

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

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Received 22 1 2007; accepted 13 3 2007

Abstract

Mixed ligand complexes of Ni^{II} ion with 1-cyano-1-carboethoxyethylene-2,2-dithiolate (CED²⁻[S₂C = C(CN)(COOC₂H₅)₂]²⁻) as a primary ligand and *o*-phenylenediamine (OPD), pyridine (py), α -picoline (α -pic), β -picoline (β -pic) or γ -picoline (γ -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 the complexes have 1:1 electrolytic nature in DMF solution. Magnetic and electronic spectral studies suggest distorted octahedral stereochemistry around Ni^{II} ion in its complexes. Infrared spectral studies suggest bidentate chelating behaviour of CED²⁻ ion and OPD while other ligands show unidentate behaviour in their complexes.

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 [1, 2]. Recently the roles 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 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 [7–14]. In addition, metal dithiolates have a number of industrial and biological applications [2, 15].

Among 1,1-dithioligands, the 1-cyano-1-carboethoxyethylene-2,2-dithiolate ion shows exciting coordination properties by virtue of its chelating and bridging behaviour which have been found in its binary, and heterobimetallic complexes [1, 2, 16]. Prior to our report, McCleverty *et al.* [17] isolated and characterized a series of mixed 1,1- and 1,2-dithio ligand 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 diamines and/or heterocyclic tertiary monoamines.

In view of the above, synthesis and structural studies on mixed ligand complexes of nickel(II) ion with K₂CED·H₂O and primary aromatic diamine(OPD) and/or heterocyclic tertiary monoamine were, therefore, undertaken and the results of our investigations are presented in this paper.

Experimental

Materials

All the chemicals used in this study, obtained from E. Merck, were of GR grade or equivalent quality. α -, β - and γ -picolines were obtained from Aldrich Chemical company. K₂CED·H₂O was prepared by a known literature procedure [18].

Synthesis of complexes

Ni(OPD)_n(CED) (1)

o-Phenylenediamine (1.08 g, 10 mM) in MeOH (50 mL) solution was added with stirring to a 50 mL aqueous solution containing (0.29 g, 10 mM) hydrated nickel nitrate, which resulted in a deep green solution. To this solution, a 50 mL aqueous solution of K₂CED·H₂O (2.83 g, 10 mM) was added with stirring which yielded a deep yellow precipitate which turned to brown-red on stirring after few minutes. The precipitate was suction filtered, washed with H₂O, alcohol, ether and dried *in vacuo* over CaCl₂.

Attempts were made to synthesize Ni(OPD)_n(CED) ($n = 2,3$) by taking Ni_(II) salt, OPD and K₂CED·H₂O in 1:2:1, 1:3:1 molar ratios respectively under the

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- 75 same condition but only one product, Ni(OPD)(CED), 120
 76 was obtained with increased percentage yield. 121
- 77 *Ni(OPD)(CED)(py)₂ (2)* 122
 78 A quantity of Ni(OPD)(CED) (0.70 g, 2 mM) was ad- 123
 79 ded to 15 mL of pyridine, slowly with stirring, and fi- 124
 80 nally filtered which yielded a dark coloured filtrate. 125
 81 The solution was evaporated naturally, and yielded a 126
 82 pasty dark green material after five days. This was 127
 83 converted to a dark green powder by washing it with 128
 84 ether several times, suction filtered and air-dried. 129
- 85 *Ni(OPD)(CED)(α -pic)₂ (3)* 130
 86 A quantity of Ni(OPD)(CED) (0.70 g, 2 mM) was dis- 131
 87 solved in 10 mL DMF followed by addition of α -pico- 132
 88 line(10 mL) and the resulted solution was kept under 133
 89 observation. After two months a black sticky precipi- 134
 90 tate was obtained. The supernatant liquid was dec- 135
 91 anted and was washed with ether several times to 136
 92 convert the sticky black mass into a powder and air- 137
 93 dried. 138
- 94 *Ni(OPD)(CED)(β -pic)₂ (4)* 139
 95 A quantity of Ni(OPD)(CED) (1.77 g, 5 mM) was dis- 140
 96 solved in 10 mL DMF followed by addition of β -pico- 141
 97 line (10 mL) with stirring, which did not yield any 142
 98 product. The solution was evaporated naturally and 143
 99 after six months a black sticky product was obtained, 144
 100 which was washed with ether several times making it a 145
 101 black powder. Finally it was suction filtered and air- 146
 102 dried. 147
- 103 *Ni(OPD)(CED)(γ -pic)₂ (5)* 148
 104 The black complex was obtained essentially by the 149
 105 same method used for the synthesis of Ni(OPD)- 150
 106 (CED)(β -pic)₂, only by replacing β -picoline by γ -pico- 151
 107 line. 152
- 108 *NiL₂(CED)[L = py (6), β -pic (7) or γ -pic (8)]* 153
 109 A quantity of pyridine (py) (2.5 mL), β -picoline (β -pic) 154
 110 (3.0 mL) or γ -picoline (γ -pic) (3.0 mL) was added with 155
 111 stirring to a 25 mL aqueous solution containing hy- 156
 112 drated nickel nitrate (1.45 g, 5 mM) resulting in a blue 157
 113 solution. To this solution, a 50 mL aqueous solution 158
 114 of K₂CED·H₂O (1.42 g, 5 mM) was added with 159
 constant stirring, which yielded, a reddish brown or 160
 orange precipitate. The precipitate was suction filtered, 161
 washed with water followed by ether and air-dried. 162
- Ni(α -pic)₂(CED) (9)* 163
 A quantity of α -picoline (9 mL, ~90 mM) was added 164
 with stirring to a 25 mL aqueous solution containing 165
 hydrated nickel nitrate (1.45 g, 5 mM) resulted in a 166
 greenish flocculent precipitate which was dissolved to 167
 give a green solution by adding 30 mL (2N) hydro- 168
 chloric acid. To this solution, 20 mL aqueous solution 169
 of K₂CED·H₂O (1.42 g, 5 mM) was added with stir- 170
 ring, produced a brown precipitate which turned into 171
 a black semi-solid sticky material. The light yellow 172
 supernatant liquid was decanted and sticky black semi- 173
 solid material was crushed, washed several times with 174
 ether and air-dried. 175
- Analysis of the complexes* 176
 The complexes were analyzed for metals using stan- 177
 dard literature procedures [19]. Sulphur was estimated 178
 as BaSO₄ gravimetrically. Carbon, hydrogen and 179
 nitrogen were determined micro-analytically. 180
- Physical measurements* 181
 The molar conductance of the millimolar solutions of 182
 the complexes in DMF was measured using Systronics 183
 direct reading conductivity meter 304 with a dip-type 184
 cell with platinumized electrodes. Magnetic suscepti- 185
 bility measurements were made at room temperature on a 186
 Cahn-Faraday electrobalance using CoHg(SCN)₄ as 187
 calibrant. Experimental magnetic susceptibility values 188
 have been corrected for diamagnetism by the proce- 189
 dures given by Figgis and Lewis [20] and Earnshaw 190
 [21]. Infrared spectra were recorded in nujol 191
 (4000–200 cm⁻¹) and in KBr pellets (4000–400 cm⁻¹) 192
 on a Bomem DA – 8 FT-IR spectrophotometer. The 193
 electronic spectra of the complexes were recorded in 194
 the 1100–200 nm range on a Perkin-Elmer Model 195
 Lambda-25 UV-Vis spectrophotometer, as a nujol mull 196
 and in DMF solution. Analytical data together with 197

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

Complex (colour)	% yield (Dec. Temp. °C)	Found (Calcd.), %					Λ_M (Ω^{-1} cm ² mol ⁻¹ (DMSO))	μ_{eff} (B.M.)
		Ni	S	N	C	H		
Ni(OPD)(CED) (1) (Brownish Red)	80 (> 300)	15.6 (16.6)	18.2 (18.1)	10.9 (11.9)	40.0 (40.7)	2.8 (3.7)	56.0	2.01
Ni(OPD)(CED)(py) ₂ (2) (Red)	55 (> 300)	10.6 (11.4)	11.3 (12.5)	12.9 (13.7)	50.7 (51.9)	3.6 (4.5)	37.0	2.93
Ni(OPD)(CED)(α -pic) ₂ (3) (Black)	45 (> 300)	10.9 (10.9)	12.2 (11.9)	12.6 (13.0)	52.8 (53.3)	4.3 (5.0)	45.0	2.85
Ni(OPD)(CED)(β -pic) ₂ (4) (Black)	40 (> 300)	10.1 (10.9)	12.6 (11.9)	12.8 (13.0)	52.7 (53.3)	4.2 (5.0)	48.0	2.84
Ni(OPD)(CED)(γ -pic) ₂ (5) (Black)	60 (> 300)	10.4 (10.9)	11.4 (11.9)	11.9 (13.0)	52.7 (53.3)	4.2 (5.0)	30.0	3.44
Ni(py) ₂ (CED) (6) (Reddish Brown)	65 (> 300)	13.9 (14.5)	16.3 (15.9)	10.1 (10.4)	48.1 (47.5)	4.2 (3.7)	54.0	2.1
Ni(β -pic) ₂ (CED) (7) (Orange)	55 (> 300)	13.0 (13.6)	14.7 (14.8)	9.1 (9.7)	49.4 (50.0)	3.9 (4.4)	58.0	3.44
Ni(γ -pic) ₂ (CED) (8) (Orange)	75 (> 300)	12.8 (13.6)	14.1 (14.8)	9.2 (9.7)	49.5 (50.0)	3.9 (4.4)	54.0	0.65
Ni(α -pic) ₂ (CED) (9) (Black)	62 (> 300)	13.0 (13.6)	14.8 (14.8)	8.9 (9.7)	49.2 (50.0)	3.8 (4.4)	62.0	2.62

Table 2. UV-Visible data for the complexes

Complex	λ_{max} (nm) (in nujol mull)	λ_{max} (nm) (in DMSO solution)
(1)	915, 805, 600, 360	820, 480
(2)	920, 810, 610, 540, 360	725w, 640, 585, 440
(3)	920, 815, 610, 545, 360	675w, 575, 510, 420
(4)	920, 815, 610, 540, 360	680w, 580, 540sh, 420
(5)	920, 815, 610, 540, 360	905w, 600, 540, 445sh
(6)	920, 815, 610, 540, 360	580w, 500, 445sh, 400
(7)	920, 810, 610, 540, 360	580w, 500, 440sh, 405
(8)	920, 810, 600, 510, 360	580w, 500, 440sh, 400
(9)	920, 815, 610, 545, 360	580w, 500, 440sh, 360

158 colour, % yield, magnetic moment and molar conduc-
159 tance values are presented in Table 1. Important elec-
160 tronic and infrared spectral data are given in Table 2
161 and Table 3 respectively.

162 Results and discussions

163 The analytical data and stoichiometries of the com-
164 plexes reveal the formation of mixed ligand com-
165 plexes of Ni^{II} ion of the compositions, NiL_x(CED)
166 [L = *o*-phenylenediamine (OPD), *x* = 1; pyridine (py),
167 α -picoline (α -pic), β -picoline (β -pic) or γ -picoline
168 (γ -pic), *x* = 2] and Ni(OPD)(CED)L₂ [L = *py*, α -pic,
169 β -pic or γ -pic]; CED = 1-cyano-1-carboethoxyethylene-
170 2,2-dithiolate ion]. The complexes are insoluble in
171 water and common organic solvents but are soluble
172 in highly coordinating solvents such as DMF and
173 DMSO, giving coloured solutions.

174 The decomposition temperatures for complexes lie
175 above 300 °C. The molar conductance values of the
176 complexes in DMF solutions fall in the region
177 30.0–62.0 Ohm⁻¹ cm² mole⁻¹ which are slightly lower
178 than that of the reported values for 1:1 electrolytes
179 [22]. The lower conductivity values may be due to low
180 mobility of large complexed cations formed in DMF
181 solution by the dissociation of complex molecules.
182 Thus the observed molar conductance values of the
183 complexes in DMF suggest their 1:1 electrolytic nat-
184 ure. This is mainly due to the dissociation of the com-
185 plexes in DMF solution suggesting strained structure
186 in the solid state.

Magnetic moments and electronic spectra

188 Magnetic susceptibility measurements and electronic
189 spectra of complexes were also obtained in order to
190 explore the probable stereochemistries around Ni^{II} in
191 these complexes.. Magnetic moments of the complexes,
192 (2–5 and 7), lie in the range 2.84–3.44 B.M. suggesting
193 paramagnetism corresponding to two unpaired elec-
194 trons and their nujol mull electronic spectra show well
195 resolved three absorption bands in the regions
196 10,880–12,330, 16,340–18,590 and 27,625 cm⁻¹ assign-
197 able to ³A_{2g} → ³T_{2g}(F)(ν_1), ³A_{2g} → ³T_{1g}(F)(ν_2) and
198 ³A_{2g} → ³T_{1g}(P)(ν_3) transitions respectively which sug-
199 gest octahedral coordination around Ni^{II} in these com-
200 plexes. The ν_1 band shows definite splitting suggesting
201 distortion of octahedral stereochemistry around Ni^{II} in
202 these complexes. The splitting of ν_2 bands are ob-
203 served in the 16,340–16,420 and 18,415–18,590 cm⁻¹
204 ranges in the spectra of these complexes which may
205 arise due to spin-orbit coupling that mixes the
206 ³T_{1g}(F) and ¹E_g states, which are very close in energy
207 at the Δ_0 value given by the ligands present in these
208 mixed ligand complexes [23]. The stoichiometry of
209 complex, (7), suggest four coordinated Ni^{II} but mag-
210 netic susceptibility and electronic spectra suggest dis-
211 torted octahedral coordination around Ni^{II} which
212 probably arises due to strong bridging through sulphur
213 donor in NiN₂S₂ units [24]. The observed magnetic
214 moments for complexes, (1,6,8 and 9), lie in the range
215 0.65–2.62 B.M. which lie in the subnormal region. The
216 subnormal magnetic moments for these complexes are
217 presumably due to the complexes having layer struc-
218 tures in which vacant axial positions around the Ni^{II}
219 ions in square planar, NiN₂S₂ units, are weakly bon-
220 ded to the sulphur atoms of the other NiN₂S₂ units
221 through bridging and provide effectively a weak to
222 strong distorted octahedral environment [24] around
223 the Ni^{II} ions. This is further supported by their elec-
224 tronic spectral data. The nujol mull electronic spectra
225 of these complexes show the same pattern as observed
226 for other complexes. The middle split band observed
227 in the range 16,370–19,610 and the third band at
228 27,625 cm⁻¹ assignable to ¹A_{1g} → ¹B_{1g} and
229 ¹A_{1g} → ¹A_{2g}, respectively, may be considered charac-
230 teristic of square planar coordination with D_{4h}

Table 3. Characteristic i.r bands (cm⁻¹) for the complexes

Complexes	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{S}_2)$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
Ni(OPD)(CED)	2206s	1630s	1383vs	1032s, 935s	868w	420w	330w
Ni(OPD)(CED)(Py) ₂	2198s	1632s	1372s	1026s, 921m	860w	360w	315w
Ni(OPD)(CED)(α -pic) ₂	2197s	1630vs	1382vs	1023s, 921m	826w	385w	310w
Ni(OPD)(CED)(β -pic) ₂	2199vs	1622vs	1385s	1021m, 984w	828w	325w	280w
Ni(OPD)(CED)(γ -pic) ₂	2199vs	1637vs	1385s	1024m	894w	365w	260w
Ni(py) ₂ (CED)	2213s	1638s	1396vs	1033m 936m	867w	390w	275w
Ni(β -pic) ₂ (CED)	2219s	1637s	1385vs	1031m, 941m	875m	395w	285w
Ni(γ -pic) ₂ (CED)	2222s	1637vs	1388s	1026m, 946m	865w	405w	265w
Ni(α -pic) ₂ (CED)	2228s	1654s	1385vs	1026s, 923m	877w	400w	280w

vs = very strong, m = medium, w = weak.



231 symmetry [25] and the additional relatively weak split-
 232 ted band in the range 10,880–12,420 cm^{-1} is attribut-
 233 able to ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)(v_1)$ transition in octahedral
 234 symmetry around the Ni^{II} ion. The strength of sulphur
 235 bridges in NiN_2S_2 units in these complexes may be
 236 correlated with the observed magnetic moment values
 237 which follow the decreasing trend, $9 > 6 > 1 > 8$.

238 The solution electronic spectra of the complexes dis-
 239 solved in DMF were recorded to examine the nature of
 240 coordination around the Ni^{II} ion in these complexes in
 241 its solution state. The complexes, (2–5), show three re-
 242 solved bands in the ranges 11,060–14,770 (v_1),
 243 15,625–19,760 (v_2) and 22,730–24,040 (v_3) cm^{-1} charac-
 244 teristic of distorted octahedral geometry around Ni^{II}
 245 ion in these complexes. The middle band shows definite
 246 splitting suggesting spin-orbit coupling [23] that mixes
 247 the ${}^3T_{1g}(F)$ and 1E_g states. The intensity of the first
 248 band (v_1) is weak with respect to other bands suggest-
 249 ing distorted octahedral stereochemistry. On dilution
 250 the second and third bands shift to higher frequencies
 251 while the first band vanishes. The complexes, (6–9),
 252 show one band in the region 19,960–20,120 cm^{-1}
 253 with a shoulder in the range 22,420–22,625 cm^{-1} while
 254 the another band is observed in the range 24,815–
 255 27,775 cm^{-1} which are characteristic of square planar
 256 geometry around Ni^{II} ion in these complexes. This
 257 solution electronic spectral observation suggests the
 258 weakening or complete disruption of sulphur bridges
 259 among NiN_2S_2 units in its proposed layer structure in
 260 solid state. This is further supported by the fact that
 261 the v_1 bands, observed for these complexes in the range
 262 10,880–12,420 cm^{-1} in its nujol mull spectra, were ab-
 263 sent in its solution spectra while a weak to very weak
 264 band at 17,300 cm^{-1} is observed. The complex,
 265 $\text{Ni}(\text{OPD})(\text{CED})$ (1), shows two bands at 12,210 and
 266 20,835 cm^{-1} suggesting distorted octahedral arrange-
 267 ment around Ni^{II} in this complex.

268 Infrared spectra

269 The i.r. spectra of the mixed ligand complexes have
 270 been interpreted in the light of earlier investigations
 271 [1, 17, 18, 26–29] on transition and non-transition
 272 metal dithiolates. The CED^{2-} ligand ion may be
 273 described by resonating structures in its complexes as
 274 shown in Figure 1.

275 The i.r. spectra of the mixed ligand complexes dis-
 276 play characteristic stretching frequencies associated
 277 with $-\text{C}\equiv\text{N}$, $>\text{C}=\text{O}$, $>\text{C}=\text{CS}_2$, $\text{C}-\text{S}$ and $\text{M}-\text{S}$ from

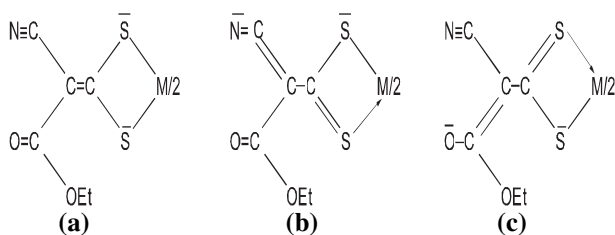


Fig. 1.

CED^{2-} ; aryl ring vibrations with metal heterocyclic
 nitrogen vibrations from py, α -pic, β -pic or γ -pic and
 amine vibrations with metal-amine nitrogen vibration
 from OPD.

The $\nu(\text{C}\equiv\text{N})$ band, appearing at 2190 cm^{-1} in
 $\text{K}_2\text{CED}\cdot\text{H}_2\text{O}$, is observed with positive shifts in the
 range 2197–2228 cm^{-1} in its mixed ligand complexes
 suggesting non-involvement of a nitrile group of the li-
 gand in bonding. Compounds containing an unconju-
 gated and a conjugated (with acetyl or benzoyl group)
 ester group show $\nu(\text{C}=\text{O})$ bands in 1720–1750 and
 1620–1630 cm^{-1} regions respectively. The $\nu(\text{C}=\text{O})$
 stretching band of ester group in these compounds ap-
 pears as a strong band in the region
 1622–1654 cm^{-1} , which is more lowered than by usual
 α,β -unsaturation, is indicative of delocalization of
 $\text{C}=\text{O}$ group with the adjacent $\text{C}=\text{C}$ bond. The exis-
 tence of $\nu(\text{C}=\text{O})$ frequency in these mixed ligand com-
 plexes in the same region as observed for
 $\text{K}_2\text{CED}\cdot\text{H}_2\text{O}$ suggests that the carbonyl oxygen is not
 involved in bonding. The complexes exhibit three
 strong to very strong bands in the region 1372–1396,
 1021–1033 and 923–984 cm^{-1} assignable to
 $v_1[\nu(\text{C}=\text{C})]$, $v_4[\nu_{\text{as}}(=\text{CS}_2)]$ and $v_2[\nu_{\text{s}}(=\text{CS}_2)]$ vibra-
 tions of $\text{C}=\text{CS}_2$ structure which were found in $\text{K}_2\text{CED}\cdot$
 H_2O at 1320, 1020 and 930 cm^{-1} respectively [16, 18].
 In some complexes $\nu(\text{C}=\text{C})$ appear as splitted (doublet
 or triplet) indicating lowering of its symmetry. The po-
 sitive shifts in $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}=\text{C})$ bands suggest
 that resonance form (a) (Figure 1) is more dominant
 in the 1-cyano-1-carboethoxyethylene-2,2-dithiolate
 complexes. The occurrence of a single weak to strong
 band in the region 828–894 cm^{-1} for $\nu(\text{C}-\text{S})$ in these
 complexes indicates symmetrical bonding of both the
 sulphur atoms of the ligand to the metal ion [30].

The mixed ligand complexes containing heterocyclic
 nitrogen donors show in-plane ring and out-of-plane
 ring deformation bands in the ranges 619–669 and
 420–435 cm^{-1} respectively indicating coordination
 through nitrogen atom as these bands have found po-
 sitive shifts with respect to its corresponding bands in
 its free form. The complexes exhibit a group of broad
 bands in the range 3231–3729 cm^{-1} attributed to
 $\nu(\text{N}-\text{H})$ (asymmetric and symmetric) stretching modes
 from the ligand, *o*-phenylenediamine. The $\text{N}-\text{H}$ bend-
 ing (scissoring) vibration mode is observed in the
 range 1651–1698 cm^{-1} in the mixed ligand complexes
 which is overlapping region with $\nu(\text{C}=\text{O})$. The $\nu(\text{C}-\text{N})$
 bending mode observed in OPD at 1272 cm^{-1} is ob-
 served in the complexes in the range 1264–1291 cm^{-1} .
 A strong absorption band found at 751 cm^{-1} in the
 spectrum of OPD attributable to out of plane $\dots\text{C}-\text{H}$
 ring (aromatic) bending mode, characteristic of substi-
 tuted benzene, is observed in the region 745–766 cm^{-1} .
 The $\nu(\text{C}-\text{H})$ (aromatic ring) arising from aromatic li-
 gands in these complexes is observed as weak band(s)
 in the region 3000–3100 cm^{-1} . The $\nu(\text{C}-\text{H})$ (aliphatic)
 for complexes containing α -pic, β -pic, γ -pic and/or
 CED^{2-} is observed as weak intensity bands in the

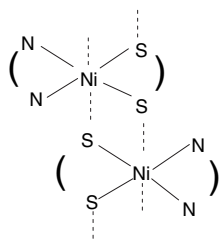


Fig. 2. [N-N = *o*-phenylenediamine, S-S = (CN)(COOC₂H₅)C = CS₂²⁻].

337 region 2833–2981 cm⁻¹ suggesting their presence in the
338 mixed ligand complexes.

339 The non-ligand bands observed in the ranges
340 325–420 and 260–330 cm⁻¹ in the spectrum of mixed
341 ligand complexes are tentatively assigned to $\nu(\text{M-N})$
342 [27] and $\nu(\text{M-S})$ [31] modes respectively.

343 Reactivity of the complex

344 When Ni(OPD)(CED) was reacted with heterocyclic
345 nitrogen bases, py, α -pic, β -pic or γ -pic, under differ-
346 ent experimental conditions then it yielded an addition
347 product of the composition Ni(OPD)(CED)L₂ [L =
348 py, α -pic, β -pic or γ -pic] whose magnetic moment and
349 electronic spectral data suggest distorted octahedral
350 arrangement around Ni^{II} ion in these complexes. The
351 formation of addition compounds suggests that the
352 interactions through S-atom bridging between NiN₂S₂
353 units in proposed layer structure in complex,
354 Ni(OPD)(CED), in its solid state were weak and were
355 broken by strong nitrogen donor molecules yielding
356 addition products.

357 Conclusions

358 Based on stoichiometries and spectrochemical studies,
359 distorted octahedral structure for complexes (2–5) and
360 a layered structure consisting of NiN₂S₂ units bridged
361 through S-atom for complexes, (1, 6–9), have been
362 proposed. The structure of one of representative com-
363 plex, Ni(OPD)(CED), has been proposed as shown in
364 Figure 2.

366 Acknowledgements

367 The authors are grateful to the Head, RSIC, NEHU,
368 Shillong for microanalysis and recording of i.r spectra.
369 Help received from Head of the Department of Chem-
370 istry, B.H.U., Varanasi for measuring magnetic sus-
371 ceptibility is also acknowledged. One of the authors
372 (Mrs.Bijaya.Paul) is grateful to Mr. P.K. Das, donor
373 of Pyari Mohan LabanyaPrabha Memorial (PMLPM)
374 Research Fellowship, for financial assistance.

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