

## Synthesis, characterization and luminescent properties of mixed ligand complexes of nickel(II) with 1,1-dicarboethoxyethylene-2,2-dithiolate and some nitrogen donors

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**Abstract :** Mixed ligand complexes of Ni<sup>II</sup> ion with 1,1-dicarboethoxyethylene-2,2-dithiolate [DED<sup>2-</sup> = {S<sub>2</sub>C=C(COOC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sup>2-</sup>] as a primary ligand and *o*-phenylenediamine (OPD), pyridine (py),  $\alpha$ -picoline ( $\alpha$ -pic),  $\beta$ -picoline ( $\beta$ -pic) or  $\gamma$ -picoline ( $\gamma$ -pic) as secondary ligands have been isolated and characterized by analytical data, molar conductance, magnetic susceptibility, electronic, infrared and fluorescence spectral studies. The molar conductance data reveal that the complexes have non-electrolytic nature in DMF solution. Magnetic and electronic spectral studies suggest distorted octahedral stereochemistry around Ni<sup>II</sup> ion in its complexes. Infrared spectral studies suggest bidentate chelating behaviour of DED<sup>2-</sup> ion and OPD while other ligands show unidentate behaviour in their complexes. These complexes show fluorescence at room temperature in solid state.

**Keywords :** Nickel(II), 1,1-dithiolates, nitrogen donors, mixed ligand complexes, luminescent properties.

### Introduction

A variety of dithiolate ligands have been used to synthesize transition as well as non-transition metal complexes to study their coordination behaviour. Thus the coordination chemistry of metal dithiolates has been an area of interest for several years<sup>1,2</sup>. Recently the roles of dithioligands have been explored in the design of many electrically conducting molecular solids<sup>3-6</sup>. The interest in this area stems from various reasons such as stabilization of transition metal ions in its unusual oxidation states, facile redox behaviour, stabilization of square planar geometry around transition metal ions, interesting spectral and magnetic properties, in catalysis, models for active sites of many enzyme systems, magnetic exchange behaviour, electron transfer reactions and electrically conducting materials<sup>7-14</sup>. In addition, metal dithiolates have a number of industrial and biological applications<sup>2,15</sup>.

Among 1,1-dithiolate ligands, 1,1-dicyanoethylene-2,2-dithiolate, 1-cyano-1-carboethoxyethylene-2,2-dithiolate and 1,1-dicarboethoxyethylene-2,2-dithiolate show exciting coordination properties by virtue of its chelating and bridging behaviour which have been found in its binary,

ternary and heterobimetallic complexes<sup>1,2,16-20</sup>. McCleverty *et al.*<sup>21</sup> have isolated and characterized a series of mixed 1,1- and 1,2-dithio ligand complexes of cobalt and iron. On the other hand mixed ligand complexes of Ni<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup> with some dithiolates and nitrogen donor have also been reported<sup>22-27</sup>. But there is no report on mixed ligand complexes of Ni<sup>II</sup> ion involving 1,1-dicarboethoxyethylene-2,2-dithiolate (DED<sup>2-</sup>) and aromatic primary diamine and/or heterocyclic tertiary monoamines.

In view of the above, we undertake the synthesis and characterization of mixed ligand complexes of Ni<sup>II</sup> ion with 1,1-dicarboethoxyethylene-2,2-dithiolate (DED<sup>2-</sup>) and *o*-phenylenediamine (OPD) and its reaction products with heterocyclic nitrogen donors such as pyridine (py),  $\alpha$ -picoline ( $\alpha$ -pic),  $\beta$ -picoline ( $\beta$ -pic) and  $\gamma$ -picoline ( $\gamma$ -pic). The results of these investigations are described in this paper.

### Results and discussion

The analytical data and stoichiometries of the complexes reveal the formation of mixed ligand complexes of

$\text{Ni}^{\text{II}}$  ion of the composition,  $\text{Ni}(\text{OPD})(\text{DED})\text{L}_2$  [OPD = *o*-phenylenediamine, DED = 1,1-dicarboethoxyethylene-2,2-dithiolate ion and L =  $\text{H}_2\text{O}$ , py,  $\alpha$ -pic,  $\beta$ -pic or  $\gamma$ -pic]. The complexes are insoluble in water and common organic solvents but are soluble in highly coordinating solvents such as DMF and DMSO, giving coloured solutions. These complexes cannot be recrystallized but TLC measurements confirm the purity of the complexes as only one spot was observed for each complex. The complexes do not decompose up to 300 °C.

The molar conductance values of the complexes in DMF solution ( $10^{-3} \text{ M}$ ) fall in the region 18.0–27.0  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating non-electrolyte nature of the complexes<sup>28</sup>.

Magnetic susceptibility measurements and electronic spectra of complexes were recorded in order to explore the probable stereochemistry around  $\text{Ni}^{\text{II}}$  in these complexes. The corrected magnetic moments of complexes (1–5) with  $\text{DED}^{2-}$  and nitrogen donors lie in the range 2.85–3.26 B.M. suggesting paramagnetism corresponding to two unpaired electrons. The solid state electronic spectra of the complexes show three absorption bands in the regions 10384–11751, 13986–17544 and 21008–21505  $\text{cm}^{-1}$  assignable to  ${}^3A_{2g} \rightarrow {}^3T_{2g} (F)$  ( $\nu_1$ ),  ${}^3A_{2g} \rightarrow {}^3T_{1g} (F)$  ( $\nu_2$ ) and  ${}^3A_{2g} \rightarrow {}^3T_{1g} (P)$  ( $\nu_3$ ) respectively suggesting octahedral coordination around  $\text{Ni}^{\text{II}}$  in these complexes. The  $\nu_1$  and  $\nu_2$  bands show definite splitting suggesting distortion of octahedral stereochemistry around  $\text{Ni}^{\text{II}}$  in these complexes. The splitting of  $\nu_2$  bands are observed in the 13986–14124 and 17094–17544  $\text{cm}^{-1}$  ranges in the spectra of these complexes which may arise due to spin-orbit coupling that mixes the  ${}^3T_{1g} (F)$  and  ${}^1E_g$  states, which are very close in energy at the  $\Delta_0$  value given by the ligands present in these mixed ligand complexes<sup>29</sup>. The electronic spectra of complexes in DMF solution show only two bands either  $\nu_1$  and  $\nu_2$  or  $\nu_1$  and  $\nu_3$  except  $\text{Ni}(\text{OPD})(\text{DED})(\text{H}_2\text{O})_2$  which yields three absorption bands with splitted  $\nu_2$  band. The distorted octahedral stereochemistry around  $\text{Ni}^{\text{II}}$  ion in these complexes has been proposed<sup>30</sup>.

#### Infrared spectra :

The IR spectra of the mixed ligand complexes have been interpreted in the light of earlier investigations<sup>1,19,20,31,32</sup> on transition and non-transition metal dithiolates. The  $\text{DED}^{2-}$  ligand ion may be described by resonating structures in its complexes as shown in Fig. 1.

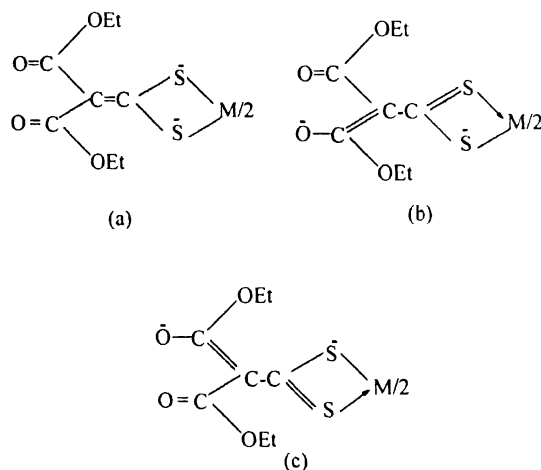


Fig. 1. Resonance form of  $\text{DED}^{2-}$  complexes.

Compounds containing an unconjugated and a conjugated (with acetyl or benzoyl group) ester group show  $\nu(\text{C}=\text{O})$  bands in 1720–1750 and 1620–1630  $\text{cm}^{-1}$  regions respectively. The  $\nu(\text{C}=\text{O})$  stretching band of ester group in these compounds appears as a strong band in the region 1618–1639  $\text{cm}^{-1}$ , which is more lowered than by usual  $\alpha,\beta$ -unsaturation, is indicative of delocalization of  $\text{C}=\text{O}$  group with the adjacent  $\text{C}=\text{C}$  bond. The existence of  $\nu(\text{C}=\text{O})$  frequency in these mixed ligand complexes in the same region as observed for  $\text{K}_2\text{DED} \cdot \text{H}_2\text{O}$  suggests that the carbonyl oxygen is not involved in bonding. The complexes exhibit three bands in the region 1340–1408, 1022–1094 and 943–984  $\text{cm}^{-1}$  assignable to  $\nu_1[\nu(\text{C}=\text{C})]$ ,  $\nu_4[\nu_{\text{as}}(=\text{CS}_2)]$  and  $\nu_2[\nu_{\text{s}}(=\text{CS}_2)]$  vibrations respectively of  $\text{C}=\text{CS}_2$  structure<sup>16,31</sup>. The  $\nu(\text{C}=\text{C})$  band appears as splitted band (doublet) suggesting lowering of its symmetry. The positive shifts in  $\nu(\text{C}=\text{C})$  band suggest that resonance form (a) (Fig. 1) is dominant in the 1,1-dicarboethoxyethylene-2,2-dithiolate complexes. The occurrence of a single weak band in the region 832–864  $\text{cm}^{-1}$  for  $\nu(\text{C}-\text{S})$  in these complexes supports symmetrical bonding of both the sulphur atoms of the ligand to the metal ion<sup>33</sup>.

The mixed ligand complexes containing heterocyclic nitrogen donors show in-plane ring and out-of-plane ring deformation bands in the ranges 611–668 and 400–420  $\text{cm}^{-1}$  respectively indicating coordination through nitrogen atom as these bands have found positive shifts with respect to its corresponding bands in its free form. The complexes show a group of broad bands in the region 3000–3600  $\text{cm}^{-1}$  which are due to combined effect of

$\nu(\text{O-H})$  and  $\nu(\text{N-H})$ . The dehydrated complexes at 200 °C exhibit a group of broad bands in the range 3224–3376  $\text{cm}^{-1}$  attributed to  $\nu(\text{N-H})$  (asymmetric and symmetric) stretching modes from the ligand, *o*-phenylenediamine. The N-H bending (scissoring) vibration mode is observed in the range 1717–1720  $\text{cm}^{-1}$  in the mixed ligand complexes which is overlapping region with  $\nu(\text{C=O})$ . The  $\nu(\text{C-N})$  bending mode observed in OPD at 1272  $\text{cm}^{-1}$  is observed in the complexes in the range 1281–1298  $\text{cm}^{-1}$ . A strong absorption band found at 751  $\text{cm}^{-1}$  in the spectrum of OPD attributable to out-of-plane  $\pi$ -C-H ring (aromatic) bending mode, characteristic of substituted benzene, is observed in the region 754–759  $\text{cm}^{-1}$ . The  $\nu(\text{C-H})$ (aromatic ring) arising from aromatic ligands in these complexes is observed as weak band(s) in the region 3000–3100  $\text{cm}^{-1}$ . The  $\nu(\text{C-H})$ (aliphatic) for complexes containing  $\alpha$ -pic,  $\beta$ -pic,  $\gamma$ -pic and/or  $\text{DED}^{2-}$  is observed as weak intensity bands in the region 2930–2986  $\text{cm}^{-1}$  suggesting their presence in the mixed ligand complexes.

The other bands observed in the ranges 400–420 and 290–320  $\text{cm}^{-1}$  in the spectrum of mixed ligand complexes are tentatively assigned to  $\nu(\text{M-N})^{34}$  and  $\nu(\text{M-S})^{32}$  modes respectively.

#### *Luminescent properties :*

The fluorescence spectra of  $\text{Ni}^{\text{II}}$  complexes (1-5), OPD and  $\text{K}_2\text{DED}\cdot\text{H}_2\text{O}$  were recorded in the solid state at RT with a Foster-Freeman Video Spectral Comparator-5000. The intensity of emission bands are measured in percentage with respect to standard sample supplied with the instrument having emission intensity equal to 100. Complexes (1-5) exhibit one intense emission band in the region 474–476 nm when they are excited at 365 nm while under the same conditions, the free ligands  $\text{K}_2\text{DED}\cdot\text{H}_2\text{O}$  and OPD display the emission bands at about 481 nm and 479 nm, respectively. The emission bands of (1-5) complexes are similar to those of ligands, indicating that intra ligand excitation is responsible for these emission bands. A blue-shift in the emission spectra of complexes with respect to the participating ligands occurs, which is probably due to the co-ordination of ligands, because photoluminescence behaviour is closely associated with the local environment<sup>35</sup>.

#### *Reactivity of the complex :*

When  $\text{Ni}(\text{OPD})(\text{DED})(\text{H}_2\text{O})_2$  was reacted with heterocyclic nitrogen bases, py,  $\alpha$ -pic,  $\beta$ -pic or  $\gamma$ -pic, under

different experimental conditions then it yielded a product of the composition  $\text{Ni}(\text{OPD})(\text{DED})\text{L}_2$  [L = py,  $\alpha$ -pic,  $\beta$ -pic or  $\gamma$ -pic] in which water molecules were replaced by stronger Lewis bases.

### Experimental

#### *Materials :*

All the chemicals used in this study, obtained from E. Merck, were of GR grade or equivalent quality,  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines were obtained from Aldrich Chemical Company.  $\text{K}_2\text{DED}\cdot\text{H}_2\text{O}$  was prepared by a known literature procedure<sup>31</sup>.

#### *Synthesis of complexes :*

##### *Ni(OPD)(DED)(H<sub>2</sub>O)<sub>2</sub> (1) :*

*o*-Phenylenediamine (1.08 g, 10 mmol) in methanol (50  $\text{cm}^3$ ) solution was added with stirring to a 50  $\text{cm}^3$  aqueous solution containing (2.9 g, 10 mmol) hydrated nickel nitrate, which resulted in a deep green solution. To this solution, a 50  $\text{cm}^3$  aqueous solution of  $\text{K}_2\text{DED}\cdot\text{H}_2\text{O}$  (3.30 g, 10 mmol) was added with stirring which yielded a deep yellowish precipitate which turned to greenish yellow on stirring after few minutes. The precipitate was suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused  $\text{CaCl}_2$ . The colour of the precipitate became greenish yellow after drying.

[UV-Vis bands (nm) : 946, 905, 570, 465 in solid state; 980, 772, 573, 451 in DMF solution].

[Fluorescence emission band (intensity) : 475 nm (79%) in solid state with excitation at 365 nm].

Attempts were made to synthesize  $\text{Ni}(\text{OPD})_n(\text{DED})$  ( $n = 2, 3$ ) by taking  $\text{Ni}^{\text{II}}$  salt, OPD and  $\text{K}_2\text{DED}\cdot\text{H}_2\text{O}$  in 1 : 2 : 1 and 1 : 3 : 1 molar ratios respectively under the same condition but only one product,  $\text{Ni}(\text{OPD})(\text{DED})(\text{H}_2\text{O})_2$ , was obtained with increased percentage yield.

##### *Ni(OPD)(DED)(py)<sub>2</sub> (2) :*

$\text{Ni}(\text{OPD})(\text{DED})(\text{H}_2\text{O})_2$  (0.875 g, 2 mmol) was dissolved in 25  $\text{cm}^3$  of pyridine slowly with vigorous stirring resulting in a deep greenish solution. The solution was allowed to evaporate at room temperature and after 15 days a sticky black product was obtained which was washed with ether several times, making it a black powder. Finally, it was suction filtered and air-dried.

[UV-Vis bands (nm) : 945, 907, 715, 575, 466 in solid state; 974, 425 in DMF solution].

[Fluorescence emission band (intensity) : 474 nm (82%) in solid state with excitation at 365 nm].

*Ni(OPD)(DED)( $\alpha$ -pic)<sub>2</sub> (3) :*

Ni(OPD)(DED)(H<sub>2</sub>O)<sub>2</sub> (0.875 g, 2 mmol) was dissolved in 10 cm<sup>3</sup> DMF followed by addition of  $\beta$ -picoline (10 cm<sup>3</sup>) and the resulted solution was kept under observation. After six months a brownish black sticky precipitate was obtained. The supernatant liquid was decanted and the precipitate was washed with ether several times which converted the sticky brownish black mass into a powder form and finally air-dried.

[UV-Vis bands (nm) : 963, 709, 584, 463 in solid state; 957, 432 in DMF solution].

[Fluorescence emission band (intensity) : 474 nm (85%) in solid state with excitation at 365 nm].

*Ni(OPD)(DED)( $\beta$ -pic)<sub>2</sub> (4) :*

Ni(OPD)(DED)(H<sub>2</sub>O)<sub>2</sub> (0.875 g, 2 mmol) was dissolved in 10 cm<sup>3</sup> DMF followed by addition of  $\beta$ -picoline (10 cm<sup>3</sup>) with stirring, which did not yield any product. The resulting solution was kept under observations and after five months a black sticky product was obtained. The supernatant liquid was decanted and the precipitate was washed with several times with ether which yielded black powder. Finally, it was suction filtered and air-dried.

[UV-Vis bands (nm) : 917, 851, 708, 585, 476 in solid state; 980, 553 in DMF solution].

[Fluorescence emission band (intensity) : 475 nm (83%) in solid state with excitation at 365 nm].

*Ni(OPD)(DED)( $\gamma$ -pic)<sub>2</sub> (5) :*

The black complex was obtained essentially by the

same method used for the synthesis of Ni(OPD)(DED)( $\beta$ -pic)<sub>2</sub>, only by replacing  $\beta$ -picoline by  $\gamma$ -picoline.

[UV-Vis bands (nm) : 981, 852, 710, 585, 467 in solid state; 977, 574 in DMF solution].

[Fluorescence emission band (intensity) : 474 nm (71%) in solid state with excitation at 365 nm].

*Analysis of the complexes :*

The complexes were analyzed for nickel using standard literature procedures<sup>36</sup>. Sulphur was estimated gravimetrically and carbon, hydrogen and nitrogen were determined micro-analytically on CE 440 Exeter, USA.

*Physical measurements :*

The molar conductance of the milli-molar solutions of the complexes in DMF was measured using Systronics direct reading conductivity meter 304 with a dip-type cell with platinized electrodes. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday electro-balance using CoHg(SCN)<sub>4</sub> as calibrant. Experimental magnetic susceptibility values have been corrected for diamagnetism by the procedures given by Figgis and Lewis<sup>37</sup> and Earnshaw<sup>38</sup>. Infrared spectra were recorded in nujol (4000–200 cm<sup>-1</sup>) and in KBr pellets (4000–400 cm<sup>-1</sup>) on a Bomem DA-8 FT-IR spectrophotometer. The electronic spectra of the complexes in solid state and DMF solution were recorded on a Foster-Freeman Video Spectral Comparator-5000 and on a Perkin-Elmer Model Lamda-25 UV-Vis spectrophotometer respectively. Solid state fluorescence spectra of the complexes were recorded on a Foster-Freeman Video Spectral Comparator-5000. Analytical data together with colour, yield, magnetic moment and molar conductance values are presented in Table 1.

**Table 1.** Analytical data, molar conductance and magnetic moments of Ni<sup>II</sup> complexes

Complex (Colour)	% Yield (Dec. temp. °C)	Analysis (%) : Found (Calcd.)					$\Lambda_M$ ( $\Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup> ) (DMF)	$\mu_{\text{eff}}$ (B.M.)
		Ni	S	N	C	H		
Ni(OPD)(DED)(H <sub>2</sub> O) <sub>2</sub> (1) (Greenish yellow)	80 (> 300)	14.21 (13.43)	15.02 (14.67)	6.90 (6.40)	39.20 (38.47)	4.40 (5.07)	27.0	3.11
Ni(OPD)(DED)(py) <sub>2</sub> (2) (Black)	70 (> 300)	10.30 (10.49)	10.82 (11.46)	10.00 (10.02)	51.45 (51.54)	5.00 (5.05)	26.0	3.26
Ni(OPD)(DED)( $\alpha$ -pic) <sub>2</sub> (3) (Brownish black)	65 (> 300)	9.40 (9.99)	10.32 (10.92)	9.40 (9.54)	53.02 (53.17)	5.32 (5.49)	22.0	2.86
Ni(OPD)(DED)( $\beta$ -pic) <sub>2</sub> (4) (Black)	60 (> 300)	9.00 (9.99)	10.60 (10.92)	9.20 (9.54)	52.80 (53.17)	5.40 (5.49)	20.0	2.93
Ni(OPD)(DED)( $\gamma$ -pic) <sub>2</sub> (5) (Black)	65 (> 300)	9.32 (9.99)	10.11 (10.92)	9.50 (9.54)	52.90 (53.17)	4.90 (5.49)	18.0	2.85

*Conclusions :*

Based on stoichiometries and spectrochemical studies, distorted octahedral structure around Ni<sup>II</sup> in these complexes have been proposed.

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