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Spectral and thermal studies of divalent transition metal complexes with indole-2-carboxylic acid and 4-substituted hydrazinethiocarbamide

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Abstract

Ternary complexes of Co(II), Ni(II) and Cu(II) with indole-2-carboxylic acid (A) and 4-substituted hydrazinethiocarbamide (L) [4-phenylhydrazinethiocarbamide (L^1), 4-benzylhydrazinethiocarbamide (L^2) and 4-(2-propenyl)hydrazinethiocarbamide (L^3)] were prepared. The structures of the complexes were proposed by molar conductance, electronic, IR, ^{1}H NMR, mass spectra as well as thermogravimetric (TG) studies. An octahedral structure is suggested for Co(II), Ni(II) and Cu(II) ternary complexes.

Keywords: Indole-2-carboxylate transition metal complexes; Hydrazinethiocarbamide complexes; Electronic spectra; IR spectra; Mass spectra

1. Introduction

Thiourea and hydrazinethiocarbamide derivatives have long history as ligands in coordination to a metal via either sulphur or nitrogen [1]. Hydrazinethiocarbamide is an interesting ligand, not only for the structural chemistry of its multifunction coordination modes, but also for the formation of complexes with antifungal, antimicrobial and antitumor properties [2–4]. Although metal complexes of hydrazinethiocarbamide derivatives have been reported either in enol or keto form [5–13], there are no reports available in the literature on synthesis or spectral studies of their mixed ligand complexes with the polyfunctional donating indole-2-carboxylic acid. Singh and Parkash [14,15] have been isolated and characterized the complexes of Fe(III), Cu(II), Hg(II), Pb(II) and Ag(I) with indole-2-carboxylic acid. The analytical studies for complexes isolated showed the stoichiometry 1:3, 1:2, 1:2, 1:2 and 1:1 (metal:ligand) for the Fe(III), Cu(II), Hg(II), Pb(II) and Ag(I) complexes, respectively [14,15]. It seems that the reaction of transition metals with substituted hydrazinethiocarbamides and indole-2-carboxylic acid is rather complicated and reaction products depend on the type of ligand used. Therefore, as a part of our program of the synthesis of several ternary complexes, we have recently reported the ternary complexes of divalent transition metal ions with the biologically active *N*-(2-acetamido)iminodiacetic acid [16–22], 8-hydroxyquinoline [23,24], creatinine [25], mercaptobenzazoles [26] and thiosemicarbazide as well as dithiocarbazate derivatives [21]. The present investigation deals with synthesis and spectral characterization of ternary metal complexes M(II)-4-substituted hydrazinethiocarbamides-indole-2-caboxylic acid. It is hoped that such study may give further insight into the type of coordination of these ligands with Co(II), Ni(II) and Cu(II).

2. Experimental

2.1. Materials and reagents

The metal salts cobalt(II) chloride, nickel(II) chloride and copper(II) chloride as well as indole-2-carboxylic acid were analytical grade (Aldrich) products of a high purity. 4-Substituted hydrazinethiocarbamides were prepared according to literature 4-phenyhydrazinethiocarbamide (L^1) [27,28], 4-benzylhydrazinethiocarbamide (L^2) [28,29] and 4-(2-propenyl)hydrazinthiocarbamide (L^3) [29,30], the purity of these compounds was verified by thin layer chromatography (TLC). Spectroscopic grade DMSO

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Table 1
Microanalytical data, physical properties, molar conductance and electronic spectra of the prepared ternary complexes

Complex (empirical formula)	Colour	Yield (%)	Found (calcd.) (%)					Λ_m (ohm^{-1} cm^2 mol^{-1})	λ_{max} (nm) (ε_{max} (mol^{-1} cm^{-1} L))
			C	H	N	S	Cl		
$[Co(A)(L^1)Cl(H_2O)]H_2O(C_{16}H_{18}ClCoN_4O_4S)$	Reddish-brown	51	41.81 (42.07)	4.29 (3.97)	12.37 (12.27)	6.84 (7.02)	7.60 (7.76)	12	302, 510 (5)
$[Ni(A)(L^1)Cl(H_2O)]H_2O(C_{16}H_{19}ClN_4NiO_4S)$	Pale green	56	42.14 (41.99)	4.10 (4.19)	12.11 (12.24)	7.17 (7.01)	7.92 (7.75)	15	284, 590 (8.6), 896 (1.25)
$H[Cu(A)(L^1)Cl_2](C_{16}H_{16}Cl_2CuN_4O_2S)$	Blue	64	41.69 (41.52)	3.36 (3.48)	12.23 (12.10)	7.11 (6.93)	15.16 (15.32)	92	276, 700 (20.8)
$[Co(A)(L^2)Cl(H_2O)]H_2O(C_{17}H_{20}ClCoN_4O_4S)$	Reddish-brown	46	43.37 (43.37)	4.66 (4.28)	11.75 (11.90)	6.63 (6.81)	7.33 (7.53)	19	306, 512 (40)
$[Ni(A)(L^2)Cl(H_2O)]H_2O(C_{17}H_{21}ClN_4NiO_4S)$	Pale green	50	43.18 (43.30)	4.31 (4.49)	12.05 (11.88)	6.94 (6.80)	7.44 (7.52)	17	282, 610 (5.3), 894 (1.45)
$H[Cu(A)(L^2)Cl_2](C_{17}H_{18}Cl_2CuN_4O_2S)$	Pale blue	53	42.57 (42.82)	3.93 (3.80)	11.61 (11.75)	6.87 (6.72)	14.69 (14.87)	110	278, 650 (30)
$[Co(A)(L^3)Cl(H_2O)]H_2OC_{13}H_{18}ClCoN_4O_4S$	Reddish-brown	60	36.84 (37.11)	4.68 (4.31)	13.42 (13.32)	7.47 (7.62)	8.26 (8.43)	12	298, 500 (33)
$[Ni(A)(L^3)Cl(H_2O)]H_2O(C_{13}H_{19}ClN_4NiO_4S)$	Green	56	29.27 (37.04)	4.10 (4.54)	12.71 (13.29)	7.75 (7.61)	8.58 (8.41)	18	288, 600 (6.5), 890 (1.35)
$H[Cu(A)(L^3)Cl_2](C_{13}H_{16}Cl_2CuN_4O_2S)$	Blue	51	36.43 (36.58)	3.93 (3.78)	12.95 (13.13)	7.34 (7.51)	16.77 (16.61)	112	271, 630 (34.1)

purchased from Aldrich was used for electronic spectral measurements.

2.2. *Synthesis of ternary metal complexes*

In a round bottomed flask an ethanolic solution (10 ml) containing 5 mmol (0.806 g) of ligand A was added to an ethanolic solution (10 ml) containing 5 mmol of each of the following metal salts: $CoCl_2\cdot6H_2O$ (1.190 g); $NiCl_2\cdot6H_2O$ (1.189 g); or $CuCl_2\cdot2H_2O$ (0.852 g). To each mixture an ethanolic solution (10 ml) containing 5 mmol of the following 4-substituted hydrazinethiocarbamides: 4-phenylhydrazinethiocarbamide (L^1) (0.836 g), 4-benzylhydrazinethiocarbamide (L^2) (0.906 g) or 4-(2-propenyl)hydrazinethiocarbamide (L^3) (0.656 g) were added slowly with stirring. The ternary mixture was refluxed for 5 h and then evaporated to half of its volume and left to cool. The ternary complexes precipitated out, were filtered and washed thoroughly with distilled H_2O and EtOH and dried in vacuo over P_4O_{10}. The microanalytical data of the isolated chelates along with their decomposition temperature are listed in Table 1.

2.3. *Physical measurements*

Melting points have been determined in open glass capillaries on Gallen Kamp melting point apparatus and are uncorrected. However, all synthesized complexes are decomposed at a high temperature (>300 °C). The C, H, N, S and Cl contents of the prepared ternary complexes were determined by the Microanalytical Unit at Cairo University. Molar conductance of DMSO solutions of the synthesized ternary complexes were measured at 25 °C using a model 31 YSI conductivity bridge with conductivity cell constant = 0.10 M. Thermogravimetric (TG) analysis was performed automatically using a Dupont 9000 thermal analyzer at a heating rate of 10 °C min^{-1} in a dynamic air atmosphere. Infrared spectra were recorded in the 4000–200 cm^{-1} range on FT-IR 1650 (Perkin Elmer) spectrophotometer using KBr disk technique. A Bruker WM 300 instrument has been used to determine ^1H NMR (300.1 MHz). Mass spectra have been obtained with a JEOL JMS 600 instrument. Electronic spectra of freshly prepared solutions of the complexes in DMSO were monitored at 25 °C in 200–1000 nm range by an Unicam Scanning UV–vis spectrophotometer model UVA 1000E with an accuracy of ±1 nm using matched silica cells of 1.0 cm path length. The spectrophotometer and its accessories were controlled by software under Windows to provide advanced operational facilities.

3. Results and discussion

3.1. *Characterization of the ternary metal complexes*

The analytical data listed in Table 1 clearly suggested two formulae $[M(A)(L)Cl\cdot H_2O]H_2O$ for the Co(II) and Ni(II)

Table 2
Tentative assignment of the most important IR frequencies (cm^{-1}) of the various synthesized ternary complexes

[M(II)-L^1-A]			M(II)-L^2-A			M(II)-L^3-A			Assignment of IR bands
Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	Co(II)	Ni(II)	Cu(II)	
3520	3525	–	3510	3520	–	3500	3495	–	ν(OH) of hydrated and coordinated H_2O
3360	3355	3330	3370	3330	3360	3360	3370	3350	ν(NH) asymm. stretching of indole-2-carboxylic acid
3280–3200	3265–3210	3280–3190	3260–3200	3245–3170	3270–3190	3280–3140	3275–3160	3280–3150	ν(NH and NH_2) of hydrazinethiocarbamides
1595	1610	1600	1605	1590	1610	1605	1615	1610	ν(COO^-) asymm. of indole-2-carboxylic acid
1550	1545	1550	1555	1545	1550	1545	1560	1550	ν(C=C) of indole and aryl rings
1510	1520	1500	1500	1505	1510	1515	1510	1510	ν(C—N) of hydrazinethiocarbamides
1410	1400	1390	1400	1390	1400	1400	1410	1400	ν(COO^-) symm. stretching of indole-2-carboxylic acid
1330	1325	1330	1335	1330	1340	1325	1335	1330	ν(C=S) of hydrazinethiocarbamides
1000	1000	1000	995	1010	1000	1010	1000	1000	ν(N—N) hydrazinethiocarbamides
870	890	–	875	865	–	890	885	–	ρ_r of rocking mode of coordinated H_2O
770	765	770	750	770	765	755	750	755	ν(C=S) of hydrazinethiocarbamides
475	480	470	490	470	475	480	485	470	ν(M—N) stretching of indole-NH—M
370	355	370	375	360	355	350	355	350	ν(M—S) stretching of hydrazinethiocarbamides – M
235	212	218	220	230	220	232	235	230	ν(M—Cl)

ternary metal complexes and $H[M(A)(L)Cl_2]$ for Cu(II) ternary metal complexes.

The prepared ternary complexes were found to be insoluble in water as well as in most common organic solvents. However, they are slightly soluble in DMF and DMSO. The measured molar conductance values (Λ_{max}) of 10^{-3} mol dm^{-3} DMSO solutions of Co(II) and Ni(II) ternary complexes are in the range 12–19 Ω^{-1} cm^2 mol^{-1} indicating the non-electrolytic nature of these complexes [31]. On the other hand, the molar conductance values of the ternary Cu(II) complexes found to be in the range 92–112 Ω^{-1} cm^2 mol^{-1} is consistent with a 1:1 electrolyte [31]. The (Λ_{max}) values obtained are in a good agreement with the values reported for various complexes measured in DMSO [31]. However, the non-zero values for the non-electrolyte and relatively high values for the 1:1 electrolyte complexes could be attributed to high polarity of solvent.

3.1.1. TG analysis

Thermogravimetric analysis of the various prepared ternary complexes have been carried out to obtain diagnostic structural evidence of the suggested molecular formula. Generally, the TG curves of Co(II) and Ni(II) ternary complexes indicate the removal of two water molecules in the temperature range up to 200 °C. These water molecules may be removed due to water of hydration and coordination. On the other hand, the TG curves of the synthesized Cu(II) ternary complexes do not display noticeable weight losses up to the relatively high temperature (≈200 °C). This behaviour reveals that such complexes do not contain hydration or coordination water. This is in accordance with the results of the microanalyses (Table 1) as well as with the infrared spectra (Table 2). However, at high temperature (>300 °C) a weight loss step is observed containing a rapid decomposition of the ternary complexes (see Fig. 1).

The TG with the corresponding DTG of Co(II)-indole-2-carboxylic acid-phenylhydrazinethiocarbamide is shown in Fig. 2. The TG curve indicates that the complex under investigation shows a remarkable stability up to ≈200 °C. Above this temperature the complex starts to decompose and the thermogram exhibits two main distinct steps, which are maximized at 274 and 478 °C on DTG curve. Finally, one can observe that we have a plateau above 550 °C. This corresponds to the formation of the metal oxide (CoO) with

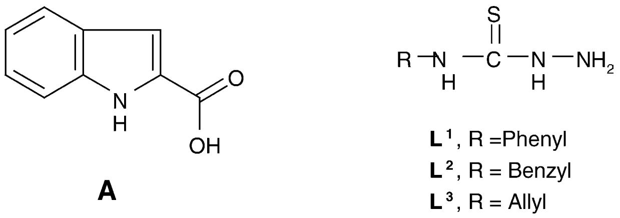

Fig. 1. The structure of the ligands.

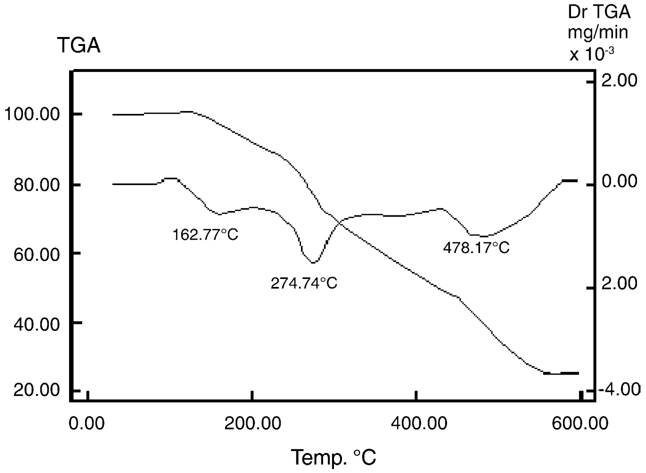

Fig. 2. TG and DTG curves of the $[Co(A)(L^1)Cl(H_2O)]H_2O$ ternary complex.

the deposition of three moles of carbon giving 24% (calcd. 24.36%).

3.1.2. Electronic spectra

The electronic absorption spectroscopic data of 10^{-3} mol dm^{-3} DMSO solutions of the various prepared ternary complexes (for example, Fig. 3) are listed in Table 1. All the spectra of the ternary complexes showed a band with λ_{max} at 306–271 nm, may be ascribed to intermolecular charge-transfer transition from the ligand molecules to the vacant orbital localized on the metal ion (L-MCT-transition) [32]. In addition to the above transitions, the electronic spectra of reddish-brown coloured Co(III) complexes demonstrate a well-defined absorption band around 512 nm ($\varepsilon = 5–40$ cm^{-1} mol^{-1} L) (Table 1). It was previously reported that the electronic spectra of six-coordinated cobalt complexes exhibit a broad absorption band near 500 nm ($\varepsilon = 23.24–32.54$ cm^{-1} mol^{-1} L), which is assigned to the $^4T_{1g} \rightarrow {}^4T_{1g}(p)$ transition of an octahedral structure in admixture with spin-forbidden transition to doublet states [32]. Accordingly, an octahedral structure could be suggested for these complexes. The spectra of the Ni(II) complexes showed a main broad absorption band in the range 590–610 nm ($\varepsilon = 5.30–8.60$ cm^{-1} mol^{-1} L), depending on the nature of the hydrazinecarbothioamide derivative ligands. An additional weak absorption band is also observed around 890 nm ($\varepsilon = 1.25–1.45$ cm^{-1} mol^{-1} L). Six-coordinated and octahedral Ni(II) complexes exhibit an absorption spectrum involving three allowed transitions in the ranges 1428–770, 909–500 and 526–370 nm of comparatively low intensity [32]. Accordingly, an octahedral structure is suggested for the Ni(II) complexes, where the observed band in the range 590–610 nm is assigned to the $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (F) transitions. The weak absorption around 890 nm is attributed to the $^3A_{2g} \rightarrow {}^2E_g$ transition [19].

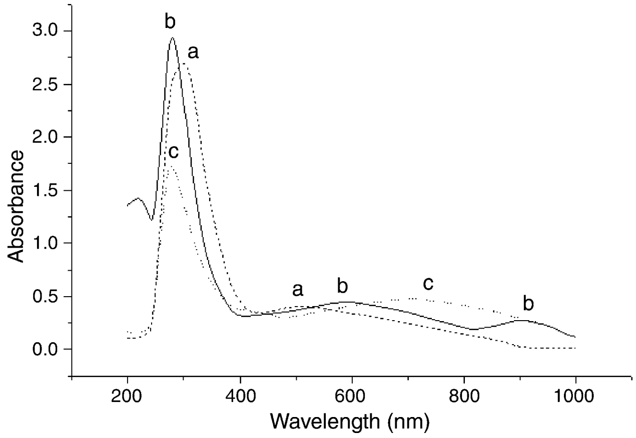

Fig. 3. UV–vis electronic absorption spectra of Co(III), Ni(II), and Cu(II) ternary complexes containing indole-2-carboxylic acid and 4-phyenylhydrazinethiocarbamide as ligands: (a) $[Co(A)(L^1)Cl(H_2O)]H_2O$; (b) $[Ni(A)(L^1)Cl(H_2O)]H_2O$; (c) $H[Cu(A)(L^1)Cl_2]$.

The spectra of the Cu(II) complexes showed a broad band with λ_{max} at 700–630 nm followed by a broad band into the near infrared region. It was reported previously that the majority of six-coordinate Cu(II) complexes have a tetragonal distorted structure giving rise to an absorption band near 630 nm. Therefore, a tetragonal distorted structure is suggested for these complexes. Accordingly, the observed band is assigned to a combination of $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_{1g}$ transitions.

3.1.3. Infrared spectra

Relevant IR bands, which provide conclusive structural evidence for the ternary complexes prepared, are listed in Table 2.

Generally, the IR spectra of ligands were compared with the spectra of the metal complexes. The IR spectra of the ternary complexes display the broad bands in the range 3525–3495 cm^{-1}, which could be attributed to the OH-stretching vibration of hydrated and coordinated water [33]. The stretching-NH vibration is observed at 3395 cm^{-1} in indole-2-carboxylic acid [34] shifts to the lower frequencies in the region 3370–3330 cm^{-1}. The lowering of these frequencies may be attributed to the formation of nitrogen–metal bond. Furthermore, the sharp band appearing in the range 1410–1390 cm^{-1} in the spectra of all synthesized ternary complexes could be attributed to symm. COO^- of indole-2-carboxylic acid. The IR spectra of 4-substituted hydrazinethiocarbamides show strong bands in the region 3460–3100 cm^{-1}, which may be assigned to NH and NH_2 groups. These bands are shifted towards lower wavenumber in all the complexes (Table 2), suggesting that the NH_2 and hydrazinethiocarbamide-^{4}NH groups are taking part in complex formation [35].

The stretching modes of C=S of free substituted hydrazinethiocarbamides observed at 1360 cm^{-1} [36] is shifted to lower frequency at 1340–1325 cm^{-1} range in the IR spectra of the complexes, revealing the participation of thione group coordinated with the metal ion. Also, bands at 770–750 cm^{-1} are assigned to free ν(C=S) [37]. The

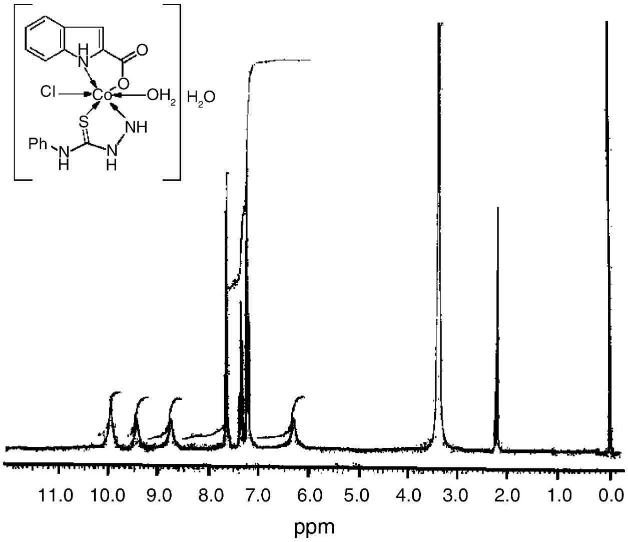

Fig. 4. ^{1}H NMR spectrum of $[Co(A)(L^1)Cl(H_2O)]H_2O$ ternary complex in DMSO-d_6.

bands at 1485 cm^{-1} assigned to ν(C–N) are shifted to higher wavenumbers (1520–1500 cm^{-1}) which is an additional evidence for the contribution of the thione group [38]. The positive shift in the ν(N–N) mode in the spectra of the complexes, indicates the involvement of only one of the hydrazine nitrogen [39] in coordination.

New bands around 490–470, 375–350 and 235–212 cm^{-1} seemed to be the spectra of complexes which are assigned to ν(M–N) [40], ν(M–S) [41,42] and ν(M–Cl) [40,43], respectively.

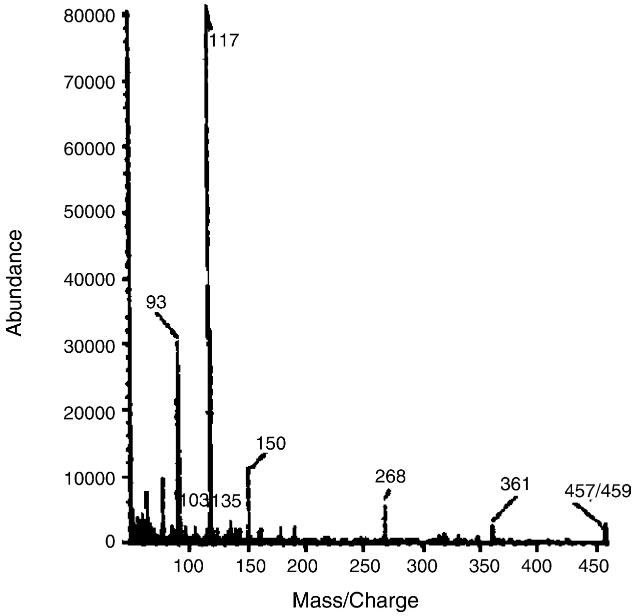

Fig. 5. Mass spectrum of $[Co(A)(L^1)Cl(H_2O)]H_2O$ ternary complex.

3.1.4. ^{1}H NMR spectrum of $[Co(A)(L^1)Cl(H_2O)]H_2O$

The ^{1}H NMR spectrum of $[Co(A)(L^1)Cl(H_2O)]H_2O$ ternary complex in DMSO-d_6 (Fig. 4), in addition to aromatic and indole-CH protons shows four broad signals at 6.40, 8.82, 9.42 and 9.87 ppm in 1:1:1:1 ratio, which are down field from TMS and disappear upon adding D_2O. These signals are attributed to the protons of hydrazinethiocarbamide-^{4}NH, hydrazinethiocarbamide-^{2}NH [44], indole-NH [45] and

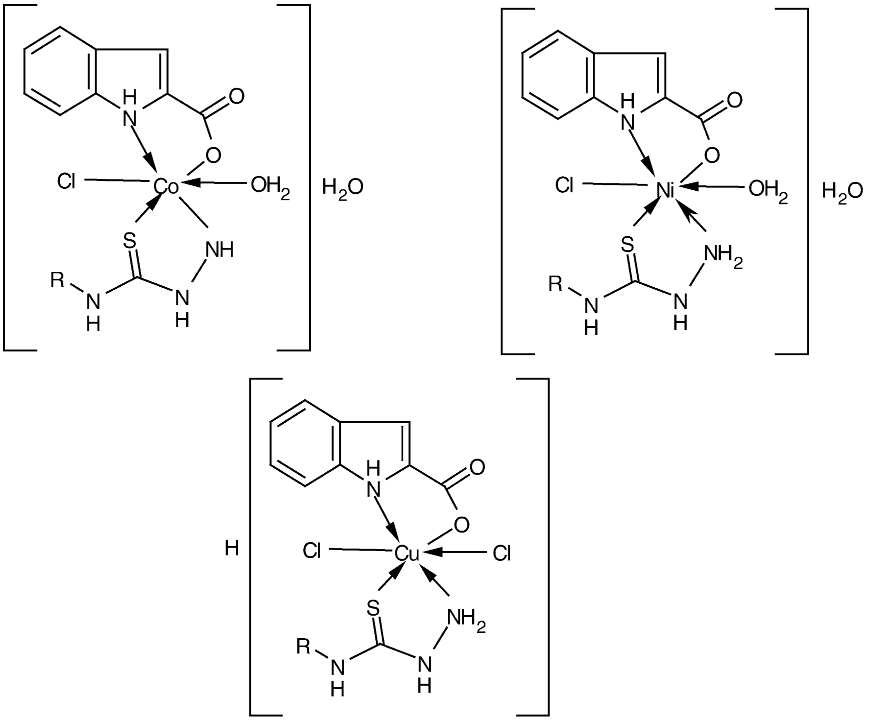

Fig. 6. Representative examples of the structures for the synthesized ternary metal complexes (R = phenyl, benzyl and allyl).

hydrazinethiocarbamide-^{1}NH [44], respectively. The presence of the previous signals in the ^{1}H NMR spectrum of $[Co(A)(L^1)Cl(H_2O)]H_2O$ ternary complex indicates that substituted hydrazinecarbothioamides act as bidentate ligands via a contribution of hydrazinethiocarbamide-^{4}NH as well as C=S groups in coordination. On the other hand, the disappearance of carboxylic proton in indole ring indicates the involvement of carboxylic group in complex formation. The $[Co^{III}(A)(L^1)Cl(H_2O)]H_2O$ ternary complexes are diamagnetic implying that their preparation proceeds via oxidation of cobalt(II) ions and only cobalt(III) chelates were isolated. A similar rapid oxidation was reported with many ligands [46].

3.1.5. Mass spectrum of $[Co(A)(L^1)Cl(H_2O)]H_2O$

For the complex $[Co(A)(L^1)Cl(H_2O)]H_2O$, the gross formula $C_{16}H_{18}CoClN_4SO_4$, was confirmed by the mass spectrometry (Fig. 5). Besides the molecular ion at $m/z = 457/459$, the characteristic fragment ion pattern of monohalo compounds was observed [47].

The mass spectrum shows fragments at 361 (8), 268 (17), 150 (11), 117 (100), 103 (21), and 93 (46). The fragments at m/z 135 (representing Ph N=C=S residue), 117 (representing indole residue), 103 (representing Ph N≡C residue), and 93 (representing aniline residue) resulting from the cleavage of Co–N and Co–S bonds.

The mass spectral fragmentation of the ternary metal complex $[Co(A)(L^1)Cl(H_2O)]H_2O$, however, is in agreement with structure in Fig. 6.

4. Conclusion

In conclusion, the following remarks may be of some interest:

(i) All complexes are stable on heating up to 200 °C, the first decomposition step for Co(III) and Ni(II) ternary complexes may be attributed to the removal of two water molecules. The other steps attributed to removal of indole and the residue of hydrazinethiocarbamide.

(ii) The isolated $[Co^{III}(A)(L^1)Cl(H_2O)]H_2O$ complexes are diamagnetic (due to the good quality of ^{1}H NMR spectrum recorded) (Fig. 4). The brown colours of Co(III) complexes are due to charge-transfer transition from ligands to cobalt [37].

(iii) The hydrazinethiocarbamide derivatives act as a bidentate ligand, coordinating via hydrazinethiocarbamide-^{4}NH and the (C=S) groups (in case of Co(III) complexes) or via NH_2 and (C=S) groups (in case of Ni(II) and Cu(II) complexes) as shown in Fig. 6. This mode of complexation can be suggested on the basis of IR and ^{1}H NMR which shows broad signals due to the protons of hydrazinethiocarbamide-^{1}NH, ^{2}NH and ^{4}NH. The IR spectra of the ternary complexes revealing the participation of thione group coordinated with the metal ions. Indole-2-carboxylic acid behaves as a mononegative bidentate ligand via indole-NH and COOH groups (in accordance with the results of ^{1}H NMR and IR spectra) with the displacement of hydrogen atom from the latter group, forming two five-membered rings as shown in Fig. 6.

(iv) The analytical data of the ternary complexes under investigation would also match for other alternative structures and could be ruled out on the basis of the above thermal and spectroscopic data.

(v) Further, the molecular mechanics PM3 program [48] for the structure of $H[Cu(A)(L^1)Cl_2]$ complex (Fig. 6), as examples suggest that the coordination by both the thiocarbonyl and the NH_2 groups towards Cu metal is more stable (steric energy = 125 kcal/mol) with respect to the other structure which involved coordination by the R–NH and NH_2 groups (steric energy = 248 kcal/mol) towards the same metal. Moreover, the coordination via the C=S group is more favorable compared with the RNH group.

(vi) The metal complexes are insoluble in ethanol, methanol, acetonitrile and various solvents, but soluble in DMSO. All attempts to prepare single crystals of the compounds failed. Thus, no definite structure can be described, but the analytical and spectroscopic data enable us to predict the possible structures as shown in Fig. 6.

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