Asian Journal of Chemistry; Vol. 35, No. 4 (2023), 910-916

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2023.27479

Mixed Ligand Complexes of Cobalt(II): Synthesis, Reactivity, Physico-Chemical and Spectroscopic Studies

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Received: 28 December 2022; *Accepted*: 17 February 2023; *Published online*: 30 March 2023; AJC-21189

The mixed ligand complexes of Co(II) metal ions with some heterocyclic nitrogen bases along with1-cyano-1-carboethoxyethylene-2,2-dithiolate ion (CED^{2-}) of the compositions, Co(N-N)(CED)·$2H_2O$ [N-N = *o*-phen/2,2′-bipy] and Co(N-N)(CED)L_2 [N-N = *o*-phen/2,2′-bipy, CED^{2-} = 1-cyano-1-carboethoxyethylene-2,2-dithiolate, L = γ-picoline (γ-pic), β-picoline (β-pic), α-picoline (α-pic), pyridine (py)] were characterized and isolated by analytical data as well as physico-chemical methods for example infrared spectroscopy, electronic, magnetic susceptibility, molar conductance. The complexes are soluble in coordinating solvents like DMSO and DMF and decompose below 250 ºC. The synthesized complexes in DMF solution are non-electrolytic as shown by their molar conductance data. The calculated magnetic moments suggest that the synthesised cobalt(II) compounds are paramagnetic and produce a low-spin environment for the Co(II) ion. Thermal studies reveal that Co(N-N) contains two coordinated water molecules (CED)·$2H_2O$. Electronic spectra of cobalt(II) complexes with mixed ligands in DMF solution are consistent with distorted octahedral stereochemistry. The IR studies indicates that the CED^{2-} ion exhibits bidentate chelating behaviour and that heterocyclic nitrogen donors coordinate to Co atoms (II). Reaction with heterocyclic nitrogen donors (γ-picoline, β-picoline, α-picoline, pyridine) signifying the ligand exchange reaction.

Keywords: 1,1-Dithiolates, Molar conductance, Mixed ligand complexes, Ligand exchange reaction.

INTRODUCTION

For many decades, researchers have been interested in the coordination chemistry of both non-transition and transition metal dithiolates [1-3]. This passion has shown itself in "biological inorganic chemistry" and the broader subject of new complex synthesis. The compounds formed by these ligand systems have found many applications *e.g.* as semiconductors, insulators, vulcanization accelerators, bacteriocides, phytocides, pesticides, herbicides, fungicides, UV stabilizers for nylon as well as polyethylene and, recently in the CdS or ZnS thin films's deposition by metal organic chemical vapour deposition [4-11]. The metal complexes of some S-containing compounds were also examined for their radioprotective effects [12]. Gallium complexes of dithiolate ligands have been studied for their anti-tumor activity and it has been found that doses ranging from 1-50 mg/kg *in vitro* in mice are efficacious [13]. Extensive research into 1,1-dithio ligand complexes and their applications to processes of commercial and biological importance has resulted in a large number of published patents [6,13]. In heterobimetallic, ternary, binary complexes [6,14-17], 1-cyano-1-carboethoxyethylene-2,2-dithiolate ion (CED^{2-}) displays intriguing coordination features due to its chelating and bridging behaviours.

According to the literature, Mecleverty *et al.* [18] synthesized a variety of cobalt mixed ligand complexes containing 1,1- and 1,2-dithiolates. Das *et al.* [19] also reported the mixed ligand Co(II) complexes *viz.* [Co(OPD)(CED)L_2], where OPD = *o*-phenylenediamine, L = γ-picoline, β-picoline, α-picoline, pyridine, H_2O] complexes are the only known mixed ligand complexes including CED^{2-} and nitrogen donors [20]. Nonetheless, no report is present on Co(II) mixed ligand complexes with aromatic diimine (such as 1,10-phenanthroline and 2,2′-bipyridine) and CED^{2-} in the literature. Therefore, it is interesting to assume the synthesis of cobalt(II) mixed ligand complexes with nitrogen donors such as aromatic heterocyclic diimine and CED^{2-} ion and their structural characterization by magnetic and spectroscopic methods.

EXPERIMENTAL

Aldrich Chemicals Company provided the α, β- and γ-picolines, while all other chemicals utilized in the research were procured from E. Merck.The method for preparing $K_2CED\cdot H_2O$ is well documented in the literature [21].

Characterization: Traditional methods from the literature [22] were used to evaluate the cobalt(II) complexes. Microanalytical determination of nitrogen, hydrogen and carbon were performed on CE 440 Exeter, USA and a $BaSO_4$ gravimetric estimate has been obtained for sulphur. The weight loss caused by heating the sample at 110-2000 ºC in oven for 4 h set between allowed us to calculate the number of water molecules present.

Physical measurements: A Systronics 304 direct conductivity instrument containing platinized electrodes and a dip-type cell was used to determine the molar conductance of the synthesized Co(II) complexes in the DMF solutions. The sample magnetometer used to assess the magnetic susceptibility at room temperature. As described by Figgis & Lewis [20] as well as Earnshaw [23], the diamagnetism correction approaches to the experimental magnetic susceptibility data was applied. Using a Bomem DA-8 FT-IR spectrophotometer equipped with KBr along with CsI lenses, infrared spectra of KBr pellets (4000-400 cm^{-1}) and nujol (4000-200 cm^{-1}) at two different wavelengths were obtained. The electronic spectra of the synthesized complexes were acquired in the region of 1100 to 200 nm using a Perkin-Elmer model Lamda-25 UV-Vis spectrophotometer in nujol nulls and a Chemito DU 2600 twin beam UV-Vis spectrophotometer in DMF.

Synthesis of Co(*o*-phen)(CED)$\cdot$2H$_2$O (1): A solution was prepared by adding ethanolic solution of 1,10-phenanthroline monohydrate (0.9912 g, 5 mM) to an ethanolic solution of $Co(NO_3)_2\cdot 6H_2O$ (1.4552 g, 5 mM) while stirring. The resulting solution was then added while being stirred with an aqueous solution of $K_2CED\cdot H_2O$ (1.4171 g, 5 mM), which results in the precipitate colour changed from green to yellow. The precipitate was filtered using suction filter and washed with ether, alcohol, water, then dried in a vacuum on fused $CaCl_2$. When completely dried, the product had a pale greenish yellow colour. Yield: 1.5310 g (66.2%).

Synthesis of Co(*o*-phen)$_2$(CED) (2): A pink solution was obtained by adding 1.9823 g of 1,10-phenanthroline monohydrate (10 mM) to 1.4552 g of cobalt nitrate dihydrate (5 mM) in 50 mL of ethanolic solution while stirring. Now, $K_2CED\cdot H_2O$ (50 mL aqueous solution, 1.4171 g, 5 mM) was added to the pink solution while being stirred, producing a dark yellow precipitate. The precipitate has been filtered through suction filter, washed with ether, alcohol, water and then dried in a vacuum on fused $CaCl_2$. Yield: 1.6240 g (53.5%).

Synthesis of Co(*o*-phen)(CED)(py)$_2$ (3): A dark-coloured solution was obtained by adding Co(*o*-phen)(CED)$\cdot 2H_2O$ (0.924 g, 2 mM) to 10 mL of pyridine while vigorously stirring. After the dark-coloured solution naturally evaporated, a black precipitate was formed. It was repeatedly washed with ether to obtain a dark-brown precipitate. Suction filtration and air drying were used on the precipitate. Yield: 0.962 g (82.3%).

Synthesis of Co(*o*-phen)(CED)(α-pic)$_2$ (4): While stirring, 0.924 g (2 mmol) of Co(*o*-phen)(CED)$\cdot 2H_2O$ (0.924 g, 2 mM) was added gradually to 10 mL of α-picoline, producing a black solution. The filtrate yielded black sticky mass after evaporation at room temperature, which was washed with ether till the precipitate became free from its sticky nature. The resulting brownish precipitate was filtered undeer suction and then finally air-dried. Yield: 0.335 g (27.3%).

Synthesis of Co(*o*-phen)(CED)(β-pic/γ-pic)$_2$ (5/6): Both Co(*o*-phen)(CED)(γ-pic)$_2$ (**6**) along with Co(*o*-phen)(CED)(β-pic)$_2$ (5) were synthesized in similar way as Co(*o*-phen)(CED)-(α-pic)$_2$, with the exception that α-picoline was substituted for γ-picoline and β-picoline in both cases. (**5**) Yield: 0.5585 g (45.6%) for Co(*o*-phen)(CED)(β-pic)$_2$ and (**6**) Yield: 1.1328 g (92.5%) for Co(*o*-phen)(CED)(γ-pic)$_2$.

Synthesis of Co(bipy)(CED)$\cdot$2H$_2$O (7): When $Co(NO_3)_2\cdot 6H_2O$ (1.4552 g, 5 mM) was added to 50 mL ethanolic solution of 2,2′-bipyridine (0.7809 g, 5 mM), the solution turned from pink to yellow. $K_2CED\cdot H_2O$ (50 mL aqueous solution, 1.4171 g, 5 mM) has been mixed to this mixture while stirring, resulting precipitate that became a dull yellow after 30 min of mixing. The precipitate has been vacuuming dried on fused $CaCl_2$ after being suction filtered, then washed with ether, alcohol followed by water. The precipitate dried to a pale greenish yellow colour. Yield: 1.451 g (66.2%).

Synthesis of Co(bipy)$_2$(CED) (8): The pink solution was turned into an orange colour when 25 mL of ethanolic solution of 2,2′-bipyridine (0.7809 g, 5 mM) was mixed to 50 mL of $Co(NO_3)_2\cdot 6H_2O$ (0.7276 g, 2.5 mM) while stirring. A brown colour precipitate was obtained after adding 25 mL aqueous solution of $K_2CED\cdot H_2O$ (0.7085 g, 2.5 mM) while mixing. The precipitate's colour become changed from brown to dull yellow when 75 mL of water was added gently. After being suction filtered, then washed in ether, alcohol, water and dried in a vacuum on fused $CaCl_2$. Yield: 0.615g (44.0%).

An attempt was made to synthesize Co(bipy)$_3$(CED) under similar experimental circumstances but Co(bipy)$_2$(CED)was the final product.

Synthesis of Co(bipy)(CED)(py)$_2$ (9): Co(bipy)(CED)$\cdot 2H_2O$ (1.090 g, 2.5 mM) was added to 10 mL of pyridine slowly while mixing, producing a dark-coloured solution. On naturally evaporating the solution, a dark precipitate was produced. After rinsing the black precipitate with ether until the washing filtrate was colourless. Yield: 0.7438 g (53.3%).

Synthesis of Co(bipy)(CED)(α-pic)$_2$ (10): Co(bipy)(CED) $\cdot 2H_2O$ (1.090 g, 2.5 mM) was added slowly to 20 mL of α-picoline for 0.5 h. The dark coloured filtrate yielded dark brown colour precipitate after natural evaporation. An dark brown precipitate had developed while using ether for washing the filtrate and then dried in air. Yield: 0.433 g (29.4%).

Synthesis of Co(bipy)(CED)(β-pic/γ-pic)$_2$ (11/12): The synthesis of Co(bipy)(CED)(γ-pic)$_2$ (**12**) as well as Co(bipy)-(CED)(β-pic)$_2$ (**11**) complexes followed the identical procedure as that of Co(bipy)(CED)(α-pic)$_2$with the exception that α-picoline was substituted with γ-picoline and β-picoline. Yield:

0.7024 g (48.0%) for Co(bipy)(CED)(β-pic)$_2$. Yield: 0.7124 g (48.6%) for Co(bipy)(CED)(γ-pic)$_2$.

RESULTS AND DISCUSSION

When Co(*o*-phen)(CED)·2H_2O (**1**) and Co(bipy)(CED)·2H_2O (**7**) were treated with monodentate heterocyclic nitrogen donors (γ-picoline, β-picoline, α-picoline, pyridine) under various experimental circumstances after that they yielded the product Co(N-N)(CED).L$_2$ [N-N = *o*-phen or bipy; L = γ-picoline, β-picoline, α-picoline, pyridine] indicating a ligand exchange process where the powerful heterocyclic nitrogen donors have been substituted for water molecules. The analytical data suggests that the successful synthesis of [Co(N-N)$_2$(CED)] as well as [Co(N-N)(CED)L$_2$] [N-N = *o*-phen/bipy, CED^{2-} = 1-cyano-1-carboethoxyethylene-2,2-dithiolate, L = H_2O, γ-picoline, β-picoline, α-picoline, pyridine] type mixed ligand complexes of cobalt(II) with sulphur and nitrogen donors.

Below 250 ºC, all the synthesized cobalt(II) complexes decompose and are sparingly soluble in polar solvents for example DMF along with DMSO, but insoluble common organic solvents (benzene, acetone, carbon tetrachloride, chloroform, ethanol, methanol, *etc.*) and water.

Weight loss experiment: Co(N-N)(CED)·2H_2O [N-N = *o*-phen or bipy] complexes were investigated for weight loss was heated for 4 h in an electric microwave set to 100, 120, 150 and 180 ºC. Weight loss between 150 and 180 ºC demonstrates the presence of two water molecules in the compounds [24].

Molar conductance: Molar conductance values in DMF solution for the synthesized cobalt(II) compounds containing mixed ligands (10^{-3} M) in the range of 29.0-54.0 ohm^{-1} cm^2 mol^{-1} indicating their non-electrolytic nature [25].

Magnetic moment: Several different chemical conformation can host cobalt(II), each with its own electronic structure and unique magnetic and spectral characteristics. The synthesized Co(II) mixed ligand complexes have substantially lower magnetic moment values than cobalt(II) high-spin octahedral complexes, in the range of 2.09 to 3.22 B.M., which is significantly less than high-spin octahedral complexes of cobalt(II). When a significant binding field is present, the ^2E state, which is derived from the ^2G state of free metal ion, may become ground state, resulting in a low spin octahedral complexes with a $t_{2g}^6e_g^1$ electronic configuration and one unpaired electron. Spin-only calculations suggest a lower (μ_s) value, but the measured μ_{eff} is higher. A significant orbital influence is always present and the efficient magnetic moments of these compounds are larger than μ_s, which happens due to the octahedral ground state's orbital angular momentum [26]. The values of magnetic moment are consistent with the presence of a low-spin Co(II) ion in the synthesized complexes (Table-1).

Electronic spectra: Cobalt(II) octahedral complexes with high spin have a ground state of ^4F, whereas those with low spin have ^2G ground state (II).The ground state of the electronic spectra of Co(II) high-spin octahedral complexes is a quartet, but the excited states can be achieved via three spin-allowed electronic transitions that can be assigned to different atomic orbitals $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1) (occurs generally in the near I.R. area),$^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2), $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3). Transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(\nu_3)$ has the greatest energy and so dominates the visible spectrum. Notably, the transitions in octahedral structures to the $^4A_{2g}$ level and the $^4T_{1g}(P)$ level are rather close together. The $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition is the weakest of the three because it involves only two electrons and both the $^4A_{2g}$

TABLE-1
ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC MOMENTS FOR THE MIXED LIGAND COMPLEXES OF Co(II) ION

Complex (Colour)	% Yield (Dec. temp., °C)	Elemental analysis (%): Found (calcd.)					Λ_M (Ω^{-1} cm^2 mol^{-1}) (DMF)	μ_{eff} (B.M.)
		Co	S	C	H	N		
Co(*o*-phen)(CED)·2H_2O (**1**)	70	12.34	13.18	46.85	3.62	9.00	29.00	2.84
(Greenish yellow)	(205)	(12.74)	(13.86)	(46.74)	(3.70)	(9.08)		
Co(*o*-phen)$_2$(CED) (**2**)	65	9.30	10.49	59.20	3.32	11.23	37.00	2.39
(Dull yellow)	(210)	(9.71)	(10.56)	(59.39)	(3.48)	(11.53)		
Co(*o*-phen)(CED)(py)$_2$ (**3**)	60	10.21	10.63	57.23	4.23	11.72	54.00	2.37
(Dark brown)	(198)	(10.08)	(10.96)	(57.52)	(3.96)	(11.97)		
Co(*o*-phen)(CED)(α-pic)$_2$ (**4**)	55	9.34	10.20	58.62	4.10	11.21	51.00	3.22
(Brown)	(220)	(9.61)	(10.46)	(58.81)	(4.33)	(11.42)		
Co(*o*-phen)(CED)(β-pic)$_2$ (**5**)	60	9.48	10.60	58.40	4.12	11.31	37.00	2.46
(Black)	(210)	(9.61)	(10.46)	(58.81)	(4.33)	(11.42)		
Co(*o*-phen)(CED)(γ-pic)$_2$ (**6**)	70	9.50	10.30	58.32	4.01	11.12	32.00	2.88
(Deep Brown)	(230)	(9.61)	(10.46)	(58.81)	(4.33)	(11.42)		
Co(bipy)(CED)·2H_2O (**7**)	80	13.36	14.34	44.10	3.73	9.21	31.00	2.71
(Greenish Yellow)	(210)	(13.44)	(14.61)	(43.83)	(3.90)	(9.58)		
Co(bipy)$_2$(CED) (**8**)	70	10.20	11.37	55.72	3.53	12.12	42.00	2.09
(Dull yellow)	(205)	(10.55)	(11.47)	(55.90)	(3.78)	(12.53)		
Co(bipy)(CED)(py)$_2$ (**9**)	65	10.30	11.30	55.42	3.92	12.01	45.00	2.78
(Black)	(230)	(10.51)	(11.43)	(55.70)	(4.13)	(12.48)		
Co(bipy)(CED)(α-pic)$_2$ (**10**)	60	9.90	10.53	56.97	4.40	11.53	35.00	2.46
(Brown)	(140)	(10.01)	(10.88)	(57.13)	(4.61)	(11.89)		
Co(bipy)(CED)(β-pic)$_2$ (**11**)	70	9.76	10.60	56.85	4.32	11.48	36.00	2.16
(Black)	(120)	(10.01)	(10.88)	(57.13)	(4.61)	(11.89)		
Co(bipy)(CED)(γ-pic)$_2$ (**12**)	65	9.97	10.40	56.92	4.34	12.61	53.00	2.78
(Brown)	(130)	(10.01)	(10.88)	(57.13)	(4.61)	(11.89)		

state and the $^4T_{1g}$(F) ground state originate mostly from $t_{2g}^3e_g^4$ electronic configurations.

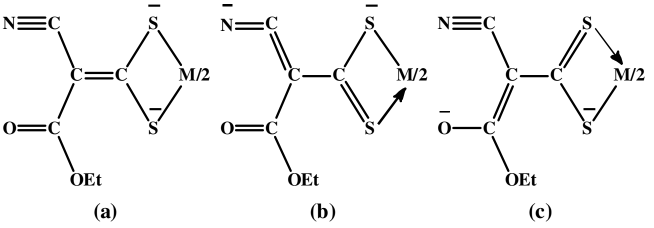
An excessively strong ligand field in low-spin octahedral cobalt(II) complexes may convert the ^{2}E state, which originates in the ^{2}G state of free ion to ground state. Since the predominant electron configuration is $t_{2g}^6e_g^1$, which is attributed due to the Jahn-Teller distortion.

The electronic spectra in DMF solution in the mixed ligand cobalt(II) complexes demonstrate the three bands in ranges 10,000-11,148, 14,577-18,553 and 19,342-22,371 assignable to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3),$^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2),$^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1), respectively signifying distorted octahedral stereochemistry around Co(II) in its complexes. The ν_1 bands observed in the synthesized mixed ligand complexes are very weak intensity while ν_2 bands are very broad and of weak intensity. The ligand absorption band indicates that the ν_3 bands, which are strong absorption bands, are not distinguishable at higher concentrations but do show as a distinct band at low concentrations. The electronic spectra of Co(II) complexes with mixed ligands were analyzed and compared to prior studies. The ν_3 bands exhibited the strong absorption bands are not distinct at higher concentration as observed by the ligand absorption band but appear as distinct band at low concentrations [27-29]. Table-2 provides the essential spectral data along with their respective assignments.

TABLE-2
ELECTRONIC SPECTRAL (cm^{-1}) DATA OF Co(II) MIXED LIGAND COMPLEXES

Complex	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1)	$^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (ν_2)	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3)
Co(*o*-phen)(CED)·$2H_2O$ (**1**)	10638	18215	21368
Co(*o*-phen)$_2$(CED) (**2**)	10650	18050	20704
Co(*o*-phen)(CED)(py)$_2$ (**3**)	10718	16051	21322
Co(*o*-phen)(CED)(α-pic)$_2$ (**4**)	10707	16129	–
Co(*o*-phen)(CED)(β-pic)$_2$ (**5**)	10000	18553	–
Co(*o*-phen)(CED)(γ-pic)$_2$ (**6**)	11086	16750	21598
Co(bipy)(CED)·$2H_2O$ (**7**)	11236	17065	22075
Co(bipy)$_2$(CED) (**8**)	11098	16667	22371
Co(bipy)(CED)(py)$_2$ (**9**)	11148	14577, 16806	22172
Co(bipy)(CED)(α-pic)$_2$ (**10**)	11013	14641, 17123	19531
Co(bipy)(CED)(β-pic)$_2$ (**11**)	11148	17361	19342
Co(bipy)(CED)(γ-pic)$_2$ (**12**)	10952	16778	22321

Infrared spectra: Previous studies [4,5,30,31] on non-transition along with transition metal 1,1-dithiolates have guided the interpretation of the mixed ligand complexes' IR spectra. Resonance structures in CED^{2-} ligand ion complexes as shown in Fig. 1, which can be used to characterize the ion.



(a) (b) (c)

Fig. 1. Resonance forms of CED complexes

Each moiety in the complexes experiences its own set of vibrations and provides its own set of peaks to the IR spectrum. Some bands in IR spectra show pure vibrations due to electron delocalization in the chelated CED^{2-} ring, which causes coupling of vibrational modes. Some of the most distinctive features of the mixed ligand cobalt(II) complexes are the stretching frequencies linked with M-S, C-S, >C=CS$_2$, >C=O, -C≡N, from CED^{2-}; aryl ring vibrations with metal heterocyclic nitrogen vibrations from bipy, *o*-phen, γ-picoline, β-picoline, α-picoline, pyridine and O-H vibrations from water.

In K_2CED·H_2O, as expected, the ν(C≡N) band is observed at 2190 cm^{-1}, whereas in cobalt(II) mixed ligand compounds it is observed in the range of 2192-2180 cm^{-1}, which is consistent with the ligand's non-involvement of the nitrile group in bonding. Ester compounds exhibit ν(C=O) bands at 1750-1720 and 1630-1620 cm^{-1} region, depending on whether the ester group is unconjugated or conjugated (with benzoyl or acetyl group). The delocalization of ν(C=O) group in the neighbouring C=C bond manifests as a strong band in 1625-1604 cm^1, which is lower than typical α,β-unsaturation. The carbonyl oxygen is not participated in the bonding since the ν(C=O) frequency of such mixed ligand complexes is identical to that of K_2CED·H_2O.

The complexes exhibit three prominent bands at 933-930, 1030-1027, 1397-1384 cm^{-1}, which are attributed due to the $\nu_2[\nu_s(=CS_2)]$, $\nu_4[\nu_{as}(=CS_2)]$, $\nu_1[\nu(C=C)]$ vibrations of >C=CS$_2$ structural unit, which was observed in K_2CED·H_2O at 930, 1020, 1320 cm^{-1}, respectively [32]. A few metal complexes exhibit split (triplet or doublet) ν(C=C) symmetry, suggesting a reduc-tion in the symmetry of the structure. Resonance form (Fig. 1a) seems to be predominate in 1-cyano-1-carboethoxy-ethylene-2,2-dithiolate complexes, as observed by the changes in ν(C≡N) and ν(C=C) bands. These mixed ligand complexes exhibit symmetric bonding between ligand's two sulphur atoms and metal ion, as shown by the presence of weak to strong band in 869-845 cm^{-1} region for ν(C-S). The changes in the spectra of out-of-plane and in-plane and ring deformation bands at 425-416 and 651-642 cm^{-1}, in mixed ligand complexes with hetero-cyclic nitrogen donors indicate coordination *via* the nitrogen atom [33]. A weak to medium intensity band can be seen at 1095-1070 cm^{-1} region, which has been attributed to the ring breathing mode of heterocyclic nitrogen donors in the Co(II) complexes. When this band is present in complexes, it means heterocyclic nitrogen donors are being coordinated to the metal centre [32]. The weak band(s) between 3083 and 3061 cm^{-1} are attributed to the n(C-H) (aromatic ring) formed by the heterocyclic aromatic ligand in these complexes. The coordination of CED^{2-} and/or γ-picoline, β-picoline, α-picoline, in the mixed ligand complexes is confirmed by the presence of weak intensity bands for the ν(C-H) (aliphatic) for complexes at 2979-2975 cm^{-1}. In the symmetric and antisymmetric stretching mode of coordinated water, the ν(O-H) frequency emerges as wide band in range 3500-3000 cm^{-1}, whereas H-O-H bending modes appear in the 1630-1610 cm^{-1} region that overlaps with ν(C=O) of CED^{2-} ion. Two water molecules are thought to be in the outside the coordination sphere surrounding the metal centre because of the weight loss shown by

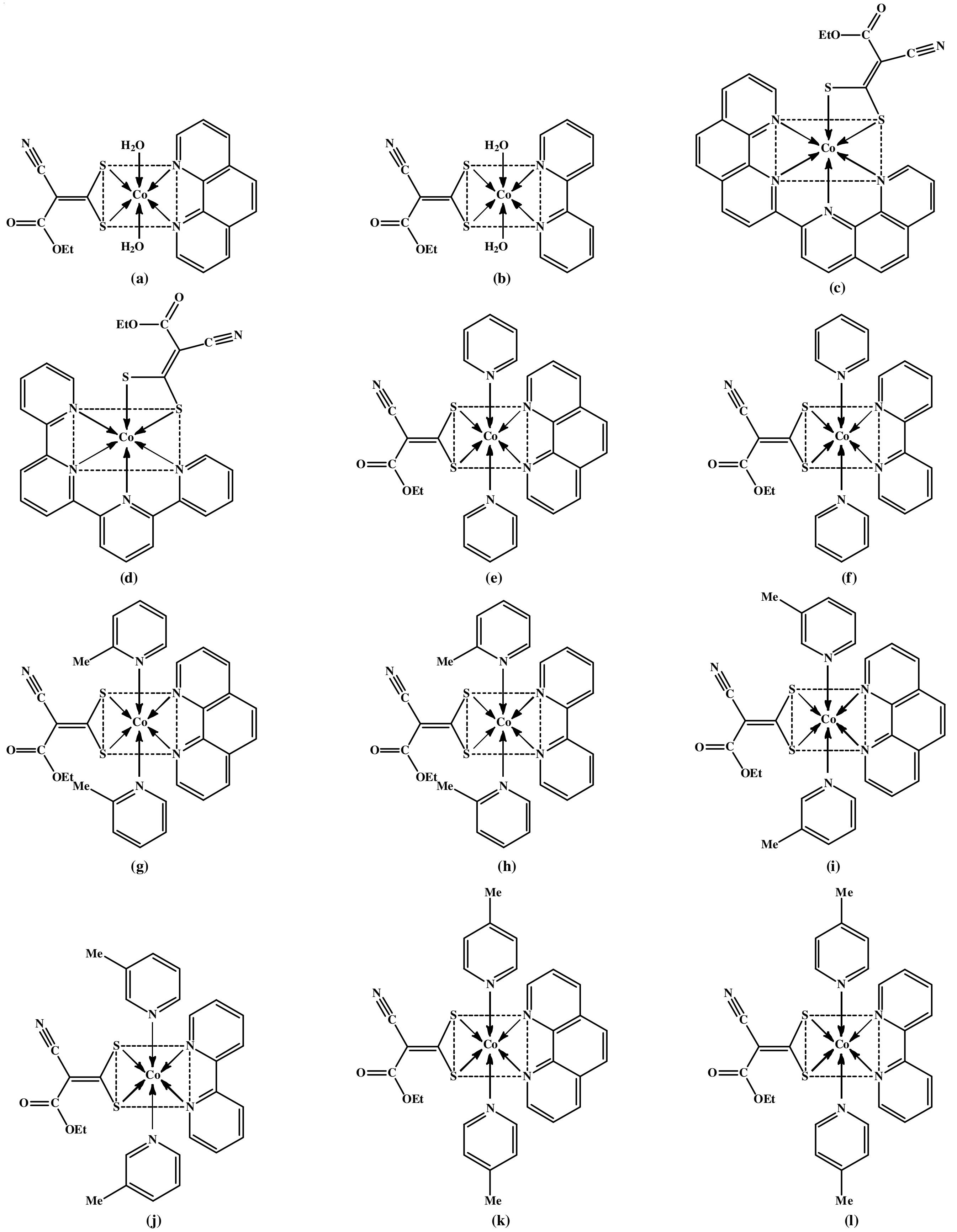


Fig. 2. Proposed structures for Co(*o*-phen)(CED)·$2H_2O$ (a), Co(bipy)(CED)·$2H_2O$ (b), Co(*o*-phen)$_2$(CED) (c), Co(bipy)$_2$(CED) (d), Co(*o*-phen)(CED)(py)$_2$ (e), Co(bipy)(CED)(py)$_2$ (f), Co(*o*-phen)(CED)(α-pic)$_2$ (g), Co(bipy)(CED)(α-pic)$_2$ (h), Co(*o*-phen)(CED)(β-pic)$_2$ (i), Co(bipy)(CED)(β-pic)$_2$ (j), Co(*o*-phen)(CED)(γ-pic)$_2$ (k) and Co(bipy)(CED)(γ-pic)$_2$ (l)

TABLE-3
CHARACTERISTIC IR BANDS (cm^{-1}) FOR THE MIXED LIGAND COMPLEXES OF Co(II) ION

Complex	ν(C≡N)	ν(C=O)	ν(C=C)	ν_{as}(=CS_2)	ν_s(=CS_2)	ν(C-S)	ν(M-N)	ν(M-S)	In-plane ring deformation	Out-of-plane ring deformation	ν(C-H) aromatic/ aliphatic
$K_2CED·H_2O$	2190vs	1642vs	1320vs 1375vs	1020s	930s	886s	-	-	-	-	2982w
Co(*o*-phen)(CED)·$2H_2O$ (**1**)	2192s	1625vs	1385vs	1029s	932m	869w	390w	321w	643w	425w	3071w/2979w
Co(*o*-phen)$_2$(CED) (**2**)	2187s	1622s	1397vs	1030s	930m	845m	410w	319w	643w	424w	3061w/2976w
Co(*o*-phen)(CED)(py)$_2$ (**3**)	2188s	1604m	1385vs	1029s	930m	845m	385w	322w	645w	425w	3064w/2979w
Co(*o*-phen)(CED)(α-pic)$_2$ (**4**)	2187s	1605m	1385vs	1029s	930m	845m	382w	313w	643w	421w	3061w/2975w
Co(*o*-phen)(CED)(β-pic)$_2$ (**5**)	2189s	1610m	1385vs	1030s	931m	847m	392w	309w	643w	422w	3061w/2977w
Co(*o*-phen)(CED)(γ-pic)$_2$ (**6**)	2180s	1619s	1385vs	1029s	931m	847m	405w	299w	644w	420w	3070w/2977w
Co(bipy)(CED)·$2H_2O$ (**7**)	2191s	1605s	1385vs	1027vs	933m	846w	421w	315w	651w	422w	3071w/2977w
Co(bipy)$_2$(CED) (**8**)	2187s	1604s	1396vs	1029s	931m	848w	423w	317w	651w	416w	3081w/2977w
Co(bipy)(CED)(py)$_2$ (**9**)	2189s	1604vs	1384vs	1027s	930m	847w	399w	319w	650w	419w	3077w/2979w
Co(bipy)(CED)(α-pic)$_2$ (**10**)	2188vs	1604vs	1385vs	1027s	930m	850w	405w	311w	650w	419w	3078w/2978w
Co(bipy)(CED)(β-pic)$_2$ (**11**)	2188vs	1605vs	1384vs	1028s	931s	850w	398w	308w	649w	420w	3078w/2977w
Co(bipy)(CED)(γ-pic)$_2$ (**12**)	2188s	1604s	1385vs	1028s	930m	850w	412w	306w	642w	419w	3083w/2976w

complexes **1** and **7** between 150 and 180 ºC [24]. The non-ligand bands in the mixed ligand complexes are probably attributed to ν(Co-S) [33] along with ν(Co-N) [34] modes, appeared at 322-299 and 423-382 cm^{-1}, respectively. Table-3 lists the impo rtant key IR bands of the synthesized cobalt(II) mixed ligand complexes. The tentative strucutres of the synthesized cobalt(II) mixed ligand complexes are shown in Fig. 2.

Conclusion

In summary, it was determined that $Co(NO_3)_2·6H_2O$ reacts with $K_2CED·H_2O$ in presence of *o*-phen or bipy in distinct molar ratio and resulted in the formation of several cobalt(II) mixed ligand complexes. The synthesized complexes Co(*o*-phen)-(CED)·$2H_2O$ along with Co(bipy)(CED)·$2H_2O$ yielded substituted products after reacting with monodentate heterocyclic nitrogen donors (γ-picoline, β-picoline, α-picoline, pyridine) where water molecules were replaced by nitrogen donors. The physical, chemical and spectroscopic analyses of these synthesized cobalt(II) mixed ligand complexes have led to the hypothesis that cobalt(II) complexes adopts a deformed octahedral stereochemistry (low-spin).

ACKNOWLEDGEMENTS

Financial support from the SERB, DST, Government of India, New Delhi is much appreciated, as expressed by the corresponding author, Arijit Das (SERB's Sanction order No. EEQ/2021/000257 dated 25/02/2022).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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