

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

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### Abstract

Mixed ligand complexes of Ni(II) ion with 1,1-dicyanoethylene-2,2-dithiolate ( $i\text{-MNT}^{2-}$ ) 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 on the basis of analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral studies. The molar conductance data reveal that most of the complexes have 1:1 electrolytic nature in DMF solution. Magnetic and electronic spectral studies suggest square planar and octahedral stereochemistries around Ni(II) ions. Infrared spectral studies suggest bidentate chelating behaviour of  $i\text{-MNT}^{2-}$  ion and OPD while other ligands show unidentate behaviour in their complexes.

### Introduction

The coordination chemistry of transition as well as non-transition metal dithiolates has been area of interest for several years [1, 2]. Recently, the role of dithioligands have been explored in the design of many electrically conducting molecular solids [3–6]. The interest in this area stems from various reasons such as stabilisation of transition metal ions in its unusual oxidation states, facile redox behaviour, stabilisation of square planar geometry around transition metal ions, interesting spectral and magnetic properties. In addition, metal dithiolates have a number of industrial and biological applications [2, 7].

Among 1,1-dithioligands, 1,1-dicyanoethylene-2,2-dithiolate ion shows exciting coordination properties by virtue of its chelating and bridging behaviour which have been found in its binary, ternary and heterobimetallic complexes [2, 8, 9]. Our earlier communications [10–13] include the studies on mixed ligand complexes of Ni(II), Cu(II), Zn(II) and Cd(II) with 1,1-dicyanoethylene-2,2-dithiolate and some nitrogen bases such as ammonia, ethylenediamine, pyridine, 2,2-bipyridine and 1,10-phenanthroline. Prior to our report, McCleverty *et al.* [14] have obtained and characterized a series of mixed 1,1- and 1,2-dithiolate complexes of cobalt and iron. But there is no report on mixed ligand complexes of nickel(II) ion involving 1,1-dithiolate and aromatic primary diamine and/or heterocyclic tertiary monoamine.

In view of the above, synthesis and structural studies on mixed ligand complexes of nickel(II) ion with  $K_2i\text{-MNT}$  and primary aromatic diamine (OPD) and/or heterocyclic tertiary monoamine were, therefore, undertaken and the results of our investigations are reported in this paper.

### Experimental

#### Materials

All the chemicals used in this study were obtained from E. Merck of GR grade or equivalent quality.  $\alpha$ -,  $\beta$ - and  $\gamma$ -picolines were obtained from Aldrich Chemical company.  $K_2i\text{-MNT}\cdot H_2O$  was prepared by a known literature procedure [15].

#### Synthesis of complexes

##### $Ni(OPD)(i\text{-MNT})$ (1)

A quantity of 50 cm<sup>3</sup> methanolic solution of *o*-phenylenediamine (10 mM) was added with stirring to a 50 cm<sup>3</sup> aqueous solution containing (10 mM) of hydrated nickel nitrate which resulted in a deep green coloured solution. To this resulting solution, a 50 cm<sup>3</sup> aqueous solution of  $K_2i\text{-MNT}\cdot H_2O$  (10 mM) was added with stirring which yielded a yellow coloured precipitate changing instantaneously to brown on stirring. The precipitate was suction filtered, washed with water, alcohol, ether and dried *in vacuo* over  $CaCl_2$ .

Attempts were made to synthesize  $Ni(OPD)_2(i\text{-MNT})$  and  $Ni(OPD)_3(i\text{-MNT})$  by taking Ni(II)salt, OPD and  $K_2i\text{-MNT}\cdot H_2O$  in 1:2:1, 1:3:1 molar ratios respectively under the same conditions but only one product,  $Ni(OPD)(i\text{-MNT})$ , was obtained with increased percentage yield.

##### $Ni(OPD)(i\text{-MNT})(py)_2$ (2)

The green micro-crystalline product of the complex was obtained when 4 mM of  $Ni(OPD)(i\text{-MNT})$  was dissolved in 10 cm<sup>3</sup> of pyridine and shaken vigorously. The precipitate was filtered and washed with ether several

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times containing a few drops of pyridine. The precipitate was dried in open air.

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

A quantity of Ni(OPD)(i-MNT) (5 mM) was added to 10 cm<sup>3</sup> of  $\alpha$ -picoline slowly with stirring and finally heated over a steam bath which resulted dark coloured solution. The solution was filtered hot and allowed to cool at room temperature, which did not yield any precipitate. The solution was evaporated naturally within 2 months, leaving a black micro-crystalline product which was washed with ether several times, suction filtered and air dried.

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

A quantity of Ni(OPD)(i-MNT) (5 mM) was mixed with 10 cm<sup>3</sup> of  $\beta$ -Picoline in a small stoppered round bottom flask. On shaking vigorously the mixture became warm and the brown precipitate turned to green and finally to ash within 2 days. On observing further, the colour of the precipitate changed from ash to brown-pink and finally to brown within 5 months. The mixture was diluted with 20 cm<sup>3</sup> ether, suction filtered and washed with ether until the filtrate became colourless. The precipitate was dried *in vacuo* over CaCl<sub>2</sub>.

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

A quantity (5 mM) of Ni(OPD)(i-MNT) was added to 10 cm<sup>3</sup> of  $\gamma$ -picoline with stirring which yielded a dark yellow solution which became warm. After 5 min, the solution yielded thick black precipitate which changed to moss colour within 30 min of stirring and no further change in the colour of the precipitate was found even after 2-days. Finally, 20 cm<sup>3</sup> of ether was added to it, stirred and suction filtered. The precipitate was washed with ether several times and dried *in vacuo* over CaCl<sub>2</sub>.

*Ni( $\beta$ -pic)<sub>4</sub>(i-MNT)* (6)

A quantity (5 mM) of Ni(OPD)(i-MNT) was added slowly in portions to 10 cm<sup>3</sup> of  $\beta$ -picoline with stirring which gave first a brown solution and then a suspension. On stirring, the mixture became warm and yielded a green to olive green precipitate within 30 min. The precipitate was suction filtered, washed with ether several times and dried in air.

*Ni( $\alpha$ -pic)<sub>2</sub>(i-MNT)* (7)

A quantity (5 cm<sup>3</sup>) of  $\alpha$ -picoline (~30 mM) was added slowly to a 25 cm<sup>3</sup> aqueous solution containing 5 mM of hydrated nickel nitrate and stirred for an hour. The solution was filtered and to this filtrate 20 cm<sup>3</sup> aqueous solution containing K<sub>2</sub>i-MNT·H<sub>2</sub>O (5 mM) was added with stirring which yielded first of all yellow coloured precipitate which changed to olive green and finally to reddish brown within a short interval. The mixture was stirred for 30 min, suction filtered, washed with water, alcohol, ether and dried *in vacuo* over CaCl<sub>2</sub>.

*Ni( $\beta$ -pic)<sub>2</sub>(i-MNT)·2H<sub>2</sub>O* (8)

To a 25 cm<sup>3</sup> aqueous solution containing 5 mM of hydrated nickel nitrate, 5 cm<sup>3</sup> of  $\beta$ -picoline (~30 mM) was added with stirring which turned the solution from green to blue. To this resulting solution, a 20 cm<sup>3</sup> aqueous solution containing 5 mM of K<sub>2</sub>i-MNT·H<sub>2</sub>O was added with stirring which yielded a yellow precipitate turning to olive green within a short interval of time. The mixture was stirred for 30 min, suction filtered, washed with water, alcohol and finally with ether and was dried *in vacuo* over CaCl<sub>2</sub>.

*Ni( $\gamma$ -pic)<sub>2</sub>(i-MNT)* (9)

A blue solution was obtained when 5 cm<sup>3</sup> of  $\gamma$ -picoline (~30 mM) was added to a 25 cm<sup>3</sup> aqueous solution containing hydrated nickel nitrate (5 mM) with stirring. To this resulting solution, 20 cm<sup>3</sup> of an aqueous solution containing 5 mM of K<sub>2</sub>i-MNT·H<sub>2</sub>O was added with stirring which yielded yellow coloured precipitate turning to green and finally to a black sticky material. The supernatant liquid was decanted and the sticky black material was washed with water several times. To this sticky black material, 50 cm<sup>3</sup> of dehydrated alcohol was added, crushed with a glass rod and stirred for about 4 h which resulted in a pinkish brown coloured precipitate. The precipitate was washed with water, alcohol, ether and dried *in vacuo* over CaCl<sub>2</sub>.

*Analysis of the complexes*

The complexes were analysed for metals using standard literature procedures [16]. Sulphur was estimated as BaSO<sub>4</sub> gravimetrically. Carbon, hydrogen and nitrogen were determined micro-analytically. 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 in weight.

*Physical measurements*

The molar conductance of the millimolar 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 vibrating sample magnetometer. Experimental magnetic susceptibility values were corrected for diamagnetism by the procedures given by Figgis and Lewis [17] and Earnshaw [18]. 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 were recorded in the range 1100–200 nm on a Perkin-Elmer Model Lambda-25 UV-VIS spectrophotometer as nujol mull and on Chemito DU 2600 double beam UV-VIS spectrophotometer in DMSO solution. Analytical data together with colour, magnetic moment and molar conductance values are presented in Table 1. Important electronic

and infrared spectral data are given in Tables 2 and 3, respectively.

## Results and discussions

The analytical data and stoichiometries of the complexes reveal the formation of mixed ligand complexes of Ni(II) ion of the compositions,  $\text{NiL}_x(\text{i-MNT})$  [L = *o*-phenylenediamine (OPD),  $x = 1$ ;  $\alpha$ -picoline ( $\alpha$ -pic) or  $\gamma$ -picoline ( $\gamma$ -pic),  $x = 2$ ;  $\beta$ -picoline ( $\beta$ -pic),  $x = 4$ ] and  $\text{Ni(OPD)(i-MNT)L}_2 \cdot x\text{H}_2\text{O}$  [L = pyridine (py),  $\alpha$ -pic,  $\gamma$ -pic,  $x = 0$ ;  $\beta$ -pic,  $x = 2$ ; i-MNT = 1,1-dicyanoethylene-2,2-dithiolate ion]. 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.

The decomposition temperatures for complexes lie above 300 °C. The water molecules were determined by estimating weight loss after heating the compound in an electric oven in the temperature range 110–200 °C. The expulsion of two water molecules above 150 °C indicates that they are held in coordination sphere of the complex. The molar conductance values of the complexes in DMF solutions fall in the region 62.0–74.0  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  except for  $\text{Ni(OPD)(i-MNT)(}\alpha\text{-pic)}_2$  which has the value 31.0  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ . The observed molar conductance values of the complexes in DMF indicate their 1:1 electrolytic nature [19]. This is mainly due to the dissociation of the complexes in DMF solution suggesting strained structures in the solid state.

### Magnetic moments and electronic spectra

Magnetic susceptibility measurements and the electronic spectra of complexes were also obtained in order to have

information on their probable geometries. Magnetic moments of the complexes, 2–6 and 8, lie in the range 2.84–3.20 B.M. suggesting paramagnetic corresponding to two unpaired electrons and their nujol mull electronic spectra show well resolved three absorption bands in the ranges 9960–10917, 14471–16611 and 18,050–21,929  $\text{cm}^{-1}$  assignable to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(v_1)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v_2)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(v_3)$  transitions respectively which suggest octahedral coordination around Ni(II) in these complexes. The complexes, (7) and (9) have magnetic moment values equal to zero and show two resolved absorption bands in the regions 16,638–18,869 and 23,923–24,797  $\text{cm}^{-1}$  assignable to  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1A_{2g}$  transitions, respectively, characteristics of square planar [20] coordination with  $D_{4h}$  symmetry around Ni(II) in these complexes. The observed magnetic moment for the complex,  $\text{Ni(OPD)(i-MNT)}$  (1) is 2.20 B.M. which lies in the abnormal region. The subnormal magnetic moment of this Ni(II) complex is presumably due to the complex having layer structure in which vacant axial positions around the Ni(II) ions in the square planar,  $\text{NiN}_2\text{S}_2$ , units are weakly bonded to the sulphur atoms of the other  $\text{NiN}_2\text{S}_2$  units through bridging and provide effectively a weak to strong distorted octahedral environment [21] around the Ni(II) ion. This is further supported by the electronic spectral data. The complex shows two absorption bands at 16,207 and 20,491  $\text{cm}^{-1}$  assignable to  ${}^1A_{1g} \rightarrow {}^1B_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1A_{2g}$ , respectively, characteristic of square planar coordination with  $D_{4h}$  symmetry and an additional weak intensity broad band at about 10,152  $\text{cm}^{-1}$  is attributable to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(v_1)$  transition in octahedral symmetry around Ni(II).

The solution electronic spectra of the complexes dissolved in DMSO were recorded to examine the nature of coordination around Ni(II) ions in these

Table 1. Analytical data, molar conductance and magnetic moments of the complexes

Complex (colour)	% yield (Dec. Temp. °C)	Found (Calcd.)%				H	$\Lambda_M$ ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) (DMSO)	$\mu_{\text{eff}}$ (B.M.)
		Ni	S	N	C			
Ni(OPD)(i-MNT) (1) (Brown)	70 (> 300)	18.91 (19.12)	20.26 (20.88)	18.01 (18.25)	38.97 (39.12)	2.53 (2.63)	72.0	2.20
Ni(OPD)(i-MNT)(py) <sub>2</sub> (2) (Green)	62 (> 300)	12.10 (12.62)	13.25 (13.78)	17.86 (18.06)	50.71 (51.64)	3.63 (3.90)	72.0	3.20
Ni(OPD)(i-MNT)( $\alpha$ -pic) <sub>2</sub> (3) (Black)	60 (> 300)	11.00 (11.89)	13.46 (12.99)	16.91 (17.04)	52.83 (53.57)	4.31 (4.49)	31.0	2.84
Ni(OPD)(i-MNT)( $\beta$ -pic) <sub>2</sub> (4) (Brown)	65 (> 300)	11.12 (11.89)	12.23 (12.99)	16.82 (17.04)	52.71 (53.57)	4.23 (4.49)	68.0	2.99
Ni(OPD)(i-MNT)( $\gamma$ -pic) <sub>2</sub> (5) (Moss)	65 (> 300)	11.37 (11.89)	13.16 (12.99)	16.85 (17.04)	52.69 (53.57)	4.21 (4.49)	71.0	2.84
Ni( $\beta$ -pic) <sub>4</sub> (i-MNT) (6) (Olive Green)	60 (> 300)	9.87 (10.27)	10.88 (11.22)	14.06 (14.71)	58.10 (58.86)	4.52 (4.94)	73.0	2.88
Ni( $\alpha$ -pic) <sub>2</sub> (i-MNT) (7) (Reddish Brown)	70 (> 300)	14.81 (15.23)	16.02 (16.65)	14.02 (14.55)	49.38 (49.89)	3.12 (3.66)	62.0	0
Ni( $\beta$ -pic) <sub>2</sub> (i-MNT)·2H <sub>2</sub> O(8) (Olive Green)	65 (> 300)	13.36 (13.94)	14.80 (15.22)	12.89 (13.30)	44.96 (45.63)	4.12 (4.31)	74.0	2.86
Ni( $\gamma$ -pic) <sub>2</sub> (i-MNT) (9) (Brown)	75 (> 300)	14.86 (15.23)	16.13 (16.65)	13.95 (14.55)	49.20 (49.89)	3.02 (3.66)	68.0	0

Table 2. Uv-vis data for the complexes

Complex	$\lambda$ max(nm) (in nujol mull)	$\lambda$ max (nm) (in DMSO solution)
(1)	985, 617, 488	789, 633, 456
(2)	916, 617, 462	633, 456
(3)	938, 652, 462	569, 533, 424
(4)	916, 604, 458	637, 456
(5)	918, 602, 493	622, 568, 456
(6)	941, 623, 456	641, 573, 456
(7)	530, 404	631, 456
(8)	1004, 691, 554	632, 456
(9)	601, 418	635, 456

complexes in its solution state. The complexes, 2, 4, 7–9, show only two absorption bands in the range 15,698–15,847 and 21,929  $\text{cm}^{-1}$  characteristic of square planar geometry around Ni(II) ion in these complexes. The complexes, 3, 5–6, also show two absorption bands in the ranges 15,600–18,761 and 21,929–23,584  $\text{cm}^{-1}$  while the first band in each case shows splitting. The absorption bands are characteristic of square planar geometry around Ni(II) but splitting of first band suggests some distortion. The complex, 1, shows three bands at 12,674, 15,797 and 21,929  $\text{cm}^{-1}$  suggesting octahedral coordination around Ni(II) ion. In solution, all complexes except Ni(OPD)(i-MNT) show square planar to distorted square planar geometry around Ni(II) ion which is probably attained by nitrogen donors present in complexes and/or coordinating solvent molecules after dissociating the sulphur ligand. This is supported by their molar conductance values which indicate 1:1 electrolytic nature of the complexes in coordinating solvent (DMF). This suggests that the mixed ligand complexes have strained structures in its solid state which are relaxed when they are dissolved in coordinating solvent and showing 1:1 electrolytic nature.

Table 3. Characteristic i.r. bands ( $\text{cm}^{-1}$ ) for the complexes

Complexes	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(=\text{CS}_2)$	$\nu(\text{C}-\text{S})$	$\nu(\text{Ni}-\text{N})$	$\nu(\text{Ni}-\text{S})$
(1)	2230s, 2213s	1367vs	948m	900s	355m	320w
(2)	2211vs, 2199vs	1356w, 1377w	963m	892s	365m	270w
(3)	2200s	1393s	984w	865w	380m	280w
(4)	2212vs, 2198vs	1380w	965m	891s	390m	300w
(5)	2209vs, 2188vs	1374m	964m	892s	340m	310w
(6)	2213vs, 2199vs	1383m	967s	893s	330m	305w
(7)	2213vs, 2199vs	1384m	969m	900s	375m	320w
(8)	2209vs	1393m	964w, 982w	897s	370m	290w
(9)	2206vs	1393m, 1380m	937m	897s	360m	285w

vs – very strong; s – strong; m – medium; w – weak.

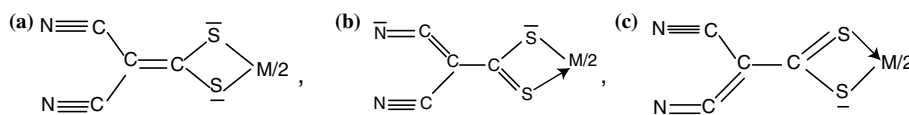


Fig. 1.

### Infrared spectra

The i.r. spectra of the mixed ligand complexes have been interpreted in the light of earlier investigations [1, 15, 22–26] on transition and non-transition metal isomaleonitriledithiolates. The i-MNT<sup>2-</sup> ligand ion may be described by resonating structures in its complexes as shown in Figure 1.

Each of the moieties in the complexes undergoes particular vibrations and contributes certain peaks to their i.r. spectra. The electron delocalization in the chelated i-MNT<sup>2-</sup> ring leads to the coupling of vibrational modes so that few bands in i.r. spectra represent pure vibrations. The i.r. spectra of the mixed ligand complexes display characteristic stretching frequencies associated with  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{C}$ ,  $\text{C}-\text{S}$  and  $\text{M}-\text{S}$  from i-MNT<sup>2-</sup>; aryl ring vibrations with metal heterocyclic nitrogen vibrations from py,  $\alpha$ -pic,  $\beta$ -pic and  $\gamma$ -pic and amine vibrations with metal-amine nitrogen vibrations from OPD.

The  $\nu(\text{C}\equiv\text{N})$  band appearing at 2195  $\text{cm}^{-1}$  with a shoulder at 2200  $\text{cm}^{-1}$  in  $\text{K}_2$ i-MNT, is observed in the range 2199–2230  $\text{cm}^{-1}$  in the mixed ligand complexes. In most of the complexes definite splitting of this peak is observed which reflects a lower symmetry for these complexes. The  $\nu(\text{C}=\text{C})$  absorption in all the complexes appears in the range 1367–1393  $\text{cm}^{-1}$  is close to that observed in free  $\text{K}_2$ i-MNT ligand (1360  $\text{cm}^{-1}$ ), which implies some delocalization of  $\pi$ -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) (Figure 1) is more dominant in these complexes of i-MNT<sup>2-</sup> ligand ion. A band at 960  $\text{cm}^{-1}$  with a shoulder at 985  $\text{cm}^{-1}$  on the higher frequency side is observed in the i.r. spectrum of  $\text{K}_2$ i-MNT due to the  $=\text{CS}_2$  group. The corresponding band in the mixed ligand complexes are found in the range 937–984  $\text{cm}^{-1}$ . The  $\nu(\text{C}-\text{S})$  band occurring in the spectrum of  $\text{K}_2$ i-MNT at

860  $\text{cm}^{-1}$  appears as a single band in the range 865–900  $\text{cm}^{-1}$  in the complexes indicating symmetrical bonding of both the sulphur atoms to metal ions. Similar bonding behaviour of  $i\text{-MNT}^{2-}$  ion is reported [26] in  $\text{K}_2[\text{Ni}(i\text{-MNT})_2]$  where a single  $\nu(\text{C}-\text{S})$  band is observed at 900  $\text{cm}^{-1}$ . The mixed ligand complexes containing heterocyclic nitrogen donors show in-plane ring and out-of-plane ring deformation bands in the ranges 607–649 and 421–430  $\text{cm}^{-1}$ , respectively, indicating coordination through nitrogen atom. Complexes, 1–5, exhibit a broad band in the range 3048–3299  $\text{cm}^{-1}$  attributed to  $\nu(\text{N}-\text{H})$  stretching modes lower than the free  $o$ -phenylenediamine ligand bands (3188–3383  $\text{cm}^{-1}$ ). The N–H bending (Scissoring) vibration mode is observed in the range 1601–1620  $\text{cm}^{-1}$  for the complexes which is lower than the free OPD band (1633  $\text{cm}^{-1}$ ). These shifts towards the lower frequency clearly suggest the amino nitrogen coordination to metal ion. Aromatic,  $\nu(\text{C}-\text{H})$  for the aromatic ligands in these complexes show a weak intensity band in the region 3028–3101  $\text{cm}^{-1}$ . Methyl,  $\nu(\text{C}-\text{H})$  for complexes containing  $\alpha$ -pic,  $\beta$ -pic and  $\gamma$ -pic, ligands show a band in the region 2923–2965  $\text{cm}^{-1}$ .

A strong absorption band observed in the range 700–811  $\text{cm}^{-1}$  in these complexes is attributed to out-of-plane  $=\text{C}-\text{H}$  ring bending mode which is found in free OPD at 751  $\text{cm}^{-1}$ , characteristic of substituted benzene. Weak combination and overtone bands appear in the 1650–2000  $\text{cm}^{-1}$  region in complexes, 1–5, and the number and relative positions of these bands are remarkably for *ortho* disubstituted benzenoid structure.

The non-ligand bands observed in the ranges 330–390 and 270–320  $\text{cm}^{-1}$  in the spectra of mixed ligand complexes are tentatively assigned to  $\nu(\text{M}-\text{N})$  [24] and  $\nu(\text{M}-\text{S})$  [27] modes, respectively.

#### Reactivity of the complex

When  $\text{Ni}(\text{OPD})(i\text{-MNT})$  was reacted with heterocyclic nitrogen bases, py,  $\alpha$ -pic,  $\beta$ -pic or  $\gamma$ -pic, under different conditions then it yielded an additional product of composition  $\text{Ni}(\text{OPD})(i\text{-MNT})\text{L}_2$  [L = py,  $\alpha$ -pic,  $\beta$ -pic or  $\gamma$ -pic] and  $\text{Ni}(\beta\text{-pic})_4(i\text{-MNT})$ , whose magnetic moment and electronic spectral data suggest an octahedral arrangement around Ni(II) ion in these complexes. The formation of addition compounds suggests that the interactions through S-atom bridging between  $\text{NiN}_2\text{S}_2$  units in layer structure in the complex,  $\text{Ni}(\text{OPD})(i\text{-MNT})$ , in its solid state were weak and were broken by strong donor molecules yielding addition products.

#### Conclusions

Based on stoichiometries and spectrochemical studies, octahedral structure for complexes 2–6 and 8 and square planar structure for complexes 7 and 9 have been

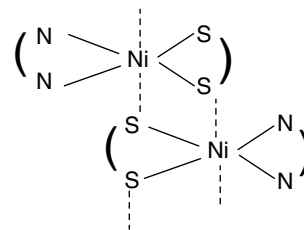


Fig. 2. [N–N = *o*-phenylenediamine, S–S =  $(\text{CN})_2\text{C}=\text{CS}_2^-$ ].

proposed. The structure of complex ,1, has been tentatively proposed as shown in Figure 2.

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#### References

1. D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1970); **26**, 301 (1979).
2. R.P. Burns, F.P. McCullough and C.A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, **22**, 303 (1979).
3. M. Bousseau, L. Valade, J.P. Legros, P. Cassoux, M. Garbouskas and L.V. Interante, *J. Am. Chem. Soc.*, **108**, 1908 (1986).
4. A. Kobayashi, Y. Sasaki, R. Kato and H. Kobayashi, *Chem. Lett.*, 387 (1986).
5. J.A. McCleverty, *Molecular Metals*, Plenum, New York, 1979.
6. D. Zhu, X.C. Xing, P.J. Wu, P. Wang, D.M. Zhang and D.L. Yang, *Synth. Met.*, **42**, 2541 (1991).
7. *Chem. Abstr.*, **100**, p115000a (1984); **102**, p195283z, p31934m (1985); **104**, p192920k, p88608d (1986); **106**, p67474h (1987).
8. U. Abram, W. Dietzsch and R. Kirmse, *Z. Chem.*, **22**, 305, (1982).
9. N.K. Singh, P.P. Agarwal and N. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **21**, 541 (1991); *Transition Met. Chem.*, **15**, 325 (1990).
10. M.K. Singh, R.C. Aggarwal and B. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **15**(4), 459 (1985).
11. M.K. Singh, *Indian J. Chem.*, **30A**, 1070 (1991).
12. M.K. Singh, *J. Indian Chem. Soc.*, **76**, 148 (1999).
13. M.K. Singh, *Indian J. Chem.*, **38A**, 1294 (1999).
14. J.A. McCleverty, D.G. Orchard and K. Smith, *J. Chem. Soc.(A)*, 707 (1971).
15. K.A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **22**, 1107 (1968).
16. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd edit., ELBS and Longmans, London, 1961.
17. B.N. Figgis and J. Lewis, *Modern Coordination Chemistry*, Eds. J. Lewis and R.G. Wilkins, Interscience, New York, 1960.
18. A. Earnshaw, *Introduction to Magnetochemistry*, Academic Press, London, 1968.
19. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
20. C.K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

21. R.C. Aggarwal, N. Singh and S. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **16**, 115 (1986).
22. M.L. Caffery and D. Coucouvanis, *J. Inorg. Nucl. Chem.*, **37**, 2081 (1975).
23. A. Devison, N. Edelstein, R.H. Holm and A.H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).
24. G. N. Schrauzer and V.P. Meyweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).
25. D.M. Adams and J.B. Cornell, *J. Chem. Soc.(A)*, 884 (1967).
26. J.P. Fackler Jr. and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).
27. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edit., Wiley-Interscience, New York, 1978.

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