

Synthesis and Characterization of mixed ligand complexes of Co(II) ion with some N and S donor

Mahesh K. Singh^{a*}, Ranajoy Laskar^a, Sanjit Sutradhar^a, Bijaya Paul^a,
S. Bhattacharjee^a and Arijit Das^{b*}

^aDepartment of Chemistry, Tripura University, Suryamaninagar-799022, Tripura, India.

^bDepartment of Chemistry, Ramthakur College, Agartala-799003, Tripura(w), Tripura, India.

Abstract: Mixed ligand complexes of Co(II) ion with some heterocyclic nitrogen donors and 1,1-dicyanoethylene-2,2-dithiolate of the compositions, $Co(N-N)_2(i-MNT)$, $Co(N-N)(i-MNT).2H_2O$ and $Co(N-N)(i-MNT)L_2$ [$N-N = 1,10$ -phenanthroline, 2,2'-bipyridine; $i-MNT^{2-} = 1,1$ -dicyano-ethylene-2,2-dithiolate; $L =$ pyridine(py), α -picoline (α -pic), β -picoline (β -pic) or γ -picoline (γ -pic)] 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 non-electrolytic nature of the complexes in DMF. Magnetic moment values suggest low spin complexes. The electronic spectral data suggest distorted octahedral stereochemistry around Co(II) ion in these complexes. Infrared spectral studies suggest bidentate chelating behaviour of $i-MNT^{2-}$, 1,10-phenanthroline and 2,2'-bipyridine while other ligands show unidentate behaviour in their complexes.

Keywords: Cobalt(II), 1,1-dicyanoethylene-2,2-dithiolate, Nitrogen donors, Mixed ligand complexes.

I. Introduction

The coordination chemistry of transition as well as non-transition metal dithiolates has been an area of interest for several decades [1,2]. Recently, the role of dithio ligands has 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 addition, metal dithiolates have a large number of industrial and biological applications [2,7].

1,1-Dicyanoethylene-2,2-dithiolate ion, shows exciting coordination properties by virtue of their chelating and bridging behaviours which have been found in their binary, ternary and heterobimetallic complexes [2, 8-10]. Our earlier communications [11-15,16,17] include the studies on mixed ligand complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with some nitrogen donors and 1,1-dithiolates. McCleverty *et. al.* [18] has also reported mixed ligand complexes of Co(II) involving 1,1- and 1,2-dithiolates.

It is evident from the literature survey that there is no report on mixed ligand complexes of cobalt(II) with 1,1-dicyanoethylene-2,2-dithiolate ion and heterocyclic nitrogen donors. Thus, it was thought of interest to undertake the synthesis and spectrochemical characterization of mixed ligand complexes of cobalt(II) ion with 1,1-dicyanoethylene-2,2-dithiolate ($i-MNT^{2-}$) ion and heterocyclic nitrogen donors, 1,10-phenanthroline or 2,2'-bipyridine and investigate their reactivity towards heterocyclic nitrogen donors, such that pyridine (py), α -picoline (α -pic), β -picoline (β -pic) or γ -picoline (γ -pic)]. The results of these investigations are reported in this article.

II. Experimental

2.1. Materials

All the chemicals used in this study were obtained from E. Merck of GR grade or equivalent quality. α -, β - and γ -picolines were obtained from Aldrich chemical company.

2.2. Analysis of the complexes

The complexes thus obtained were analyzed for cobalt using standard literature procedures [20]. Carbon, hydrogen and nitrogen were determined micro-analytically on CE 440 Exeter, USA and sulphur was estimated as $BaSO_4$ gravimetrically. The water molecules were determined by heating the sample for 4h in an electric oven maintained at 110-200^oC and determining the loss of weight.

2.3. 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 Cahn-Faraday electro balance using $[\text{CoHg}(\text{SCN})_4]$. Experimental magnetic susceptibility values have been corrected for diamagnetism by the procedures given by Figgis and Lewis [21] and Earnshaw [22]. Infrared spectra were recorded in nujol ($4000\text{-}200\text{ cm}^{-1}$) and in KBr pellets ($4000\text{-}400\text{ cm}^{-1}$) on a Bomem DA – 8 FT-IR spectrophotometer using CsI and KBr optics, respectively. The electronic spectra of the complexes were recorded in the range $1100\text{-}200\text{ nm}$ on a Perkin-Elmer Model Lamda-25 UV-Vis spectrophotometer in DMF 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 Table 2 and Table 3, respectively.

2.4. Preparation of ligands

The potassium-1,1-dicyanoethylene-2,2-dithiolate ($\text{K}_2\text{i-MNT.H}_2\text{O}$) was prepared by a known literature procedure [19].

2.5. Preparation of $\text{Co}(o\text{-phen})_2(\text{i-MNT})$ (1)

A 25 cm^3 ethanol solution of 1,10-phenanthroline(*o-phen*) (0.9911g, 5mmol) was added with stirring to a 25 cm^3 aqueous solution containing hydrated cobalt(II) nitrate (0.7276g, 2.5mmol) resulting orange coloured solution. To this resulting solution, a 25 cm^3 aqueous solution of $\text{K}_2\text{i-MNT.H}_2\text{O}$ (0.5909g, 2.5mmol) was added with stirring which yielded reddish brown precipitate. The precipitate was suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused CaCl_2 . After drying, the colour of the product was brown.

Attempt was made to synthesize $\text{Co}(o\text{-phen})_3(\text{i-MNT})$ by taking Co(II) salt, *o-phen* and $\text{K}_2\text{i-MNT.H}_2\text{O}$ in 1:3:1 molar ratio respectively under the same conditions but the product obtained was $\text{Co}(o\text{-phen})_2(\text{i-MNT})$.

2.6. Preparation of $\text{Co}(\text{bipy})_2(\text{i-MNT})$ (2)

A quantity of 2,2-bipyridine (bipy) (1.5619g, 10 mmol) was added to a 150 cm^3 of aqueous solution containing hydrated cobalt(II) nitrate (1.4552g, 5 mmol) and stirred the mixture which resulted wine red solution. To this solution, a 50 cm^3 aqueous solution of $\text{K}_2\text{i-MNT.H}_2\text{O}$ (1.1819g, 5mmol) was added with stirring giving olive green precipitate. The precipitate was suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused CaCl_2 . After drying, the colour of the product was brown. After drying the colour of product turned to brown.

Attempt was made to synthesize $\text{Co}(\text{bipy})_3(\text{i-MNT})$ by taking Co(II) salt, bipy and $\text{K}_2\text{i-MNT.H}_2\text{O}$ in 1:3:1 molar ratio under the same conditions was unsuccessful.

2.7. Preparation of $\text{Co}(o\text{-phen})(\text{i-MNT}).2\text{H}_2\text{O}$ (3)

A 20 cm^3 ethanol solution of 1,10-phenanthroline(*o-phen*) (0.9911g, 5mmol) was added with stirring to a 20 cm^3 ethanol solution containing hydrated cobalt(II) nitrate (1.4552g, 5mmol) resulting yellow solution. To this resulting solution, a 20 cm^3 aqueous solution of $\text{K}_2\text{i-MNT.H}_2\text{O}$ (1.1819g, 5mmol) was added with stirring resulted olive green precipitate. The precipitate was suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused CaCl_2 .

2.8. Preparation of $\text{Co}(\text{bipy})(\text{i-MNT}).2\text{H}_2\text{O}$ (4)

The complex, $\text{Co}(\text{bipy})(\text{i-MNT}).2\text{H}_2\text{O}$ was prepared similar to $\text{Co}(o\text{-phen})(\text{i-MNT}).2\text{H}_2\text{O}$ by taking Co(II) salt, 2,2'-bipyridine(bipy) and $\text{K}_2\text{i-MNT.H}_2\text{O}$ in 1:1:1 molar ratio. The colour of precipitate found was olive green.

2.9. Preparation of $\text{Co}(o\text{-phen})(\text{i-MNT})(\text{py})_2$ (5)

$\text{Co}(o\text{-phen})(\text{i-MNT}).2\text{H}_2\text{O}$ (0.8306g, 2mmol) was added to 25 cm^3 of pyridine slowly with vigorous shaking which resulted dark solution. The solution was filtered which did not yield any precipitate. The filtrate was evaporated naturally for a month, leaving a microcrystalline black product which was washed with ether containing traces of pyridine several times, suction filtered and air dried.

2.10. Preparation of $\text{Co}(o\text{-phen})(\text{i-MNT})(\alpha\text{-pic}/\gamma\text{-pic})_2$ (6,7)

The blackish brown complex, $\text{Co}(o\text{-phen})(\text{i-MNT})(\alpha\text{-pic})_2$ and $\text{Co}(o\text{-phen})(\text{i-MNT})(\gamma\text{-pic})_2$ were obtained essentially by the same method used for synthesis of $\text{Co}(o\text{-phen})(\text{i-MNT})(\text{py})_2$, only replacing pyridine by α -picoline and γ -picoline respectively.

2.11. Preparation of Co(bipy)(i-MNT)(py/ α -pic/ γ -pic)₂ (8,9,10)

Co(bipy)(i-MNT).2H₂O (0.7826g, 2 mmol) was added slowly to 25cm³ of pyridine / α -picoline / γ -picoline with constant stirring yielding dark solutions. The solution was filtered and filtrate was allowed to evaporated naturally for a month, leaving blackish green product.

The product was washed several times with ether containing traces of corresponding bases, suction filtered and air dried.

2.12. Preparation of Co(o-phen/bipy)(i-MNT)(β -pic)₂ (11, 12)

Co(o-phen)(i-MNT).2H₂O (0.8306g, 2mmol) and Co(bipy)(i-MNT).2H₂O (0.7826g, 2 mmol) was dissolved in 20cm³ of DMF followed by addition of β -picoline (β -pic) (10 cm³) with stirring. The solution was evaporated naturally and after 6 months a dark colour product was obtained, which was washed with ether several times yielding olive green/ blackish green powder respectively. The products were suction filtered and air dried.

III. Results and discussion

The analytical data indicate the formation of mixed ligand complexes of cobalt(II) of the compositions Co(N-N)₂(i-MNT), Co(N-N)(i-MNT).2H₂O and Co(N-N)(i-MNT)L₂ [N-N =1,10-phenanthroline (o-phen) or 2,2'-bipyridine (bipy); i-MNT²⁻ = 1,1-dicyanoethylene-2,2-dithiolate ; L = pyridine(py), α -picoline(α -pic), β -picoline(β -pic) or γ -picoline(γ -pic)].

The complexes do not decompose up to 200^oC and are insoluble in water and common organic solvents (methanol, ethanol, chloroform, carbon tetrachloride, acetone, benzene etc) but soluble in coordinating solvents such as DMF and DMSO. These complexes cannot be re-crystallized but TLC measurements confirm the purity of the complexes as only one spot was observed for each complex.

The weight loss experiments for the complexes were carried out by heating a small amount of sample in a glass tube for 4 hrs in an electric oven maintained at 100, 120, 150 and 180^oC. The complexes, Co(o-phen)(i-MNT).2H₂O and Co(bipy)(i-MNT).2H₂O show loss of weight in the temperature range 150-180^oC corresponding to two water molecules suggesting that they possess two water molecules in their coordination sphere.

3.1.Molar conductance

The low molar conductance values (15.5 - 27.0 ohm⁻¹cm²mole⁻¹) in DMF solution (10⁻³M) for complexes (2-7,11) indicate non-electrolytes while values (51.0-74.0 ohm⁻¹cm²mole⁻¹) for complexes (1,8-10,12) indicate (1:1) electrolytic nature [23].

3.2. Magnetic moment

Magnetic susceptibility measurements and the electronic spectra of complexes were recorded for ascertaining the stereochemistry around Co(II) ion in these mixed ligand complexes. The corrected magnetic moments of Cobalt(II) complexes with i-MNT²⁻ and heterocyclic nitrogen donors lie in the range 2.0 – 3.3 B.M. suggesting low-spin, Co(II) (t_{2g} e_g¹), distorted octahedral stereochemistry around the Co(II) ion in these complexes. The observed (μ_{eff}) value is higher than calculated by the spin only formula (μ_s) value. This suggests that there is also an orbital contribution.

3.3. Electronic spectra

In the electronic spectra of Co(II) complexes, there is a quartet ground state and three spin - allowed electronic transitions to the excited quartet states, ⁴T_{1g}(F) → ⁴T_{2g}(v₁), (generally occurs in the near i.r. region), ⁴T_{1g}(F) → ⁴A_{2g}(v₂) and ⁴T_{1g}(F) → ⁴T_{1g}(P) (v₃) are possible. The visible spectrum is dominated by highest energy transition ⁴T_{1g}(F) → ⁴T_{1g}(P). Usually the ⁴A_{2g} level is usually close to the ⁴T_{1g}(P) level, so transitions to these two levels are close in energy. Since the ⁴A_{2g} state is derived mainly from a t_{2g}³e_g⁴ electronic configuration and the ⁴T_{1g}(F) ground state is derived mainly from a t_{2g}⁵e_g² configuration, the ⁴T_{1g}(F) → ⁴A_{2g} transition is essentially a two-electron process and weaker than the other transitions. The electronic spectra of mixed ligand complexes of Co(II) have been discussed in the light of earlier studies [24, 25,26].

The electronic spectra of complexes in DMF solution show three bands in the ranges 10141-11111, 16611-16694 and 21186 – 238089 cm⁻¹ assignable to ⁴T_{1g}(F) → ⁴T_{2g}(v₁), ⁴T_{1g}(F) → ⁴A_{2g}(v₂) and ⁴T_{1g}(F) → ⁴T_{1g}(P) (v₃), respectively suggesting distorted octahedral stereochemistry around Co(II) in its complexes. The v₁ and v₂ bands are weak bands with respect to splitting of the third band reflects distortion in octahedral stereochemistry in these complexes. The v₁ and v₂ bands are of weak intensity with respect to v₃ band. The v₃ band in these complexes is not very distinct as obscured by the tail of the ligand absorption band.

The nujol-mull reflectance spectra of the complexes are not well resolved but most of the complexes show similar trends.

3.4. Infrared spectra

IR spectra of the mixed ligand complexes have been interpreted in the light of earlier investigations [1, 19, 27-32] on transition and non transition metal 1,1-dithiolates. The *i*-MNT²⁻ ligand may be described by the following resonating structures as shown in Fig. 1 in which Fig 1(a) be the dominant resonating form in all the newly synthesized complexes.

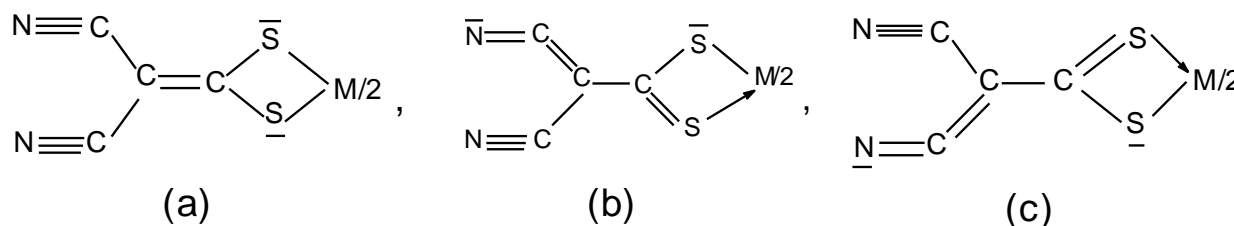


Fig. 1: Resonance forms of *i*-MNT²⁻ ligand ion.

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*-MNT²⁻ ring leads to the coupling of vibrational modes so that few bands in i.r. spectra represent pure vibrations. IR spectra display characteristic stretching frequencies associated with C≡N, C=C, C-S and M-S from complexes of *i*-MNT²⁻; aryl ring vibrations with metal heterocyclic nitrogen vibrations from *o*-phen, bipy, py, α -pic, β -pic and γ -pic.

The $\nu(\text{C}\equiv\text{N})$ band appearing at 2195cm^{-1} with a shoulder at 2200cm^{-1} in $\text{K}_2\text{i-MNT}\cdot\text{H}_2\text{O}$, is a sharp absorption band and is found in the range $2197\text{-}2204\text{cm}^{-1}$ in the mixed ligand complexes. The $\nu(\text{C}=\text{C})$ absorption in all the complexes appears in the range $1381\text{-}1425\text{cm}^{-1}$ observed in free $\text{K}_2\text{i-MNT}$ ligand at 1360cm^{-1} , implying delocalization of π -electron out of the C=C bond. In most of the complexes $\nu(\text{C}=\text{C})$ was splitted band (doublet or triplet) indicating lowering of symmetry. The positive shifts observed in stretching frequencies of C≡N and C=C support resonance form (a) (Fig.1) as dominant in these complexes. A band at 960cm^{-1} with a shoulder at 985cm^{-1} in the i.r. spectrum of $\text{K}_2\text{i-MNT}\cdot\text{H}_2\text{O}$ due to =CS₂ group is found in the range $939\text{-}967\text{cm}^{-1}$ in the complexes. The $\nu(\text{C-S})$ band occurring in the spectrum of $\text{K}_2\text{i-MNT}\cdot\text{H}_2\text{O}$ at 860cm^{-1} appears as a single band in the range $876\text{-}903\text{cm}^{-1}$ in the complexes indicating symmetrical bonding of both the sulphur atoms to metal ion. Similar bonding behaviour of *i*-MNT²⁻ ion is reported [28] in $\text{K}_2[\text{Ni}(\text{i-MNT})_2]$ where a single $\nu(\text{C-S})$ band is observed at 900cm^{-1} .

Mixed ligand complexes show heterocyclic in-plane and out-of-plane ring deformation bands in the ranges $604\text{-}632$ and $425\text{-}435\text{cm}^{-1}$, respectively indicating coordination through nitrogen atom as these bands show positive shifts with respect to the corresponding bands in the free form. Complexes, 3 and 4, show a broad bands in the region $3200\text{-}3500\text{cm}^{-1}$ which are due to $\nu(\text{O-H})$. The weight loss experiment shows weight loss corresponding to two water molecules in each complex, 3 and 4, above 180°C indicates the presence of coordinated water in these complexes. The $\nu(\text{C-H})$ (aromatic ring) arising from aromatic ligands in these complexes is observed as weak band(s) in the region $3000\text{-}3100\text{cm}^{-1}$. The $\nu(\text{C-H})$ (aliphatic) for complexes containing α -pic, β -pic or γ -pic is observed as very weak intensity bands in the region $2820\text{-}2950\text{cm}^{-1}$ suggesting their presence in the mixed ligand complexes.

The non-ligand bands observed in the ranges $330\text{-}430$ and $255\text{-}330\text{cm}^{-1}$ in the complexes are tentatively assigned to $\nu(\text{M-N})$ [30] and $\nu(\text{M-S})$ [33] modes respectively.

Based on stoichiometries and above mentioned studies distorted octahedral stereochemistry around the cobalt(II) ion for these complexes have been proposed.

IV. Reactivity of the complexes

The reactions of heterocyclic nitrogen donors (py, α -pic, β -pic or γ -pic) with $\text{Co}(\textit{o}$ -phen/bipy)(*i*-MNT) $\cdot 2\text{H}_2\text{O}$ were studied separately under different conditions then they yielded addition products of the composition $\text{Co}(\textit{o}$ -phen/bipy)(*i*-MNT)L₂ [L = pyridine (py), α -picoline (α -pic), β -picoline (β -pic) or γ -picoline (γ -pic)] approving the Lewis acid character of the mixed ligand complexes.

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Table 1. Analytical data, molar conductance and magnetic moments for the mixed ligand complexes of Co(II) ion.

Complex (colour)	% yield (Dec. Temp. °C)	Found (Calcd.),%					Λ_M ($\Omega^{-1}\text{cm}^2$ mol^{-1} (DMF))	μ_{eff} (B.M.)
		Co	S	N	C	H		
Co(o-phen) ₂ (i-MNT) (1) (Olive green)	(270) 72	10.19 (10.53)	11.41 (11.45)	14.83 (15.01)	59.82 (60.10)	2.32 (2.88)	51.00	3.30
Co(bipy) ₂ (i-MNT) (2) (Greenish yellow)	70 (220)	10.97 (11.52)	12.44 (12.53)	15.92 (16.43)	55.84 (56.36)	3.02 (3.15)	27.00	2.80
Co(o-phen)(i-MNT).2H ₂ O (3) (Olive green)	65 (269)	15.53 (14.18)	16.30 (16.87)	12.99 (13.48)	45.92 (46.26)	2.62 (2.91)	23.00	2.90
Co(bipy)(i-MNT).2H ₂ O (4) (Olive green)	68 (225)	15.72 (15.05)	17.02 (16.38)	14.31 (17.02)	42.43 (42.96)	2.89 (3.09)	19.00	2.95
Co(o-phen)(i-MNT)(py) ₂ (5) (Black)	72 (240)	10.36 (10.96)	11.90 (11.92)	15.21 (15.63)	57.85 (58.09)	3.12 (3.37)	15.50	3.25
Co(o-phen)(i-MNT)(α -pic) ₂ (6) (Blackish brown)	77 (242)	10.61 (10.41)	10.90 (11.33)	14.32 (14.85)	58.97 (59.46)	3.45 (3.92)	25.00	3.00
Co(o-phen)(i-MNT)(γ -pic) ₂ (7) (Blackish brown)	71 (220)	10.19 (10.41)	11.20 (11.35)	14.62 (14.85)	59.12 (59.46)	3.79 (3.92)	20.00	2.00
Co(bipy)(i-MNT)(py) ₂ (8) (Blackish green)	65 (220)	10.99 (11.47)	12.02 (12.48)	16.02 (16.36)	55.87 (56.13)	3.13 (3.53)	54.00	2.95
Co(bipy)(i-MNT)(α -pic) ₂ (9) (Blackish green)	67 (170)	10.52 (10.88)	11.60 (11.84)	15.10 (15.51)	57.23 (57.66)	3.97 (4.09)	61.00	2.90
Co(bipy)(i-MNT)(γ -pic) ₂ (10) (Blackish green)	70 (214)	10.48 (10.88)	11.37 (11.84)	15.23 (15.51)	57.35 (57.66)	3.87 (4.09)	74.00	3.30
Co(o-phen)(i-MNT)(β -pic) ₂ (11) (Olive green)	70 (230)	10.22 (10.41)	11.00 (11.33)	14.63 (14.85)	59.01 (59.46)	3.58 (3.92)	22.00	3.00
Co(bipy)(i-MNT)(β -pic) ₂ (12) (Blackish green)	72 (190)	10.42 (10.88)	11.36 (11.84)	15.33 (15.51)	57.08 (57.66)	3.92 (4.09)	60.00	2.92

Table 2. UV-Vis data for the mixed ligand Complexes of Co(II) ion in DMF solution

Complexes	λ_{max} (nm), ϵ (L mol ⁻¹ cm ⁻¹)			Ligand bands
	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
Co(<i>o</i> -phen) ₂ (i-MNT) (1)	986 (20)	601 (203)	436(1000)	404(1966)
Co(bipy) ₂ (i-MNT) (2)	-	599 (209)	460(98)	403(1970)
Co(<i>o</i> -phen)(i-MNT).2H ₂ O (3)	-	600 (199)	430(1800)	365(1120), 302(1820)
Co(<i>bipy</i>)(i-MNT).2H ₂ O (4)	-	599 (207)	465(900)	398(1890)
Co(<i>o</i> -phen)(i-MNT)(py) ₂ (5)	900 (53)	601 (120)	466(625), 436(1000)	395(1808)
Co(<i>o</i> -phen)(i-MNT)(α -pic) ₂ (6)	-	600 (259)	459(1344)	404(1970)
Co(<i>o</i> -phen)(i-MNT)(γ -pic) ₂ (7)	-	600 (190)	470(900)	396(1996)
Co(<i>bipy</i>)(i-MNT) (py) ₂ (8)	903 (23)	600 (159)	472(640)	409 (1187)
Co(<i>bipy</i>)(i-MNT)(α -pic) ₂ (9)	900 (12)	602 (178)	460(702)	415(1129)
Co(<i>bipy</i>)(i-MNT)(γ -pic) ₂ (10)	902 (17)	-	420(750)	397(1700)
Co(<i>o</i> -phen)(i-MNT)(β -pic) ₂ (11)	-	601(175)	432(820)	395(1700)
Co(<i>bipy</i>)(i-MNT)(β -pic) ₂ (12)	900(16)	-	445(725)	396(1685)

Table 3. Characteristic i.r bands (cm⁻¹) for the mixed ligand complexes of Co(II) ion

Complexes	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(=\text{CS}_2)$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{S})$
Co(<i>o</i> -phen) ₂ (i-MNT) (1)	2197vs	1408vs	944w	897s	430w	255w
Co(bipy) ₂ (i-MNT) (2)	2201vs	1402s, 1384s	941m	897s	425m	265w
Co(<i>o</i> -phen)(i-MNT).2H ₂ O (3)	2199vs	1382vs	962w	898m	428m	330w
Co(<i>bipy</i>)(i-MNT).2H ₂ O (4)	2202s	1405vs, 1383vs	943m	899m	385m	328w
Co(<i>o</i> -phen)(i-MNT)(py) ₂ (5)	2199vs	1402vs, 1382vs	940m	896m	350m	260w
Co(<i>o</i> -phen)(i-MNT)(α -pic) ₂ (6)	2199vs	1402vs, 1381vs	939m	895m	330w	272w
Co(<i>o</i> -phen)(i-MNT)(γ -pic) ₂ (7)	2200vs	1426s	939m	876m,	335w	274w
Co(<i>bipy</i>)(i-MNT) (py) ₂ (8)	2196vs	1384vs	956s	903s	365m	283w
Co(<i>bipy</i>)(i-MNT)(α -pic) ₂ (9)	2203vs	1394vs	950m	903s	380w	287w
Co(<i>bipy</i>)(i-MNT)(γ -pic) ₂ (10)	2196vs	1387vs	967w	896s	375w	292w
Co(<i>o</i> -phen)(i-MNT)(β -pic) ₂ (11)	2200vs	1384vs	939m	897s	340w	302w
Co(<i>bipy</i>)(i-MNT)(β -pic) ₂ (12)	2204vs	1384vs	944m	896s	376w	304w

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