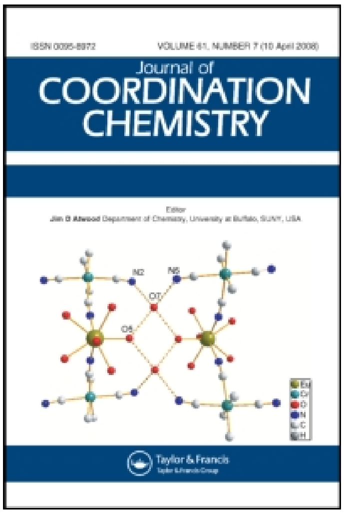

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Synthesis and characterization of mixed ligand complexes of cobalt(II) with some nitrogen and sulfur donors

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Synthesis and characterization of mixed ligand complexes of cobalt(II) with some nitrogen and sulfur donors

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Mixed ligand complexes of Co(II) with nitrogen and sulfur donors, $Co(OPD)(S–S) \cdot 2H_2O$ and $Co(OPD)(S–S)L_2$ [OPD = *o*-phenylenediamine; S–S = 1,1-dicyanoethylene-2,2-dithiolate (i-MNT^{2-}) or 1-cyano-1-carboethoxyethylene-2,2-dithiolate (CED^{2-}); L = pyridine (py), α-picoline (α-pic), β-picoline (β-pic), or γ-picoline (γ-pic)], have been isolated and characterized by analytical data, molar conductance, magnetic susceptibility, electronic, and infrared spectral studies. The molar conductance data reveal non-electrolytes in DMF. Magnetic moment values suggest low-spin and high-spin complexes. The electronic spectral studies suggest distorted octahedral stereochemistry around Co(II) in these complexes. Infrared spectral studies suggest bidentate chelating behavior of i-MNT^{2-}, CED^{2-}, or OPD while other ligands are unidentate in their complexes.

Keywords: Cobalt(II); 1,1-Dithiolates; Nitrogen donors; Mixed ligand complexes

1. Introduction

Coordination chemistry of transition as well as non-transition metal dithiolates has been an area of interest [1, 2]. Recently, the role of dithio ligands has been explored in the design of electrically conducting molecular solids [3–6]. Interest in dithiolates stems from the stabilization of transition metal ions in unusual oxidation states, facile redox behavior, stabilization of square planar geometry around transition metal ions, and interesting spectral and magnetic properties. In addition, metal dithiolates have a large number of industrial and biological applications [2, 7].

1,1-Dithioligands, 1,1-dicyanoethylene-2,2-dithiolate, and 1-cyano-1-carboethoxyethylene-2,2-dithiolate show chelating and bridging behaviors which have been found in binary, ternary, and heterobimetallic complexes [2, 8–10]. Our manuscripts [11–15] include the studies on mixed ligand complexes of Ni(II), Cu(II), Zn(II), and Cd(II) with nitrogen donors and 1,1-dithiolates.

There is no report on mixed ligand complexes of cobalt(II) with 1,1-dithiolate ions and nitrogen donors except the mixed ligand complexes of cobalt involving 1,1- and

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1,2-dithiolate reported by McCleverty *et al.* [16]. Thus, we undertake the synthesis and characterization of complexes of cobalt(II) with some 1,1-dithiolate[1,1-dicyanoethylene-2,2-dithiolate (i-MNT^{2-}) or 1-cyano-1-carboethoxyethylene-2,2-dithiolate (CED^{2-})] and a nitrogen donor *o*-phenylenediamine, OPD, and investigate their reactivity toward heterocyclic nitrogen donors [pyridine (py), α-picoline (α-pic), β-picoline (β-pic), or γ-picoline (γ-pic)]. The results are reported in this article.

2. Experimental

2.1. *Materials*

All 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. K_2i-MNT $\cdot$ H_2O and K_2CED $\cdot$ H_2O were prepared by a known literature procedure [17].

2.2. *Analysis of the complexes*

The complexes were analyzed for cobalt using standard literature procedures [18]. Carbon, hydrogen, and nitrogen were determined microanalytically on CE 440 Exeter, USA, and sulfur was estimated as $BaSO_4$ 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.

2.3. *Physical measurements*

The molar conductances of millimolar solutions of the complexes in DMF were measured using a Systronics direct reading conductivity meter 304 with a dip-type cell with platinized electrodes. Magnetic susceptibility measurements were made at room temperature on a vibrating sample magnetometer. Experimental magnetic susceptibility values have been corrected for diamagnetism by the procedures given by Figgis and Lewis [19] and Earnshaw [20]. Infrared spectra were recorded in nujol (4000–200 cm^{-1}) and in KBr pellets (4000–400 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 1100–200 nm on a Perkin–Elmer Model Lamda–25 UV–Vis spectrophotometer as nujol mulls and on a Chemito DU 2600 double beam UV–Vis spectrophotometer in DMF. Analytical data, colors, magnetic moments, and molar conductances are presented in table 1. Important electronic and infrared spectral data are given in tables 2 and 3, respectively.

2.4. *Preparation of Co(OPD)(i-MNT)$\cdot$2H_2O (1)*

A 50 cm^3 methanolic solution of *o*-phenylenediamine (1.08 g, 10 mmol) was added with stirring to a 50 cm^3 aqueous solution containing hydrated cobalt(II) nitrate (2.91 g, 10 mmol) resulting in a dark solution. To this solution, a 50 cm^3 aqueous

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

Complex (color)	% Yield (dec. temp. °C)	Found (calcd) %					Λ_M (Ω^{-1} cm^2 mol^{-1}) (DMF)	μ_{eff} (B.M.)
		Co	S	N	C	H		
Co(OPD)(i-MNT) · $2H_2O$ (**1**)	75	16.68	18.19	16.10	34.54	3.21	34.00	3.38
(Black)	(>280)	(17.16)	(18.68)	(16.32)	(34.93)	(3.52)		
Co(OPD)(i-MNT)$(py)_2$ (**2**)	60	12.14	13.20	17.80	51.32	3.63	26.00	2.12
(Black)	(>280)	(12.66)	(13.77)	(18.05)	(51.60)	(3.89)		
Co(OPD)(i-MNT)$(\alpha\text{-pic})_2$ (**3**)	50	12.34	13.40	16.90	53.10	4.41	20.00	2.53
(Black)	(>280)	(11.94)	(12.99)	(17.02)	(53.54)	(4.49)		
Co(OPD)(i-MNT)$(\beta\text{-pic})_2$ (**4**)	65	11.75	12.52	16.82	53.23	4.23	28.00	4.34
(Black)	(>280)	(11.94)	(12.99)	(17.02)	(53.54)	(4.49)		
Co(OPD)(i-MNT)$(\gamma\text{-pic})_2$ (**5**)	55	11.57	13.10	16.85	53.10	4.20	25.00	1.82
(Black)	(>280)	(11.94)	(12.99)	(17.02)	(53.54)	(4.49)		
Co(OPD)(CED) · $2H_2O$ (**6**)	80	14.70	15.70	10.60	36.40	2.52	26.00	2.80
(Black)	(>280)	(15.09)	(16.42)	(10.76)	(36.92)	(2.32)		
Co(OPD)(CED)$(py)_2$ (**7**)	75	10.94	12.12	14.00	51.11	4.23	23.00	2.21
(Black)	(>280)	(11.49)	(12.51)	(13.66)	(51.55)	(4.52)		
Co(OPD)(CED)$(\alpha\text{-pic})_2$ (**8**)	60	11.00	11.48	12.65	52.90	4.82	28.00	4.41
(Black)	(>280)	(10.90)	(11.86)	(12.95)	(53.32)	(5.03)		
Co(OPD)(CED)$(\beta\text{-pic})_2$ (**9**)	70	10.43	11.73	12.67	53.20	4.90	26.00	4.30
(Black)	(>280)	(10.90)	(11.86)	(12.95)	(53.32)	(5.03)		
Co(OPD)(CED)$(\gamma\text{-pic})_2$ (**10**)	65	10.40	11.60	12.72	52.95	4.80	25.00	4.97
(Black)	(>280)	(10.90)	(11.86)	(12.95)	(53.32)	(5.03)		

Table 2. UV–Vis data for complexes of Co(II) in DMF.

	$\lambda_{\max}$ (nm), ε(L mol^{-1} cm^{-1})			
Complexes	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$	${}^4T_{1g}(F) \rightarrow {}^4T^{1g}(P)$	
1	931 (191)	806 (796)	633(1112), 575(1080)	359(31), 300(513)
2	930 (192)	806 (511)	632(1125), 574(1083)	354(153), 296(507)
3	928 (617)	806 (774)	636(1120), 581(1085)	363(272), 296(507)
4	933 (364)	809 (452)	644(573), 575(574)	360(221), 300(409)
5	928 (664)	815 (741)	638(884), 573(862)	362(350), 297(269)
6	928 (464)	811 (561)	630(612), 575(605)	363(360), 300(503)
7	933 (533)	820 (630)	636(896), 578(887)	365(368), 296(661)
8	933 (473)	809 (661)	624(929), 570(913)	365(37), 296(381)
9	931 (381)	811 (635)	629(930), 576(910)	367(52), 300(400)
10	933 (548)	805 (672)	625(944), 572(924)	361(44), 296(425)

solution of K_2i-MNT · H_2O (2.36 g, 10 mmol) was added with stirring giving greenish yellow precipitate, changing to olive green and finally to moss green on stirring. The precipitate was suction filtered, washed with water, alcohol, ether and dried *in vacuo* over fused $CaCl_2$. After drying, the color of the product was black.

Attempts were made to synthesize Co(OPD)$_x$(i-MNT) [$x = 2$ or 3] by taking Co(II) salt, OPD, and K_2i-MNT · H_2O in 1 : 2 : 1 or 1 : 3 : 1 molar ratios, respectively, under the same conditions, but only one product, Co(OPD)(i-MNT) · $2H_2O$, was obtained.

2.5. *Preparation of Co(OPD)(i-MNT)(py)$_2$ (2)*

Co(OPD)(i-MNT) · $2H_2O$ (0.68 g, 2 mmol) was added to 15 cm^3 of pyridine slowly with vigorous shaking resulting in a dark solution. The solution was filtered giving no precipitate and evaporated naturally for 1 month, leaving a microcrystalline black product, which was washed with ether several times, suction filtered and air dried.

2.6. *Preparation of Co(OPD)(i-MNT)(α-pic)$_2$ (3)*

Co(OPD)(i-MNT) · $2H_2O$ (0.68 g, 2 mmol) was dissolved in 10 cm^3 of DMF followed by addition of α-picoline (10 cm^3) with stirring; the solution was evaporated naturally and after 1 month a black product was obtained, which was washed with ether several times yielding a black powder which was suction filtered and air dried.

2.7. *Preparation of Co(OPD)(i-MNT)(β-pic/γ-pic)$_2$ (4,5)*

The black complexes, Co(OPD)(i-MNT)(β-pic)$_2$ and Co(OPD)(i-MNT)(γ-pic)$_2$, were obtained essentially by the same method used for the synthesis of Co(OPD)(i-MNT)(α-pic)$_2$, only by replacing α-picoline by β-picoline and γ-picoline, respectively.

2.8. *Preparation of Co(OPD)(CED) • 2H$_2$O (6)*

o-Phenylenediamine (3.24 g, 30 mmol) in MeOH (50 cm^3) was added with stirring to a 50 cm^3 aqueous solution containing hydrated cobalt(II) nitrate (2.91 g, 10 mmol)

Table 3. Characteristic IR bands (cm^{-1}) for the complexes of Co(II).

Complexes	ν(O–H) + ν(N–H)/ν(N–H)	ν(C≡N)	ν(C=O)	ν(C=C)	ν(=CS_2)	ν(C–S)	ν(M–N)	ν(M–S)
1	3432 br, 3252 br	2202 vs	–	1363 vs	1151 m, 1029 w, 950 m	903 s	425 m	320 w
2	3429 br, 3325 br	2200 vs	–	1406 vs, 1384 vs, 1346 vs	1148 m, 1067 m, 1012 m, 944 m	899 s	375 m	270 w
3	3491 br, 3283 br	2204 s	–	1383 vs	1149 m, 1097 m	903 m	370 m	280 w
4	3474 br, 3204 br	2203 s	–	1385 vs	1147 s, 1101 s, 947 w	901 m	388 m	300 w
5	3479 br, 3346 br	2199 vs	–	1385 vs	1153 m, 1099 m	901 m	356 m	310 w
6	3449 br, 3248 br	2190 vs	1641 s	1376 vs	1172 s, 1149 s, 1092 m, 1025 m	934 m	420 w	330 w
7	3408 br, 3235 br	2187 vs	1656 s	1385 vs	1169 m, 1144 m, 1092 m, 1067 w, 1026 m	930 m, 914 m	365 w	315 w
8	3439 br, 3292 br	2193 s	1653 vs	1400 vs	1145 s, 1097 s, 1026 s	935 m	378 m	310 w
9	3383 br, 3332 br	2191 s	1655 vs	1389 vs	1143 s, 1097 s, 1028 s	931 m	320 w	280 w
10	3447 br, 3342 br	2191 s	1661 vs	1387 vs	1170 m, 1147 m, 1093 m, 1028 m	931 m	365 w	260 w

br = broad, vs = very strong, s = strong, m = medium, w = weak.

resulting in a dark violet solution. To this solution, a 50 cm^3 aqueous solution of $K_2CED \cdot H_2O$ (2.83 g, 10 mmol) was added with stirring, giving dark olive green precipitate. The precipitate was suction filtered, washed with water, MeOH, ether, and dried *in vacuo* over fused $CaCl_2$. The color of the precipitate became black after drying.

2.9. *Preparation of Co(OPD)(CED)(py)$_2$ (7)*

Co(OPD)(CED) $\cdot$ $2H_2O$ (0.78 g, 2 mmol) was added to 25 cm^3 of pyridine slowly with vigorous shaking resulting in a blackish solution. The solution was filtered yielding no precipitate and evaporated naturally for 1 month leaving a sticky black product, which was washed with ether several times, making it a black powder. Finally, it was suction filtered and air dried.

2.10. *Preparation of Co(OPD)(CED)(α-pic)$_2$ (8)*

Co(OPD)(CED) $\cdot$ $2H_2O$ (0.78 g, 2 mmol) was dissolved in 10 cm^3 of DMF followed by addition of α-picoline (5 cm^3) with stirring, which did not yield product. The solution was evaporated naturally, and after 1 month a black product was obtained which was washed with ether several times, resulting in a black powder. Finally, it was suction filtered and air dried.

2.11. *Preparation of Co(OPD)(CED)(β-pic/γ-pic)$_2$ (9, 10)*

The black complexes, Co(OPD)(CED)(β-pic)$_2$ and Co(OPD)(CED)(γ-pic)$_2$, were obtained essentially by the same method used for the synthesis of Co(OPD)(CED)(α-pic)$_2$, only by replacing α-picoline by β-picoline, and γ-picoline, respectively.

3. Results and discussion

The analytical data indicate formation of mixed ligand complexes of cobalt(II), Co(S–S)(N–N) $\cdot$ $2H_2O$, and [Co(S–S)(N–N)L_2] [S–S = 1,1-dicyanoethylene-2,2-dithiolate (i-MNT^{2-}) or 1-cyano-1-carboethoxyethylene-2,2-dithiolate (CED^{2-}); N–N = *o*-phenylenediamine (OPD); L = pyridine (py), α-picoline (α-pic), β-picoline (β-pic), and/or γ-picoline (γ-pic)]. The complexes do not decompose up to 280°C, and are insoluble in water and common organic solvents (methanol, ethanol, chloroform, carbon tetrachloride, acetone, benzene, etc.), but soluble in strong coordinating solvents such as DMF and DMSO. These complexes cannot be recrystallized, 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 h in an electric oven maintained at 100, 120, 150, and 180°C. Only Co(OPD)(i-MNT) $\cdot$ $2H_2O$ and Co(OPD)(CED) $\cdot$ $2H_2O$ show weight loss from 150 to 180°C corresponding to two coordinated water molecules.

3.1. *Molar conductance*

The low molar conductance values (20.0–34.0 ohm^{-1} cm^2 mole^{-1}) in DMF solution (10^{-3} M) indicate non-electrolytes [21].

3.2. *Magnetic moment*

The magnetic susceptibility measurements and electronic spectra of complexes were obtained to indicate stereochemistry around the Co(II). The corrected magnetic moments of complexes with i-MNT^{2-} and nitrogen donors lie in the range 1.82–4.34 B.M. suggesting low-spin and high-spin octahedral stereochemistry. The observed (μ_{eff}) value is higher than calculated by the spin only formula (μ_s) value, suggesting an orbital contribution. Complexes **2**, **3**, and **5** with magnetic moments from 1.82 to 2.53 B.M. suggest low-spin Co(II) ($t_{2g}^6e_g^1$). Complex **1** shows μ_{eff} of 3.38 B.M. which is slightly higher than the low-spin and slightly lower than the high-spin Co(II) complex, suggesting low-spin and high-spin equilibrium in this complex. Complex **4** shows normal magnetic moment for high-spin Co(II) octahedral complexes.

The magnetic moments of Co(II) complexes with CED and nitrogen donors lie in the range 2.21–4.97 B.M. Complexes **6** and **7** show μ_{eff} values 2.80 and 2.21 B.M., respectively, suggesting low-spin Co(II) while **8**–**10** show magnetic moment values 4.41, 4.30, and 4.97 B.M., respectively, suggesting high-spin Co(II) ($t_{2g}^5e_g^2$).

The oxidation of Co(II) to Co(III) [22] lead to lowering the magnetic moments. However, this possibility can be excluded since the magnetic moment of the complexes remain unchanged on exposure to air for different periods of time.

3.3. *Electronic spectra*

In electronic spectra of Co(II) high-spin octahedral complexes, there is a quartet ground state and three possible spin-allowed electronic transitions to the excited quartet states, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1) (generally occurs in the near IR region), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) [23, 24]; the visible spectrum is dominated by ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. Usually the ${}^4A_{2g}$ level is 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 $t_{2g}^3e_g^4$ electronic configuration and the ${}^4T_{1g}(F)$ ground state is derived mainly from a $t_{2g}^5e_g^2$ configuration, the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition is essentially a two-electron process and weaker than the other transitions.

The electronic spectra of complexes in DMF show three well-resolved bands in the ranges 10,718–10,776, 12,195–12,422, and a split band 15,528–16,025 and 17,301–17,544 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(\nu_1)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$, and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively, suggesting octahedral stereochemistry around Co(II). The splitting of the third band reflects distortion in octahedral stereochemistry. The ν_1 and ν_2 bands are of weak intensity with respect to the third one.

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 complexes have been interpreted in the light of earlier investigations [1, 17, 25–30] on transition and non-transition metal 1,1-dithiolates. The i-MNT^{2-} and

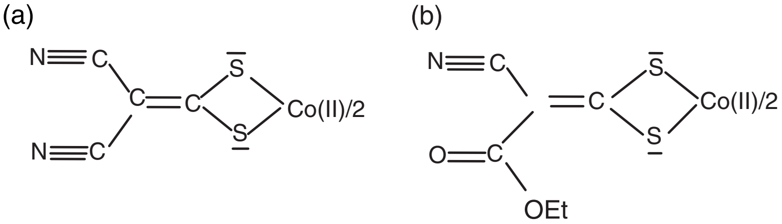

Figure 1. Dominant resonance forms of (a) i-MNT^{2-} and (b) CED^{2-} complexes.

CED^{2-} ligand ions may be described by resonating structures in their complexes as shown in figure 1.

The electron delocalization in the chelated i-MNT^{2-} and CED^{2-} rings leads to coupling of vibrational modes so that few bands represent pure vibrations. IR spectra display characteristic stretching frequencies associated with C≡N, C=C, C–S, and M–S from complexes of i-MNT^{2-}; C≡N, C=O, $>C{=}CS_2$, C–S, and M–S from complexes of CED^{2-}; aryl ring vibrations with metal heterocyclic nitrogen vibrations from py, α-pic, β-pic, and γ-pic and amine vibrations with metal-amine nitrogen vibrations from OPD.

The ν(C≡N) at 2195 cm^{-1} with a shoulder at 2200 cm^{-1} in K_2i-MNT · H_2O is a sharp absorption in the range 2199–2204 cm^{-1} in the complexes. The ν(C=C) absorption in all the complexes appears in the range 1363–1385 cm^{-1}, observed in free K_2i-MNT at 1360 cm^{-1}, implying delocalization of π-electron out of the C=C bond. The positive shifts observed in stretching frequencies of C≡N and C=C support resonance form (a) (figure 1) as dominant in complexes of i-MNT^{2-}. A band at 960 cm^{-1} with a shoulder at 985 cm^{-1} in the IR spectrum of K_2i-MNT · H_2O due to $=CS_2$ group is found in the range 944–1099 cm^{-1} in the complexes. The ν(C–S) band of K_2i-MNT · H_2O at 860 cm^{-1} appears as a single band in the range 899–903 cm^{-1} in the complexes, indicating symmetrical bonding of both the sulfurs. Similar bonding behavior of i-MNT^{2-} ion is reported [26] in $K_2[Ni(i\text{-}MNT)_2]$ where a single ν(C–S) band is observed at 900 cm^{-1}.

The ν(C≡N) band at 2190 cm^{-1} in K_2CED · H_2O is observed from 2187 to 2193 cm^{-1} in complexes suggesting non-involvement of nitrile in bonding. Compounds containing unconjugated and conjugated (with acetyl or benzoyl group) ester show ν(C=O) bands in 1720–1750 and 1620–1630 cm^{-1} regions, respectively. The ν(C=O) stretching band of the ester in these compounds is a strong band from 1622 to 1654 cm^{-1}, lowered more than usual by α,β-unsaturation, and indicative of delocalization of the C=O. The ν(C=O) (1641–1661 cm^{-1}) in the same region as observed for K_2CED · H_2O suggests that the carbonyl oxygen is not involved in bonding. The complexes exhibit three strong to very strong bands in the region 1376–1400, 1025–1028, and 930–935 cm^{-1} assignable to $\nu_1[\nu(C{=}C)]$, $\nu_4[\nu_{as}(=CS_2)]$, and $\nu_2[\nu_s(=CS_2)]$ vibrations of $C{=}CS_2$ structure which were found in K_2CED · H_2O at 1320, 1020, and 930 cm^{-1}, respectively [10, 17]. In some complexes ν(C=C) was split (doublet or triplet) indicating lowering of symmetry. The positive shifts in ν(C≡N) and ν(C=C) bands suggest that resonance form (b) (figure 1) is dominant in the 1-cyano-1-carboethoxyethylene-2,2-dithiolate complexes. The occurrence of a single weak to strong band in the region 930–935 cm^{-1} for ν(C–S) in these complexes indicates symmetrical bonding of both the sulfurs [31].

Complexes containing heterocyclic nitrogen donors show in-plane and out-of-plane ring deformation bands in the ranges 606–635 cm^{-1} and 420–435 cm^{-1}, respectively,

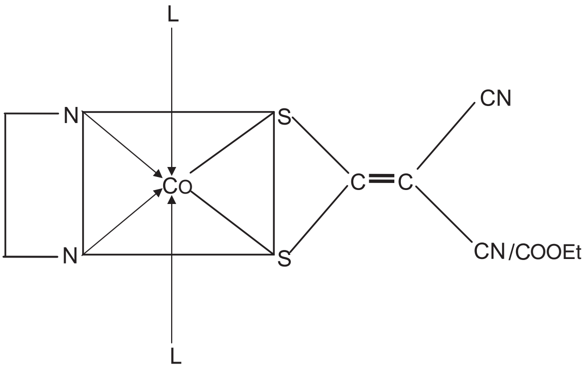

Figure 2. [Co(N–N)(S–S)L_2] [N–N = *o*-phenylenediamine (OPD), S–S = $(CN)_2C{=}CS_2^{2-}$ (i-MNT^{2-}) or (CN)(COOEt)$C{=}CS_2^{2-}$ (CED^{2-}), L = H_2O, py, α-pic, β-pic, or γ-pic].

indicating coordination through nitrogen as these bands show positive shifts with respect to the corresponding bands in the free form. Complexes **1** and **6** show a group of broad bands in the region 3000–3600 cm^{-1} which are due to combined ν(O–H) and ν(N–H). The dehydrated complexes **1** and **6** at 200°C, and all other complexes, exhibit a group of broad bands in the range 3204–3491 cm^{-1} attributed to ν(N–H) (asymmetric and symmetric) stretching modes from *o*-phenylenediamine. The ν(N–H) bending (scissoring) vibration mode is observed at 1570–1653 cm^{-1} in the complexes, overlapping with ν(C=O). The ν(C–N) bending mode observed in OPD at 1272 cm^{-1} is observed in the complexes from 1216 to 1283 cm^{-1}. A strong absorption at 751 cm^{-1} in the spectrum of OPD attributable to out of plane ....C–H ring (aromatic) bending mode, characteristic of 1,2-disubstituted benzene, is observed at 754–764 cm^{-1}. The ν(C–H) (aromatic ring) arising from aromatic ligands is observed as weak band(s) in the region 3000–3100 cm^{-1}. The ν(C–H) (aliphatic) for complexes containing α-pic, β-pic, γ-pic, and/or CED^{2-} is very weak bands in the region 2830–2980 cm^{-1}.

Non-ligand bands observed in the ranges 320–425 cm^{-1} and 260–320 cm^{-1} in the complexes are tentatively assigned to ν(M–N) [28] and ν(M–S) [32] modes, respectively.

Based on stoichiometries and above-mentioned studies, distorted octahedral stereochemistry around Co(II) have been proposed as shown in figure 2.

3.5. *Reactivity of the complexes*

The reactions of heterocyclic nitrogen donors (py, α-pic, β-pic, or γ-pic) with Co(OPD)(i-MNT) · $2H_2O$ and Co(OPD)(CED) · $2H_2O$ yielded addition products Co(OPD)(S–S)L_2 [S–S = i-MNT^{2-} or CED^{2-}; L = pyridine (py), α-picoline (α-pic), β-picoline (β-pic), or γ-picoline (γ-pic)] proving Lewis acid character of the mixed ligand complexes.

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