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Spectroscopic, thermal and biocidal studies on Mn(II), Co(II), Ni(II) and Cu(II) complexes of tridentate ligand having semicarbazone moieties

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Abstract Mn(II), Co(II), Ni(II) and Cu(II) complexes having the general composition $M(L)_2X_2$ [where L = 2-pyridinecarboxaldehyde semicarbazone, M = Mn(II), Co(II), Ni(II) and Cu(II), $X = Cl^-$ and NO_3^-] have been synthesized. All the synthesized compounds were identified and confirmed by elemental analysis, molar conductance, magnetic susceptibility measurements, mass, IR, EPR, electronic spectral studies and thermogravimetric analysis (TG). The Molar conductance measurements of the complexes lie in the range 209–228 Ω^1 cm^{-1} mol^{-1} indicating that the complexes are 1:2 electrolytic in nature. Thus the complexes may be formulated as $[M(L)_2]X_2$. The magnetic moment measurements of the complexes indicate that all the complexes are in high-spin state. On the basis of spectral studies an octahedral geometry has been assigned for Mn(II), Co(II) and Ni(II) complexes whereas tetragonal geometry for Cu(II) complexes. The thermal studies suggested that the complexes are more stable compared with free ligand. This fact was supported by calculating the thermodynamic parameters by using Horowitz–Metzger (HM) and Coats–Redfern (CR) equations. The free ligand and its metal complexes were also evaluated against the growth of phytopathogenic fungi and bacteria in vitro.

Keywords Biological activity · 3d Metals · Semicarbazone · Spectroscopic · Thermal

Introduction

Semicarbazones, as well as their sulphur analogs, thiosemicarbazones, are compounds possessing a wide variety of biological applications. The formation of a variety of metal complexes from these ligands speaks for their spectacular progress in coordination and bioinorganic chemistry [1]. Semicarbazones are reported to possess versatile structural features and very good antifungal, antibacterial, antitrypanosomal and anticonvulsant properties [2–6]. Spectral studies of semicarbazones of furaldehyde, salicylaldehyde, 2-hydoxyacetophenone, 4-formylpyridine and 4 acetylpyridine were also reported [7–9]. Rhenium(V) and Ruthenium(II) complexes of 5-nitrofurylsemicarbazone were tested against the trypanocidal activity [10]. Ni(II) complexes of thiosemicarbazones and semicarbazones were tested against the antimicrobial activity in vitro [11]. Keeping the above view in mind, we reported the synthesis, spectroscopic, thermal and biocidal studies of Mn(II), Co(II), Ni(II) and Cu(II) complexes with biologically relevant ligand. The structure of ligand and scheme for the synthesis is shown in Fig. 1.

Experimental

All the chemicals used were of Anala R grade and received from Sigma-Aldrich and Fluka companies. Metal salts were purchased from E. Merck and were used as received.

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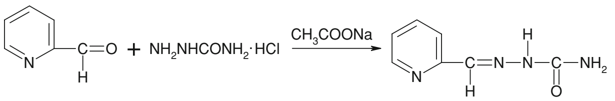

Fig. 1 Synthesis and structure of ligand (L)

Synthesis of ligand

An aqueous solution of semicarbazide hydrochloride (2.22 g, 0.02 mol) and 2-pyridinecarboxaldehyde (1.9 mL, 0.02 mol) were mixed in the presence of sodium acetate (2.72 g, 0.02 mol). This solution was stirred vigorously with the help of mechanical stirrer for an hour. On cooling a white product was formed, filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}.

Synthesis of complexes

Hot ethanolic solution (20 mL) of corresponding metal salts (0.01 mol) was mixed with hot ethanolic solution of the respective ligand (0.01 mol). This solution was refluxed for 4–5 h at 70–80 °C .On cooling a colored complex was separated out. It was filtered, washed and re-crystallized with ethanol and dried under vacuum over P_4O_{10}. The purity of the complexes was checked by thin layer chromatography (TLC). TLC analysis was performed on silica gel (Fluka F_{60} 254 20 × 20; 0.2 mm) using the solvent system *n*-heptane/acetone (2:1) as eluent.

Physical measurements

The C, H and N were analyzed on Carlo-Erba 1106 elemental analyzer. The Nitrogen content of the complexes was determined using Kjeldahl's method. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature using $CuSO_4{\cdot}5H_2O$ as callibrant. Electronic impact mass spectrum was recorded on Jeol, JMS-DX-303 mass spectrometer. IR spectra (KBr) were recorded on FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the complexes were recorded as polycrystalline sample and in the DMSO solution, at liquid nitrogen temperature for Co(II), and at room temperature for the Mn(II) and Cu(II) complexes on E_4-EPR spectrometer using the DPPH as the g-marker.

Results and discussion

The metal ion and ligand was condensed in the ratio of 1:2 for the preparation of mononuclear complexes. The reaction sequence is given below

$$MX_2 \cdot nH_2O + 2\ \text{Ligand} \xrightarrow[70-80\ ^\circ C]{\text{Reflux}} [M(\text{Ligand})_2]X_2 + nH_2O$$

The molar conductance (Table 1) of the complexes in DMSO lies in the range 209–228 Ω^{-1} cm^2 mol^{-1} indicating that the complexes are 1:2 electrolytic in nature [12]. Thus they may be formulated as $[M(L)_2]X_2$ [where M = Co(II), Ni(II), Cu(II), X = Cl^-, $NO_3{}^-$].

Mass spectrum

The electronic impact mass spectrum of the ligand shows a molecular ion (M^+) peak at m/z = 165 amu corresponding to species $[C_7H_8N_4O]^+$, which confirms the proposed formula. It also shows series of peaks like 16, 44, 59, 78, 86, 91, 105, 130 and 158 amu correspond to various fragments. Their intensities give the idea of the stabilities of the fragments.

Infrared spectra

A band appeared at ~1,588 cm^{-1} in the IR spectrum of the ligand is due to the *v*(C=N) group. On complex formation, this band is shifted towards lower side [13]. The pyridine ring vibration at ~624 cm^{-1} in the free ligand is also shifted toward higher frequency [14]. This indicates that the nitrogen atom of the pyridine ring is involved in coordination. The *v*(C=O) vibration appeared at ~1,689 cm^{-1} in the ligand is shifted towards lower side on complexation [15]. Thus it has been concluded that ligand act as tridentate coordinate through the pyridine N, imine N and Oxygen atom. In the IR spectra of the nitrate complexes of Mn(II), Co(II), Ni(II) and Cu(II) show a broad band at 1,376–1,396 cm^{-1} corresponding to uncoordinated nitrate group [16].

Magnetic moments and (electronic and EPR) spectra

Manganese(II) complexes

The magnetic moment recorded at room temperature lies at 5.91–5.97 B.M. corresponding to five unpaired electrons. Electronic spectra of Mn(II) complexes display four weak intensity absorption bands in the range 18,621–18,650, 24,630–24,632, 28,540–28,750 and 30,769–31,250 cm^{-1}. These bands may be assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ (^{4}G) (10B + 5C), $^6A_{1g} \rightarrow {}^4E_g$ (^{4}D) (17B + 5C) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}P) (7B + 7C) respectively [17] transitions. The position of these bands suggest an octahedral geometry around the Mn(II) ion (Fig. 2). The EPR spectra of Mn(II) complexes were recorded at room temperature as polycrystalline samples and in DMSO

Table 1 Molar conductance and elemental analysis data of the complexes

Compounds	Molar Conductance/ Ω^{-1} cm^2 mol^{-1})	Color	Yield/ %	m.p./ °C	Mwt	Elemental analysis found (calcd.)/%			
						M	C	H	N
$C_7H_8N_4O$ (L)	–	White	65	137	164	–	51.29 (51.22)	4.82 (4.88)	34.18 (34.14)
$[Mn(L)_2]Cl_2$ $MnC_{14}H_{16}N_8O_2Cl_2$	225	Off White	62	280	454	12.15 (12.11)	37.05 (37.00)	3.49 (3.52)	24.61 (24.67)
$[Mn(L)_2](NO_3)_2$ $MnC_{14}H_{16}N_{10}O_8$	220	Off White	64	286	507	10.80 (10.84)	33.18 (33.13)	3.19 (3.15)	27.67 (27.61)
$[Co(L)_2]Cl_2$ $CoC_{14}H_{16}N_8O_2Cl_2$	218	Pink	60	220	458	12.82 (12.86)	36.62 (36.68)	3.55 (3.49)	24.52 (24.45)
$[Co(L)_2](NO_3)_2$ $CoC_{14}H_{16}N_{10}O_8$	214	Shiny Pink	58	235	511	11.58 (11.52)	32.92 (32.87)	3.17 (3.13)	27.42 (27.39)
$[Ni(L)_2]Cl_2$ $NiC_{14}H_{16}N_8O_2Cl_2$	222	Light Green	62	256	458	12.76 (12.81)	36.65 (36.68)	3.52 (3.49)	24.50 (24.45)
$[Ni(L)_2](NO_3)_2$ $NiC_{14}H_{16}N_{10}O_8$	228	Bluish Green	64	284	511	11.52 (11.48)	32.90 (32.87)	3.19 (3.13)	27.36 (27.39)
$[Cu(L)_2]Cl_2$ $CuC_{14}H_{16}N_8O_2Cl_2$	209	Light green	69	185	463	13.87 (13.82)	36.25 (36.28)	3.52 (3.45)	24.22 (24.19)
$[Cu(L)_2](NO_3)_2$ $CuC_{14}H_{16}N_{10}O_8$	212	Shiny green	65	187	516	12.36 (12.40)	32.59 (32.55)	3.17 (3.10)	27.18 (27.13)

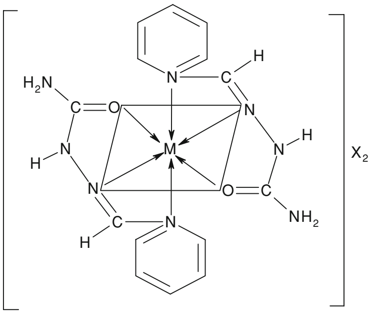

Fig. 2 Suggested structure of the complexes where M = Mn(II), Co(II), Ni(II), Cu(II) and X = Cl$^-$ and NO$_3$$^-$

solution. The polycrystalline spectra give an isotropic signal centered at 1.96–2.07 ($A^0 = 109$–112). The spectra recorded in DMSO solution gives well resolved six line spectra due to the hyperfine interaction between the unpaired electrons with the ^{55}Mn nuclear (l = 5/2).

Cobalt(II) complexes

At room temperature Co(II) complexes show magnetic moment in the range 4.85–4.90 B.M. The electronic spectra of Co(II) complexes, recorded in DMSO solution, exhibit absorption in the region, 10,718–11,223, 14,696–15,240, and 18,057–18,416 cm^{-1}. These bands may be assigned to $^4T_{1g}$ (F) → $^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) transitions respectively. The position of these bands suggests an octahedral environment around the Co(II) ion. The EPR spectra of Co(II) complexes were recorded as polycrystalline sample and in DMSO solutions at liquid nitrogen temperature. The '*g*' values are found to be almost same in both cases in polycrystalline sample as well as in the solution. This indicates that the complexes have same geometry in solid form as well as in the solution.

Nickel(II) complexes

At room temperature the magnetic moments of the Ni(II) complexes lie in the range 2.85–2.92 B.M., corresponding to two unpaired electrons. The electronic spectra of Ni(II) complexes display three absorption bands in the range 10,823–12,670, 14,326–15,420 and 23,570–24,436 cm^{-1}. The ground state of Ni(II) in an octahedral coordination [18] is $^3A_{2g}$. Thus, these bands may be assigned to three spin allowed transitions $^3A_{2g}$ (F) → $^3T_{2g}$ (F) (ν_1), $^3A_{2g}$ (F) → 3T$_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) (ν_3), respectively. The position of these bands indicates that the complexes have an octahedral geometry around the Ni(II) complexes.

Copper(II) complexes

The magnetic moments of Cu(II) complexes were recorded at room temperature. The complexes show magnetic moments in the range 1.83–1.89 BM corresponding to one unpaired electron. The electronic spectra of these complexes display bands in the range 10,430–10,542, 14,792–15,432 and 25,316–25,510 cm^{-1}. These bands correspond to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x2-y2} \rightarrow d_{z2}$), $^2B_{1g} \rightarrow {}^2B_{2g}$($d_{x2-y2} \rightarrow d_{zy}$) and $^2B_{1g} \rightarrow {}^2E_g$($d_{x2-y2} \rightarrow d_{zy}$ d_{yz}) respectively. Therefore, the complexes may be considered to possess a tetragonal geometry [19]. EPR spectra of the Cu(II) complexes were recorded, at room temperature as polycrystalline samples, on the X-band at 9.1 GHz under the magnetic field range 3,000 G. The analysis of spectra give $g_{||}$ 2.0842–2.0972 and $g_{\perp}$ 2.0145–2.0365. The trend $g_{||} > g_{\perp} > 2.0023$, observed for the complexes, under study, indicate that the unpaired electron is localized in the d_{x2-y2} orbital of the Cu(II) ion and the spectral features are characteristic for the axial symmetry. Tetragonally elongated geometry is thus confirmed for the aforesaid complexes. $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between the metal centers in a polycrystalline solid has been calculated. According to Hathaway [20], if $G > 4$ the exchange interaction is negligible, but $G < 4$ indicates considerable exchange interaction in the solid complexes. The complexes reported in this paper gives the 'G' value in the range <4, which indicates exchange interaction in the solid complexes.

Thermal studies

2-Pyridinecarboxaldehyde semicarbazone and its metal complexes were studied by thermogravimetric analysis from ambient temperature to 800 °C in nitrogen atmosphere. The TG curves were redrawn as % mass loss versus temperature (TG) curves. Typical TG curves are presented in Fig. 3 and the temperature ranges and percentage mass losses of the decomposition reaction are given in Table 2, together with evolved moiety and the theoretical percentage mass losses. Thermal techniques, such as thermogravimetric analysis (TG and DTG), has been successfully employed for the study of the energetic of interactions of metal cations with biological species, such as amino acids [21]. The weight loss profiles are analyzed the amount or percent of weight loss at any given temperature, and the temperature ranges of the degradation process were determined. Thermal stability domains, melting points, decomposition phenomena and their assignments for the 2-pyridinecarboxaldehyde semicarbazone complexes are summarized in Table 2. The simultaneous TG–DTG curves of: 2-pyridinecarboxaldehyde semicarbazide (Ligand; L), $[Cu(L)_2]Cl_2$, $[Cu(L)_2](NO_3)_2$, $[Co(L)_2]Cl_2$ $[Co(L)_2](NO_3)_2$, $[Ni(L)_2]Cl_2$, $[Ni(L)_2](NO_3)_2$, $[Mn(L)_2]Cl_2$ and $[Mn(L)_2](NO_3)_2$ compounds at the heating rate of 10 °C/min in the static nitrogen atmosphere are given in Fig. 3. The overall loss of mass from the TG curves is 100% for 2-pyridinecarboxaldehyde semicarbazone, 83.12% for $[Cu(L)_2]Cl_2$, 84.93% for $[Cu(L)_2](NO_3)_2$, 83.66% for $[Co(L)_2]Cl_2$, 85.23% for $[Co(L)_2](NO_3)_2$, 83.42% for $[Ni(L)_2]Cl_2$, 85.76% for $[Ni(L)_2](NO_3)_2$, 80.12% for $[Mn(L)_2]Cl_2$, and 82.52% for $[Mn(L)_2](NO_3)_2$ compounds, respectively. All the complexes have two essential maxima peaks mass loss. The first sharp endothermic peak concerning metal(II) chlorides Cu(II), Co(II), Ni(II) and Mn(II)) of 2-pyridinecarboxaldehyde semicarbazone complexes: occurring between 20 and 302 °C may be due to loss of hydrazine molecule (N_2H_2) and the second decomposition step in the range of 214–800 °C, correspond to the pyrolysis of the 2-pyridinecarboxaldehyde semicarbazone rest.

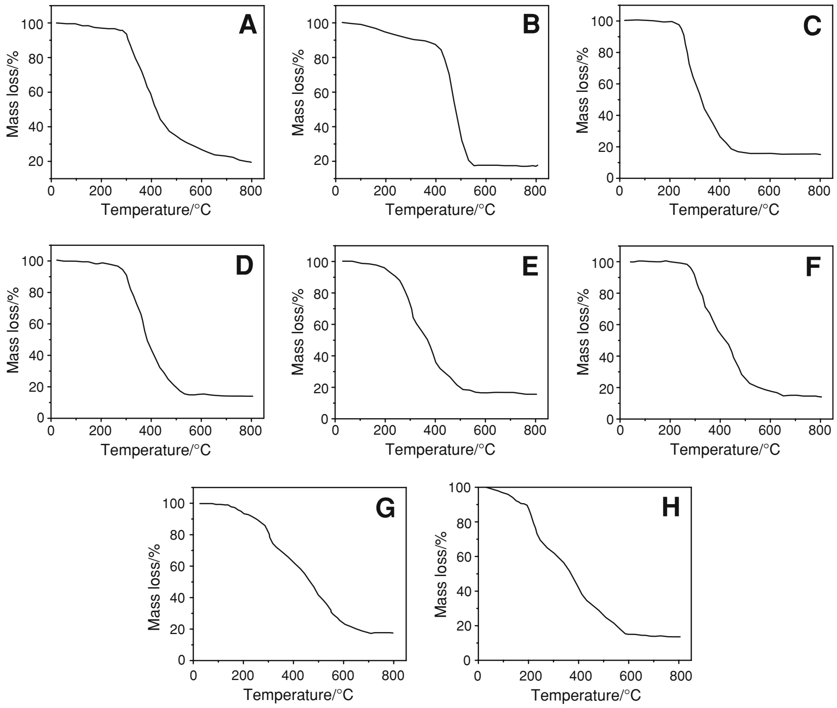

Fig. 3 TG curves of:
a $[Mn(L)_2]Cl_2$,
b $[Mn(L)_2](NO_3)_2$,
c $[Co(L)_2]Cl_2$,
d $[Co(L)_2](NO_3)_2$,
e $[Ni(L)_2]Cl_2$, **f** $[Ni(L)_2](NO_3)_2$,
g $[Cu(L)_2]Cl_2$ and
h $[Cu(L)_2](NO_3)_2$ complexes

Table 2 Thermoanalytical results (TG and DTG) for the ligand and its complexes

Compounds	Steps	Temperature range/°C	DTG_{max}/°C	TG mass loss/%		Assignments
				Calc.	Found	
$C_7H_8N_4O$ (L)	1st	20–480	143	52.44	52.06	$–C_2H_4N_3O$ (organic moiety)
	2nd	480–800	581	47.56	47.94	C_5H_4N (pyridine ring)
$[Mn(L)_2]Cl_2$ $MnC_{14}H_{16}N_8O_2Cl_2$	1st	20–302	281	7.05	7.04	$–H_4N_2$ (hydrazine molecule)
	2nd	302–800	438	73.79	73.08	$C_{14}H_{12}N_6Cl_2$ (organic moiety)
				19.16	19.88	MnO_2 (residue)
$[Mn(L)_2](NO_3)_2$ $MnC_{14}H_{16}N_{10}O_8$	1st	20–425	292	17.36	17.74	$–C_2H_4N_2O_2$ (2 amido group)
	2nd	425–800	477	65.49	64.78	$C_{12}H_{12}N_8O_4$ (organic moiety)
				17.15	17.48	MnO_2 (residue)
$[Co(L)_2]Cl_2$ $CoC_{14}H_{16}N_8O_2Cl_2$	1st	20–251	225	6.99	6.41	$–H_4N_2$ (hydrazine molecule)
	2nd	251–800	318	76.64	77.25	$C_{14}H_{12}N_6OCl_2$ (organic moiety)
				16.37	16.34	CoO (residue)
$[Co(L)_2](NO_3)_2$ $CoC_{14}H_{16}N_{10}O_8$	1st	20–316	238	17.23	17.88	$–C_2H_4N_2O_2$ (2 amido group)
	2nd	316–800	393	68.10	67.35	$C_{12}H_{12}N_8O_5$ (organic moiety)
				14.67	14.77	CoO (residue)
$[Ni(L)_2]Cl_2$ $NiC_{14}H_{16}N_8O_2Cl_2$	1st	20–214	125	7.00	6.44	$–H_4N_2$ (hydrazine molecule)
	2nd	214–800	403	76.68	76.98	$C_{14}H_{12}N_6OCl_2$ (organic moiety)
				16.32	16.58	NiO (residue)
$[Ni(L)_2](NO_3)_2$ $NiC_{14}H_{16}N_{10}O_8$	1st	20–318	267	17.24	17.40	$–C_2H_4N_2O_2$ (2 amido group)
	2nd	318–800	387	68.13	68.36	$C_{12}H_{12}N_8O_5$ (organic moiety)
				14.63	14.24	NiO (residue)
$[Cu(L)_2]Cl_2$ $CuC_{14}H_{16}N_8O_2Cl_2$	1st	20–300	190	6.92	6.64	$–H_4N_2$ (hydrazine molecule)
	2nd	300–800	488	75.88	76.48	$C_{14}H_{12}N_6OCl_2$ (organic moiety)
				17.20	16.88	CuO (residue)
$[Cu(L)_2](NO_3)_2$ $CuC_{14}H_{16}N_{10}O_8$	1st	20–212	188	17.07	17.53	$–C_2H_4N_2O_2$ (2 amido group)
	2nd	212–800	418	67.50	67.40	$C_{12}H_{12}N_8O_5$ (organic moiety)
				15.43	15.07	CuO (residue)

Kinetic calculations

The main kinetic parameters such as activation energy (E^*), enthalpy (H^*), entropy (S^*) and free energy change of the decomposition (G^*) were determined graphically by using the Coats–Redfern relation [22].

The Coats–Redfern equation (1), which is a typical integral method, can be represented as

$$\int_0^\infty d\alpha/(1-\alpha)^n = (A/\phi)\int_{T_1}^{T_2} e^{-E^*/RT}dt \qquad (1)$$

For convenience of integration, the lower limit T_1 is usually taken as zero. This equation on integration gives (Eq. 2);

$$\mathrm{Ln}\left[-\ln(1-\alpha)/T^2\right] = -E^*/RT + \ln[AR/\phi E]. \qquad (2)$$

A plot of left-hand side (LHS) against $1/T$ was drawn. E^* is the energy of activation in $kJmol^{-1}$ and calculated from the slop and A in (s^{-1}) from the intercept. The entropy of activation ΔS^* in (JK^{-1} mol^{-1}) was calculated by using the equation (Table 3)

$$\Delta S^* = R\ \ln(Ah/kT_s) \qquad (3)$$

where k is the Boltzmann constant, h is the Plank's constant and T_s is the DTG peak temperature.

Taking the activation energy of the first step as a criterion, the following stability sequence can be observed in 2-pyridinecarboxaldehyde semicarbazone complexes: $[Mn(L)_2]Cl_2 > [Mn(L)_2](NO_3)_2 > [Ni(L)_2]Cl_2 > [Ni(L)_2](NO_3)_2 > [Cu(L)_2]Cl_2 > [Cu(L)_2](NO_3)_2 > [Co(L)_2]Cl_2 > [Co(L)_2](NO_3)_2$. This order of stability points to the dependence of decomposition of the metal cations and the ionic radius. The activation energy of Cu^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+} complexes is expected increase in relation with decrease in their radius. The entropy in all complexes has a negative value, this meaning that the complexes have more ordered systems than reactants.

Table 3 Thermodynamic parameters of the ligand and its complexes using the Coats–Redfern (CR) equation

Complexes	Radius metal ion/pm	DTG_{max}/ °C	E^*/ $kJmol^{-1}$	A/s^{-1}	$\Delta S^*/JK^{-1}$ mol^{-1}	ΔH^*/ kJg^{-1}	ΔG^*/ $kJmol^{-1}$	r
$C_7H_8N_4O$ (L)	–	143	15.1	5.64×10^4	−2.13	16.5	13.2	0.9652
$[Mn(L)_2]Cl_2$ $MnC_{14}H_{16}N_8O_2Cl_2$	46	281	38.1	2.65×10^7	−1.68	19.8	21.6	0.9812
$[Mn(L)_2](NO_3)_2$ $MnC_{14}H_{16}N_{10}O_8$		292	35.2	2.34×10^6	−1.77	20.6	21.1	0.9652
$[Co(L)_2]Cl_2$ $CoC_{14}H_{16}N_8O_2Cl_2$	74.5	225	21.2	3.21×10^8	−1.29	12.4	21.3	0.9564
$[Co(L)_2](NO_3)_2$ $CoC_{14}H_{16}N_{10}O_8$		238	20.6	2.98×10^9	−1.32	11.9	20.8	0.9953
$[Ni(L)_2]Cl_2$ $NiC_{14}H_{16}N_8O_2Cl_2$	69	125	27.5	3.55×10^8	−1.65	12.8	21.9	0.9971
$[Ni(L)_2](NO_3)_2$ $NiC_{14}H_{16}N_{10}O_8$		267	26.5	2.98×10^9	−1.88	13.5	30.7	0.9987
$[Cu(L)_2]Cl_2$ $CuC_{14}H_{16}N_8O_2Cl_2$	73	190	24.3	5.11×10^5	−2.45	26.2	19.8	0.9876
$[Cu(L)_2](NO_3)_2$ $CuC_{14}H_{16}N_{10}O_8$		188	23.3	3.91×10^6	−2.32	20.9	19.5	0.9965

Biological screening

Cultures of phytopathogenic fungi and bacteria such as *Rhizoctonia bataticola*, *Alernaria alternata*, *Fusarium odum*, *Stapyloccocus aureus*, *Bacillus striata* and *Escherichia coli* were procured from Indian type of culture, Division of Plant Pathology, Indian Agriculture Research Institute.

Antifungal activities

The preliminary fungitoxicity screening of the compounds were performed against the phytopathogenic fungi *R. bataticola*, *A. alternata* and *F. Odum* in vitro by the agar plate technique [23]. The appropriate quantity of the compounds in DMSO were directly mixed to the potato agar dextrose(PDA) medium in different concentrations. The activities of the compounds have been compared with the activity of standard fungicide Ketoconazol. All the compounds show fungal growth inhibition following the order Cu(II) > Ni(II) > Co(II) > Mn(II) > ligand.

Antibacterial activities

The antibacterial action of the ligand and its Mn(II), Co(II), Ni(II) and Cu(II) complexes was checked by disc diffusion method [24]. This was done by the bacterial species *Stapyloccocus aureus*, *Pseudomonas striata* and *Escherichia coli*. DMSO served as control and Streptomycin used as standard drug. The bacterial growth inhibitory capacity of the ligand and its complexes follow the order Cu(II) > Ni(II) > Co(II) > Mn(II) > ligand.

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