)(i-MNT)·2H₂O] (1.965 g, 5 mM) was added to 20 mL of α-picoline slowly with vigorous shaking resulting dark blackish solution. The solution was filtered and no precipitate was obtained. The filtrate was allowed to evaporate naturally, leaving sticky black microcrystalline product after one month. The product was washed with ether several times, making it black powder. Finally, it was suction, filtered and air dried.

[Ni(dan)(i-MNT)(β-pic)₂] (5): [Ni(dan)(i-MNT)·2H₂O] (1.965 g, 5 mM) was dissolved in 25 mL of DMF followed by addition β-picoline (6 mL) with stirring which did not yield any product. The solution was allowed to evaporate at room temperature yielding black precipitate after about a month. The precipitate was suction filtered, washed with ether several times and air dried.

[Ni(dan)(i-MNT)(γ-pic)₂]·2H₂O (6): [Ni(dan)(i-MNT)·2H₂O] (1.965 g, 5 mM) was dissolved in 20 mL of γ-picoline slowly with constant stirring and stirred for 1 h. A greenish yellow precipitate was obtained, which was suction filtered, washed with ether several times and air dried.

An attempt was made to synthesize [Ni(dan)(i-MNT)(py)₂] from the reaction of [Ni(dan)(i-MNT)·2H₂O] and pyridine but

the reaction yielded green coloured precipitate of the composition [Ni(py)₂(i-MNT)]·4H₂O.

Analysis of the complexes: The complexes were analyzed for nickel using standard literature procedure [30]. Carbon, hydrogen and nitrogen were analyzed micro-analytically on CE 440 Exeter, USA and sulphur was estimated as BaSO₄ gravimetrically. The water molecules were determined by heating the sample for 4 h in an electric oven maintained at 110-200 °C and determining the loss of weight. The complexes have also been analyzed by thermogravimetrically using Perkin-Elmer, STA-60 thermal analyzer.

Physical measurements: The molar conductance values of mill-molar solutions of the complexes in DMF were measured using systronics direct reading conductivity 304 with a dip-type cell with platinized electrodes. Magnetic susceptibility measurements were made on room temperature on Sherwood Scientific, MSB (auto). Experimental magnetic susceptibility values have been corrected for diamagnetism by the procedures given by Figgis and Lewis [31] and Earnshaw [32]. Infrared spectra were recorded in nujol (4000-200 cm⁻¹) and in KBr pellets (4000-400 cm⁻¹) on a Bomen DA-8 FTIR and spectrum 100 FT-IR spectrophotometer (Perkin Elmer) using CSI and KBr optics, respectively. The UV-visible spectra of the complexes were recorded in the range 1100-200 nm on a Shimadzu UV-1800 spectrophotometer in the solid state (as KBr pellets) and in the range 1100-200 nm on a Lamda 25 UV-visible spectrophotometer (Perkin Elmer) in DMF solution. The antifungal study of the complexes have been carried out *in vitro* by the disk diffusion method. Thermal investigations (TGA) were carried out using Perkin-Elmer STA-60 thermal analyser under nitrogen atmosphere with a heating rate of 10 °C min⁻¹ and α-alumina as standard. Fluorescence spectra of the complexes in the solid state were recorded on a Foster-Freeman VSC-5000.

RESULTS AND DISCUSSION

The analytical data (Table-1) indicate the formation of mixed ligand complexes of nickel(II) of the compositions, Ni(dan)_x(i-MNT)·yH₂O and Ni(dan)(i-MNT)L₂·zH₂O [dan = 1,8-diamino-naphthalene; i-MNT²⁻ = 1,1-dicyanoethylene-2,2-dithiolate, x = 1, y = 2; x = 2,3, y = 0; L = α-picoline (α-pic), β-picoline (β-pic), z = 0; L = γ-picoline (γ-pic), z = 2]. The complexes decompose in the temperature range 120-130 °C while some of them do not decompose upto 300 °C and are insoluble in common organic solvents but slightly soluble in coordinating solvents such as DMF and DMSO. The complexes could not be recrystallized, but TLC measurements confirmed their purity as only one spot was observed for every complex. The weight loss experiments for complexes were carried out by heating a small amount of sample in a glass tube for 4 h in an electric oven maintained at 100, 120, 150 and 180 °C. Only [Ni(dan)(i-MNT)·2H₂O] and [Ni(dan)(i-MNT)(γ-pic)₂]·2H₂O showed weight loss in the temperature range 150-180 °C corresponding to two coordinated water molecules.

Molar conductance: The low molar conductance values 29.0 and 23.0 ohm⁻¹ cm² mol⁻¹ for [Ni(dan)(i-MNT)(α-pic)₂] and [Ni(dan)(i-MNT)(β-pic)₂], respectively in DMF solution (10⁻³ M) indicate their non-electrolytic nature while the rest

TABLE-1
 ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC MOMENT VALUES OF THE Ni(II) COMPLEXES

Complex (colour)	Yield (%) (Dec. temp. °C)	Elemental analysis (%): Found (calcd.)					$\Lambda_M (\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	μ_{eff} (BM)
		Ni	S	N	C	H		
[Ni(dan) ₃](i-MNT) (1) (Mid buff)	51 (198)	9.19 (8.71)	9.53 (9.52)	16.62 (16.64)	60.21 (60.64)	4.44 (4.49)	78.0	2.92
[Ni(dan) ₂ (i-MNT)] (2) (yellow)	79 (190)	11.55 (11.39)	11.70 (12.44)	16.31 (16.32)	55.94 (55.89)	3.91 (3.94)	76.0	2.23
[Ni(dan)(i-MNT)·2H ₂ O] (3) (yellow)	65 (230)	15.17 (14.93)	15.69 (16.31)	13.92 (14.24)	42.53 (42.78)	3.02 (3.59)	81.0	2.11
[Ni(dan)(i-MNT)(α -pic) ₂] (4) (Black)	92 (>300)	10.23 (10.80)	11.36 (11.80)	15.01 (15.46)	57.02 (57.47)	4.21 (4.45)	29.0	2.38
[Ni(dan)(i-MNT)(β -pic) ₂] (5) (Black)	88 (>300)	10.52 (10.80)	11.44 (11.80)	15.10 (15.46)	57.00 (57.47)	3.98 (4.45)	23.0	2.93
[Ni(dan)(i-MNT)(γ -pic) ₂]·2H ₂ O (6) (Greenish yellow)	81 (120)	9.88 (10.13)	10.86 (11.07)	14.02 (14.51)	52.36 (53.92)	4.52 (4.87)	75.0	2.84

complexes show values in the range 74.0 to 81.0 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (Table-1) indicating their 1:1 electrolytic nature [33].

Magnetic moment: The complexes, [Ni(dan)₃](i-MNT) (1), [Ni(dan)(i-MNT)(β -pic)₂] and [Ni(dan)(i-MNT)(γ -pic)₂]·2H₂O (6) show magnetic moment values 2.92, 2.93 and 2.84 BM, respectively while the complexes, [Ni(dan)₂(i-MNT)] (2), [Ni(dan)(i-MNT)·2H₂O] (3) and [Ni(dan)(i-MNT)(α -pic)₂] (4) show subnormal magnetic moment values 2.23, 2.11 and 2.38 BM, respectively. The magnetic moment values suggest paramagnetic corresponding to two unpaired electrons. The subnormal magnetic moments for the complexes 2, 3 and 4 may be due to strong distortion in octahedral stereochemistry around Ni(II) which is supported by their 1:1 electrolytic nature in solution.

Electronic spectra: The diffuse reflectance spectra of complexes 1, 5 and 6 show three bands in the region 9542-12062, 13280-15408 and 18726-19763 cm^{-1} assignable to $^3A_{2g} \rightarrow ^3T_{2g}$ (F) (ν_1), $^3A_{2g} \rightarrow ^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow ^3T_{1g}$ (P) (ν_3), respectively suggesting octahedral coordination around Ni(II) in these complexes. The complex 2 shows two absorption bands at 13495 and 22123 cm^{-1} while complex 3 shows one absorption band at 23923 cm^{-1} . The complex 4 does not show any characteristic absorption bands. The electronic spectra of complexes were also recorded in DMF solution to get behaviour of these mixed ligand complexes in solution (Table-2).

The complexes 1-5 show three absorption bands in the region 10162-13351, 14556-18797 and 18621-23364 cm^{-1} assignable to $^3A_{2g} \rightarrow ^3T_{2g}$ (F) (ν_1), $^3A_{2g} \rightarrow ^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow ^3T_{1g}$ (P) (ν_3) suggesting distorted octahedral stereochemistry around Ni(II) in these complexes [34]. The ν_3 band of complex 1 shows blue shift from 20408 to 21882 cm^{-1} on recording spectra on more diluted solutions. The complex 6 shows two absorption bands at 15873 and 21882 cm^{-1} characteristic of distorted octahedral stereochemistry around Ni(II).

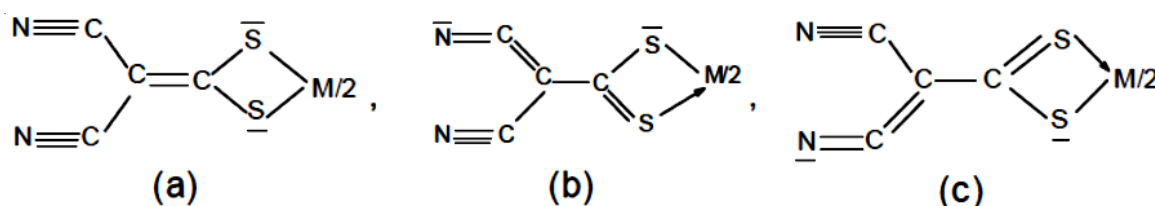
Infrared spectra: The IR spectra of the mixed ligand complexes have been discussed in the light of earlier investigation [18,25-40] on isomaleonitrile dithiolate complexes of transition and non-transition metal ions. The i-MNT²⁻ ligand ion may be described by resonating structure in its complexes as shown in Fig. 1.

The organic moiety in the mixed ligand complexes undergo particular vibrations and contributes certain peaks to their IR spectra. The IR spectra of the mixed ligand complexes display characteristic stretching frequencies associated with C \equiv N, C=C, C-S and M-S from i-MNT²⁻; aryl ring vibrations with metal heterocyclic nitrogen vibrations from α -pic, β -pic and γ -pic and amine vibrations with metal-amine nitrogen vibrations from dan.

The $\nu(\text{C}\equiv\text{N})$ band appearing at 2195 cm^{-1} with a shoulder at 2200 cm^{-1} in K₂i-MNT·H₂O, is observed in the range 2214-

 TABLE-2
 UV-VISIBLE SPECTRAL DATA OF Ni(II) COMPLEXES

Complex	λ_{max} (nm) (solid state)	λ_{max} (nm) (DMF solution)
[Ni(dan) ₃](i-MNT) (1)	1009, 753, 529	749, 553, 490
[Ni(dan) ₂ (i-MNT)] (2)	741, 452	750, 542, 457
[Ni(dan)(i-MNT)·2H ₂ O] (3)	418	800, 532, 456
[Ni(dan)(i-MNT)(α -pic) ₂] (4)	No characteristic bands	932, 534, 428
[Ni(dan)(i-MNT)(β -pic) ₂] (5)	829, 649, 534	984, 687, 537
[Ni(dan)(i-MNT)(γ -pic) ₂]·2H ₂ O (6)	1048, 690, 506	630, 457

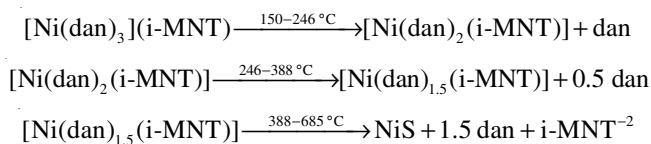

 Fig. 1. Resonance forms of i-MNT²⁻ ligand ion

2193 cm^{-1} in the mixed ligand complexes. The splitting of this band in some of the complexes has been found which reflects the lowering of symmetry for these complexes. The $\nu(\text{C}=\text{C})$ absorption band in all the complexes in the range 1385–1357 cm^{-1} is close to that observed in free $\text{K}_2\text{i-MNT}\cdot\text{H}_2\text{O}$ ligand (1360 cm^{-1}) which implies some delocalization of π -electron out of the $\text{C}=\text{C}$ bond. The positive shifts observed in stretching frequencies of $\text{C}\equiv\text{N}$ and $\text{C}=\text{C}$ suggest that resonance form (a) (Fig. 1) is more dominant in these complexes. The complex **1** shows $\nu(\text{C}\equiv\text{N})$ frequency at 2196 and 2182 cm^{-1} suggests that i-MNT^{2-} ion is associated in the complex ionically. A band at 960 cm^{-1} with a shoulder at 985 cm^{-1} on the higher frequency side is observed in the IR spectrum of $\text{K}_2\text{i-MNT}\cdot\text{H}_2\text{O}$ due to the $=\text{CS}_2$ group. The corresponding band in the mixed ligand complexes are found in the range 1002–963 cm^{-1} . The $\nu(\text{C-S})$ band occurring in the spectrum of $\text{K}_2\text{i-MNT}\cdot\text{H}_2\text{O}$ at 860 cm^{-1} appears as a single band in the range 898–883 cm^{-1} in the complexes indicating symmetrical bonding of both the sulphur atoms to metal ions (Table-3). The mixed ligand complexes **4-6** containing heterocyclic nitrogen donors show in-plane ring and out-of-plane ring deformation weak bands in the regions 632–609 and 417–410 cm^{-1} , respectively suggesting coordination through nitrogen atom. The presence of multiple weak intensity bands in the region 3059–2855 cm^{-1} suggest the presence of $\nu(\text{C-H})$ (aromatic) and $\nu(\text{C-H})$ (aliphatic) vibrations.

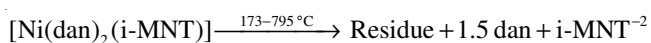
The free 1,8-diaminonaphthalene shows the characteristic bands anti symmetric and symmetric $\nu(\text{N-H})$ in the region 3417–3305 cm^{-1} , degenerate deformation, $\delta_a(\text{NH}_2)$ at 1615, $\delta_s(\text{NH}_2)$ at 1582 and $\rho_r(\text{NH}_2)$ at 813 and 757 cm^{-1} . The negative shifts in $\nu(\text{N-H})$ in these complexes suggest the coordination of amino group to metal ion. The $\delta_a(\text{NH}_2)$ and $\delta_s(\text{NH}_2)$ deformation bands are less sensitive and show bands almost in the same regions or a little higher frequencies. The $\rho_r(\text{NH}_2)$ is a sensitive band and positive shift in this band found in these complexes suggest bonding through the nitrogen atoms of 1,8-diaminonaphthalene to metal ions, The $\nu(\text{C-N})$ frequency is found at 1403 cm^{-1} in free dan and shows positive shift in this band on complexation. The shift in $\nu(\text{N-H})$, $\delta_a(\text{NH}_2)$, $\delta_s(\text{NH}_2)$, $\rho_r(\text{NH}_2)$ and $\nu(\text{C-N})$ bands of dan in its complexes suggest dan is behaving as bidentate ligand. Similar behaviour has been observed for Ni(II) [4], Co(II) [4] and Cu(II) [4] complexes containing dan. The non-ligand

bands observed in the regions 390–340 and 330–280 cm^{-1} in the spectra of mixed ligand complexes are tentatively assigned to $\nu(\text{M-N})$ [40] and $\nu(\text{M-S})$ [40] modes, respectively.

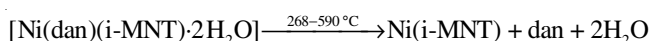
Thermogravimetric analysis: The thermo gram of complex **1**, $[\text{Ni}(\text{dan})_3](\text{i-MNT})$, contains three horizontal platues in the temperature range 150–246, 246–388 and 388–685 $^\circ\text{C}$ and weight losses suggest decomposition of complexes in three steps as shown below.



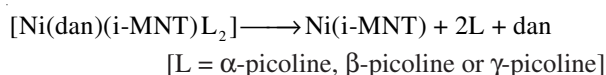
The complex **2**, $[\text{Ni}(\text{dan})_2(\text{i-MNT})]$, does not show any stable horizontal platue in its thermogram and suggests one step decomposition in the temperature range 173–795 $^\circ\text{C}$ and weight loss suggests the following decomposition pattern of the complex.



The complex **3**, $[\text{Ni}(\text{dan})(\text{i-MNT})\cdot 2\text{H}_2\text{O}]$, show one step decomposition in the temperature range 268–590 $^\circ\text{C}$ without any horizontal platue and weight loss suggests the following decomposition pattern.



The weight losses in the complexes **4**, **5** and **6** $[\text{Ni}(\text{dan})(\text{i-MNT})(\alpha\text{-pic})_2]$, $[\text{Ni}(\text{dan})(\text{i-MNT})(\beta\text{-pic})_2]$ and $[\text{Ni}(\text{dan})(\text{i-MNT})(\gamma\text{-pic})_2]$, have been observed in the temperature ranges 31–843, 31–842 and 86–844 $^\circ\text{C}$, respectively. The thermograms do not contain any stable horizontal platue suggesting that the decomposition takes place in one step. The decomposition patterns are as given below.



Luminescent properties: Three representative complexes show fluorescence emission bands at 518, 508 and 487 nm, respectively in solid sate at room temperature when they are excited at 456 nm (Fig. 2) while free ligand $\text{K}_2\text{iMNT}\cdot\text{H}_2\text{O}$ observed emission band at 477 nm under similar condition. This indicates that intra ligand excitation is responsible for

TABLE-3
CHARACTERISTIC IR BANDS (cm^{-1}) OF Ni(II) COMPLEXES

Complex	$\nu(\text{N-H})$	$\nu(\text{C}\equiv\text{N})$	$\delta(\text{NH}_2)$	$\nu(\text{C}=\text{C})$	$\nu(\text{C-N})$	$\nu(=\text{CS}_2)$	$\nu(\text{C-S})$	$\rho_r(\text{NH}_2)$	$\nu(\text{Ni-N})$	$\nu(\text{Ni-S})$
$[\text{Ni}(\text{dan})_3](\text{i-MNT})$ (1)	3392s, 3286s 3254s	2196s 2182vs	1609vs 1584vs	1367vs	1398s	987vs	883s	815vs 760vs	390w	280w
$[\text{Ni}(\text{dan})_2(\text{i-MNT})]$ (2)	3437vs 3319s 3243s	2206vs	1614vs 1585vs	1385vs	1402vs	1000s	896m	818s 761s	385w	302w
$[\text{Ni}(\text{dan})(\text{i-MNT})\cdot 2\text{H}_2\text{O}]$ (3)	3435b 3290s	2214vs	1612vs	1357vs	1374s	1002s	898s	816s 761s	375w	330w
$[\text{Ni}(\text{dan})(\text{i-MNT})(\alpha\text{-pic})_2]$ (4)	3250vb	2201vs	1622vs	1370vs	1456vs	984s	898m	816s 761s	385w	315w
$[\text{Ni}(\text{dan})(\text{i-MNT})(\beta\text{-pic})_2]$ (5)	3234vb	2193vs	1623vs 1592vs	1385vs	1469vs	984s	890s	816s 762s	345w	320w
$[\text{Ni}(\text{dan})(\text{i-MNT})(\gamma\text{-pic})_2]\cdot 2\text{H}_2\text{O}$ (6)	3436vb	2203vs	1620vs 1504m	1375s	1421s	963m	893s	815s 761s	340w	321w

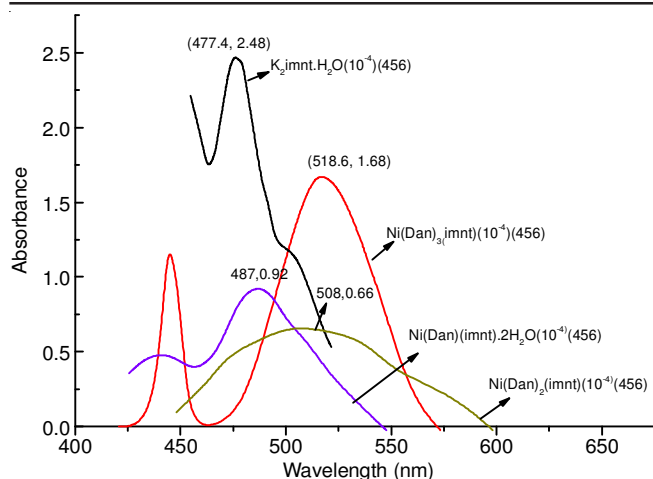


Fig. 2. Emission spectrum of free ligand and three representative complexes of Ni(II)

this emission of complexes. It is clear that red shift emission occurs, which is probably due to the coordination of ligand, because photoluminescence behaviour is closely associated with the local environment [41].

Antifungal activity study: Antifungal activity of synthesized complexes have been done by the disk diffusion method [42,43] against plants and animal fungi, *Synchytrium endobioticum* (wild type), *Pyricularia oryzae* (wild type), *Helminthosporium oryzae* (wild type), *Candida albicans* (ATCC10231) and *Trichophyton mentagrophytes* (clinically isolated) and compared with K_2 i-MNT and standard griseofulvin (10 μ g/disk). In this study, the strains were maintained and tested on sabouraud dextrose agar.

In disk diffusion method, a 20 % (w/v) stock solution of each dry extract (complexes **1-6** and K_2 i-MNT) were prepared in pure DMSO. For molds, suspensions of mature spores were obtained by gently washing the surface of solid media with a 0.05 % (v/v) solution of Tween 80 and the resulting suspension was adjusted to 106 spores mL^{-1} . Filter paper disks (6 mm diameter, Whatman No. 4) were placed on the inoculated agar surfaces and impregnated with 15 μ L of stock solutions. Pure DMSO (15 μ L) was used as a negative control while griseofulvin (10 μ g/disk) disks were used as positive controls. The plates were observed after 96 h at 25 $^{\circ}\text{C}$ for molds. All tests were performed in 5 replicates.

There is growing interest in new biologically important coordination compounds as metal binding with ligand can change their activity. The synthesized complexes were screened for their antifungal activity *in vitro* against some fungi and were compared with standard griseofulvin and corresponding ligand K_2 i-MNT \cdot H $_2$ O. The complexes show better antifungal activity than its corresponding primary ligand K_2 i-MNT \cdot H $_2$ O. The standard sample griseofulvin shows no effect on *Candida albicans* whereas complexes **3** and **6** show their effectiveness on *Candida albicans*. The results were accumulated in Table-4. The variation in effectiveness of synthesized complexes against different fungi depends either on the impermeability of the cells of the microbes or on differences in ribosome of microbial cells.

Reactivity of the complex: When $[\text{Ni}(\text{dan})(\text{i-MNT})\cdot 2\text{H}_2\text{O}]$ was treated with heterocyclic nitrogen bases, α -pic, β -pic or γ -pic under different experimental conditions then it yielded addition product of the composition, $[\text{Ni}(\text{dan})(\text{i-MNT})\text{L}_2]\cdot x\text{H}_2\text{O} = \alpha\text{-pic}, \beta\text{-pic or } \gamma\text{-pic}$ whereas $[\text{Ni}(\text{i-MNT})(\text{py})_2]\cdot 4\text{H}_2\text{O}$ was obtained with pyridine in which 1,8-diaminonaphthalene is completely displaced from the complex. This study suggests that coordinated water molecule in $[\text{Ni}(\text{dan})(\text{i-MNT})\cdot 2\text{H}_2\text{O}]$ complex were loosely bound and were replaced by strong nitrogen donors. At the same time, it has also been found that the adduct with nitrogen donors has normal magnetic moments for octahedral coordination around Ni(II) whereas $\text{Ni}(\text{dan})(\text{i-MNT})\cdot 2\text{H}_2\text{O}$ has subnormal magnetic moment.

Conclusion

Based on stoichiometries and spectrochemical studies, distorted octahedral structure around nickel(II) in these complexes have been proposed.

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TABLE-4
ANTIFUNGAL ACTIVITY STUDY OF Ni(II) COMPLEXES AGAINST FUNGI

Material (1 mg/mL)	Minimum inhibitory concentration (mg/mL)				
	<i>Pyricularia oryzae</i>	<i>Helminthosporium oryzae</i>	<i>Synchytrium endobioticum</i>	<i>Candida albicans</i>	<i>Trichophyton mentagrophytes</i>
Control (DMSO)	NE	NE	NE	NE	NE
K_2 i-MNT \cdot H $_2$ O	NE	NE	NE	NE	NE
Griseofulvin (10 μ g/disc) (standard sample)	0.10 (FC)	0.10 (FC)	0.90 (FC)	NE	0.40 (FS)
$[\text{Ni}(\text{dan})_3(\text{i-MNT})]$ (1)	14	NE	13	NE	16
$[\text{Ni}(\text{dan})_2(\text{i-MNT})]$ (2)	11	NE	09	NE	16
$[\text{Ni}(\text{dan})(\text{i-MNT})\cdot 2\text{H}_2\text{O}]$ (3)	13	13	09	16	NE
$[\text{Ni}(\text{dan})(\text{i-MNT})(\alpha\text{-pic})_2]$ (4)	11	17	10	NE	18
$[\text{Ni}(\text{dan})(\text{i-MNT})(\beta\text{-pic})_2]$ (5)	11	NE	16	NE	NE
$[\text{Ni}(\text{dan})(\text{i-MNT})(\gamma\text{-pic})_2]\cdot 2\text{H}_2\text{O}$ (6)	NE	10	13	18	18

All the readings based on 5 replicates \pm SEM, (NE) = No effect.

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