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Spectroscopic, thermal and antibacterial studies on Mn(II) and Co(II) complexes derived from thiosemicarbazone

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Abstract: Mn(II) and Co(II) complexes having the general composition $[M(L)_2X_2]$ (where L = 2-pyridinecarboxaldehyde thiosemicarbazone, M = Mn(II) and Co(II), X = Cl^- and NO_3^-) were synthesized. All the metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, mass, IR, EPR, electronic spectral studies and thermogravimetric analysis (TG). Based on the spectral studies, an octahedral geometry was assigned for all the complexes. Thermal studies of the compounds suggest that the complexes are more stable than the free ligand. This fact was supported by the kinetic parameters calculated using the Horowitz–Metzger (H–M) and Coats–Redfern (C–R) equations. The antibacterial properties of the ligand and its metal complexes were also examined and it was observed that the complexes are more potent bactericides than the free ligand.

Keywords: thiosemicarbazone; Mn(II) and Co(II) complexes; thermal; antibacterial studies.

INTRODUCTION

During the last two decades, thiosemicarbazones have emerged as an important class of sulphur donor ligands for transition metal ions. The interest in the development of the coordination chemistry of thiosemicarbazones is due to their biological and medicinal properties.[1] They present a variety of biological activities ranging from antitumour, antifungal, antibacterial, anticancer anti-inflammatory and antiviral activities.[2–10] The bacterial and fungicidal activities of transition metal complexes are due to the formation of chelates with the essential metal ions bonding through the nitrogen and the sulphur donor atom of the ligand. The activity of these compounds is also dependent on the nature of the heteroaromatic ring and the position of attachment to the ring, as well as the form of the thiosemicarbazone moiety.[11,12] Manganese(II) and cobalt(II) complexes of

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thiosemicarbazones have been reported as compounds that present biological activity.[13–15]

In view of the above applications, a spectroscopic, thermal and antimicrobial study of 2-pyridinecarboxaldehyde thiosemicarbazone (L) and its Mn(II), and Co(II) complexes is presented in this paper. The structure of the free ligand is shown in Fig. 1.

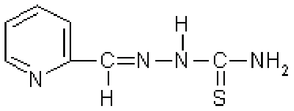

Fig. 1. Structure of the ligand (L).

EXPERIMENTAL

All the employed chemicals were of analytical grade and procured from Sigma-Aldrich and Fluka. The metal salts were purchased from Merck and were used as received.

Synthesis of ligand

A hot ethanolic solution (20 ml) of thiosemicarbazide (4.55 g, 0.0500 mol) and an ethanolic solution (20 ml) of 2-pyridinecarboxaldehyde (4.75 ml, 0.0500 mol) were mixed slowly under constant stirring. This mixture was refluxed at 75–80 °C for 4 h. On cooling, a white coloured compound precipitated out, which was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}. Yield: 68 %; m.p. 180 °C. Anal. Calcd. for $C_7H_8N_4S$ (FW = = 180): C, 46.67; H, 4.45; N, 31.11 %. Found: C, 46.62; H, 4.49; N, 31.20 %.

Synthesis of the complexes

A hot ethanolic (20 ml) solution of the ligand (0.36 g, 0.0020 mol) and an ethanolic (20 ml) solution of the required metal salt ($MnCl_2·4H_2O$, $Mn(NO_3)_2·2H_2O$, $CoCl_2·6H_2O$, $Mn(NO_3)_2·2H_2O$ (0.0010 mol) were mixed together under constant stirring. This reaction mixture was refluxed for 3–4 h at 70–80 °C. The completion of the reaction was confirmed by TLC using ethanol and acetone in a 2:1 ratio as the solvent and silica gel as the adsorbent. The reaction mass was degassed on a rotary-evaporator over a water bath. On cooling, a coloured complex separated out, which was filtered, washed and recrystalized from 50 % ethanol and dried under vacuum over P_4O_{10}.

Physical measurements

C and H were analyzed on a Carlo–Erba EA 1106 elemental analyzer. The nitrogen content of the complexes was determined using the Kjeldahl method.[16] The content of manganese was determined gravimetrically as $Mn_2P_2O_7$ and cobalt volumetrically using Xylol Orange as the indicator.[17] The molar conductance was measured on an Elico CM82T conductivity bridge. The magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4·5H_2O$ as the calibrant. Correction for diamagnetism was realised using Pascal constants. The electronic impact mass spectrum was recorded on a JEOL, JMS-DX-303 mass spectrometer. The ^{1}H-NMR spectra of the ligand was recorded at room temperature on a Brucker Advance DPX-300 spectrometer using DMSO-d_6 as the solvent. The IR spectra were recorded as KBr pellets on a FTIR BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. The EPR spectra of the Mn(II) complexes were recorded as polycrystalline sample at room temperature and the Co(II) complexes at liquid nitrogen temperature on an E_4-EPR spectrometer using DPPH as the g-marker. The thermogravimetric curves were obtained using a Shimadzu TG-50H instrument under a N_2 atmosphere at a heating rate of 15 °C min^{-1}.

RESULTS AND DISCUSSION

Based on elemental analyses, the complexes were found to have the composition shown in Table I. The molar conductance measurements of the complexes in DMSO corresponded to non-electrolytes. Thus, these complexes may be formulated as $[M(L)_2X_2]$ [where M = Mn(II) or Co(II), L = 2-pyridinecarboxaldehyde thiosemicarbazone and X = Cl^- or NO_3^-]. The electron-impact mass spectrum of the ligand is shown in Fig 2. The IR spectra (KBr, cm^{-1}) of the ligand displayed a highest frequency band at 3433 cm^{-1}, which can be assigned to the asymmetric ν(N–H) vibration of the terminal NH_2 group. The other bands at 3261 and 3156 cm^{-1} may be due to the symmetric ν(N–H) vibrations of the imino and amino groups. The other important IR bands of the ligand and their metal complexes are given in Table II.

TABLE I. Molar conductance and elemental analysis data of the complexes

Complex	Molar conductance S cm^2 mol^{-1}	Colour	M.p. °C	Yield %	Elemental analysis Found (Calcd.), %			
					M	C	H	N
$[Mn(L)_2Cl_2]$	16	Cream	285	65	11.28	34.50	3.24	23.08
$MnC_{14}H_{16}N_8S_2Cl_2$					(11.32)	(34.57)	(3.29)	(23.04)
$[Mn(L)_2(NO_3)_2]$	12	Cream	289	62	10.16	31.14	2.92	25.92
$MnC_{14}H_{16}N_{10}S_2O_6$					(10.20)	(31.17)	(2.97)	(25.97)
$[Co(L)_2Cl_2]$	17	Light	298	59	12.06	34.25	3.23	22.82
$CoC_{14}H_{16}N_8S_2Cl_2$		pink			(12.02)	(34.29)	(3.26)	(22.86)
$[Co(L)_2(NO_3)_2]$	20	Shiny	295	62	10.82	30.96	2.99	25.72
$CoC_{14}H_{16}N_{10}S_2O_6$		pink			(10.85)	(30.94)	(2.95)	(25.78)

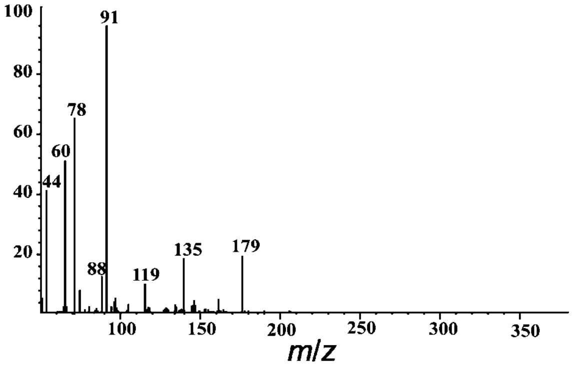

Fig. 2. Electron impact mass spectrum of the ligand (L).

The magnetic moment of the Mn(II) complexes lay in the range 5.92–5.98 μ_B, corresponding to five unpaired electrons. At room temperature, the magnetic moment of the Co(II) complexes lay in the range 4.85–4.90 μ_B, corresponding to

TABLE II. IR Spectral data (cm^{-1}) of ligand and its metal complexes

Compound	ν(C=N)	ν(Py–N)	ν(C=S)	ν(M–N)
L	1610	559	742	--
[Mn(L)$_2$Cl$_2$]	1590	575	742	440
[Mn(L)$_2$(NO$_3$)$_2$]	1595	572	742	448
[Co(L)$_2$Cl$_2$]	1587	580	742	452
[Co(L)$_2$(NO$_3$)$_2$	1592	585	742	445

three unpaired electrons (Table III). The electronic spectra of the Mn(II) complexes exhibited four weak intensity absorption bands in the ranges of 533–546, 433–439, 361–364 and 261–274 nm. These bands may be assigned to the transitions: $^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}G), $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ (^{4}G) (10B + 5C), $^6A_{1g} \rightarrow {}^4E_g$ (^{4}D) (17B + 5C) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}P) (7B + 7C), respectively.[18,19] The positions of these bands suggest an octahedral geometry around the Mn(II) ion. The electronic spectra of the Co(II) complexes, recorded in DMSO solution, exhibited absorption in the ranges of 962–965, 679–696 and 533–539 nm. These bands may be assigned to the transitions: $^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$ and $^4T_{1g}$ (F) $\rightarrow$ $\rightarrow {}^4T_{1g}$ (P), respectively.[20,21] The position of these bands suggests an octahedral environment around the Co(II) ion. The EPR spectra of the Mn(II) and Co(II) complexes were recorded as polycrystalline samples and in DMSO solution at room temperature and liquid nitrogen temperature, respectively. The polycrystalline spectra of the Mn(II) complexes gave an isotropic signal cantered at approximately the free electron g-value (g_0 = 2.0023). The broadening of the spectra is probably due to spin relaxation. In DMSO solution, the complexes gave six well-resolved lines due to hyperfine interaction between the unpaired electrons with the Mn nucleus (I = 5/2). In the spectra of the Co(II) complexes, the g-va-

TABLE III. Magnetic moments and electronic spectral data of the complexes

Complexes	μ_{eff}/μ_B	λ_{max} / nm	ε / l mol^{-1} cm^{-1}	Assignments
[Mn(L)$_2$Cl$_2$]	5.98	546	30	$^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$
		439	41	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ (^{4}G) (10B+5C)
		364	112	$^6A_{1g} \rightarrow {}^4E_g$ (^{4}D) (17B+5C)
		261	132	$^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}P) (7B+7C)
[Mn(L)$_2$(NO$_3$)$_2$]	5.92	533	34	$^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$
		433	48	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ (^{4}G) (10B+5C)
		361	119	$^6A_{1g} \rightarrow {}^4E_g$ (^{4}D) (17B+5C)
		275	136	$^6A_{1g} \rightarrow {}^4T_{1g}$ (^{4}P) (7B+7C)
[Co(L)$_2$Cl$_2$]	4.85	965	56	$^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F)
		696	72	$^4T_{1g} \rightarrow {}^4A_{2g}$
[Co(L)$_2$(NO$_3$)$_2$]	4.90	533	87	$^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P)
		962	61	$^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$ (F)
		679	75	$^4T_{1g} \rightarrow {}^4A_{2g}$
		539	92	$^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P)

lues were found to be almost the same in both the polycrystalline sample and in solution. This indicates that the complexes had the same geometry in the solid form as in solution (Table IV). Based on of above spectral studies, the structures shown in Fig. 3 may be suggested for the complexes.

TABLE IV. EPR Spectral data of the complexes

Complexes	Temp.	$g_{\parallel}$	$g_{\perp}$	g_{iso}	A^0
$[Mn(L)_2Cl_2]$	RT	–	–	1.9980	109.65
$[Mn(L)_2(NO_3)_2]$	RT	–	–	2.0178	112.82
$[Co(L)_2Cl_2]$	LNT	2.7090	1.8060	2.1070	–
$[Co(L)_2(NO_3)_2]$	LNT	2.4951	1.8301	2.0517	–

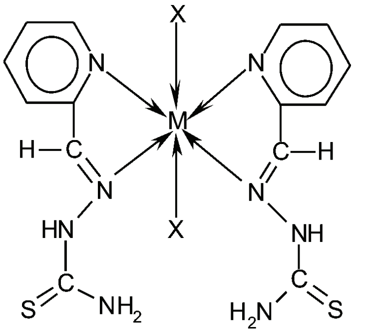

Fig. 3. Suggested structures of the complexes.

Thermogravimetric analysis

The thermal analysis data of the ligand and its metal complexes are given in Table V.

TABLE V. Thermogravimetric results (TG and DTG) for the ligand and its complexes

Compund	Stage	Temperature range, °C	DTG_{max} °C	Residual species	Decomposition species	Total losses, %	
						Found	Calc.
Ligand (L)	1st	270–800	310	C	$C_2H_2 + N_2 + S$	93.30	93.34
	2nd		600		$2C_2H_2 + N_2 + H_2$		
	3rd		725				
$[Mn(L)_2Cl_2]$	1st	40-800	216	MnS	$7C_2H_2 + Cl_2 +$ $+ 4N_2 + H_2S$	83.06	82.11
	2nd		463				
	3rd		603				
$[Mn(L)_2(NO_3)_2]$	1st	200-800	260	MnO_2	$7C_2H_2 + SO_2 +$ $+ 2NO + 4N_2 +$ $+ H_2S$	84.63	83.87
	2nd		443				
	3rd		562				
$[Co(L)_2Cl_2]$	1st	78-800	145	CoS	$7C_2H_2 + Cl_2 +$ $+ 4N_2 + H_2S$	81.32	81.44
	2nd		436				
	3rd		699				
$[Co(L)_2(NO_3)_2]$	1st	59-800	195	$CoSO_4$	$7C_2H_2 + 2NO +$ $+ 4N_2 + H_2S$	72.19	71.46
	2nd		480				
	3rd		628				

Kinetic Parameters. Two methods mentioned in the literature related to decomposition kinetics studies were applied in this study, i.e., the Coats–Redfern[22] and Horowitz–Metzger[23] method.

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

$$\int_0^{\infty} \frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \frac{A}{\varphi} \int_{T_1}^{T_2} \mathrm{e}^{\frac{E^*}{RT}} \mathrm{d}T \tag{1}$$

For convenience of integration, the lower limit, T_1, is usually taken as zero. This equation on integration gives:

$$\ln(-\ln(1-\alpha)/T^2] = -E^*/RT + \ln(AR/\Phi e) \tag{2}$$

A plot of the left-hand side (LHS) against $1/T$ was drawn. E^* is the energy of activation in kJ mol^{-1} and is calculated from the slope, and A in s^{-1} from the intercept. The entropy of activation, ΔS^* in J K^{-1} mol^{-1}, was calculated from the equation:

$$\Delta S^* = R \ln(Ah/kT_s) \tag{3}$$

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

The Horowitz–Metzger Equation was written in the form:

$$\log(\log(w_\alpha/w_\gamma)) = E^*\theta/2.303RT_s^2 - \log 2.303 \tag{4}$$

where $\theta = T - T_s$, $w_\gamma = w_\alpha - w$; w_α is the mass loss at the completion of the reaction; w is the mass loss up to time t. From the slope of the linear plot of log (log (w_α/w_γ)) *vs.* θ, the value of E^* is calculated. The pre-exponential factor, A, is calculated from the equation:

$$E^*\theta/RT_s^2 = A/[\varphi \exp(-E^*/RT_s)] \tag{5}$$

The entropy of activation, ΔS^*, enthalpy of activation, ΔH^*, and Gibbs free energy, ΔG^*, are calculated from:

$$\Delta H^* = E^* - RT \text{ and } \Delta G^* = \Delta H^* - T\Delta S^*$$

The kinetic parameters for the main degradation stages around 700–740 K (decomposition of the ligand) obtained employing the Coats–Redfern and Horowitz–Metzger equations are summarized in Table VI together with the radii of the metal ions. The results show that the values obtained by various methods are comparable. The activation energy of the Mn(II) and Co(II) complexes is expected to increase in relation with the decrease in their radius. The E^* values calculated using the Coats–Redfern method for the definite decomposition stages of the complexes are: E^*(Mn(II)) = 1.70×10^5 kJ mol^{-1} > E^*(Co(II)) = 1.24×10^5 kJ mol^{-1}; r(Mn(II)) = 46.0 pm < r(Co(II)) = 74.5 pm.

TABLE VI. Thermal behaviour and kinetic parameters determined using the Coats–Redfern (C–R) and Horowitz–Metzger (H–M) method

Compound	Radius pm	T_s K	Method	E^* kJ mol^{-1}	A s^{-1}	ΔS^* J K^{-1} mol^{-1}	ΔH^* kJ mol^{-1}	ΔG^* kJ mol^{-1}	R
Ligand (L)	–	583	CR	139	25.4	–0.513	134	164	0.9513
			HM	143	86.4	–0.411	138	162	0.9506
$[Mn(L)_2Cl_2]$	46.0	736	CR	170	1.44×10^{6}	–1.35	114	213	0.9855
			HM	167	7.98×10^{6}	–1.20	121	210	0.9814
$[Mn(L)_2(NO_3)_2]$		716	CR	178	20.1	–0.550	172	212	0.9906
			HM	188	5.94×10^{11}	–0.268	182	202	0.9916
$[Co(L)_2Cl_2]$	74.5	709	CR	124	7.76×10^{9}	–0.628	158	203	0.9962
			HM	135	8.15×10^{10}	–0.432	169	199	0.9955
$[Co(L)_2(NO_3)_2]$		753	CR	131	6.15×10^{6}	–1.23	124	217	0.9954
			HM	149	1.74×10^{8}	–0.994	143	214	0.9920

Antibacterial studies

The antibacterial action of the ligand and its Mn(II) and Co(II) complexes was measured by the disc diffusion method[24–27] against the bacterial species: *Stapyloccocus aureus*, *Pseudomonas striata* and *Escherchi*a *coli*. Sterilized nutrient agar media (NA) (25 ml) was poured into Petri dishes. After solidification, 0.10 ml of test bacteria was spread over the medium using a spreader. Discs of Whatman No. 1 filter paper, diameter 6 mm, were soaked in DMSO solutions in the compounds (1.0 mg cm^{-1}). All the compounds were placed at 4 equidistant places at a distance of 2 cm from the centre of the inoculated Petri dishes. DMSO served as the control and Streptomycin was used as the standard drug. The Petri dishes were kept in a refrigerator for 24 h for pre-diffusion. Finally, the Petri dishes were incubated at 30 °C for 24 h. All determinations were performed in duplicate for each of the compounds. The average of two independent readings for each compound was recorded.

The results of the antibacterial study are given in Fig. 4, from which it can be seen that the bacterial growth inhibitory capacity of the ligand and its complexes followed the order Co(II) > Mn(II) > ligand.

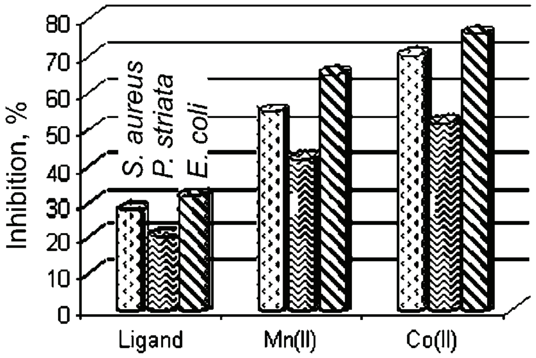

Fig. 4. Antibacterial activity of the compounds.

CONCLUSIONS

The present study confirmed an octahedral geometry around the Mn(II) and Co(II) complexes with the bidentate ligand coordinating through the nitrogen atoms of the of ν(Py–N) and ν(C=N) groups. The thermal stability sequence decreased in the following order: Mn(II) > Co(II) > ligand. The activation energy of the Mn(II) and Co(II) complexes, as expected, increased in accordance with their decreasing radius. The activation entropy change in all the complexes had a negative value, meaning that the complexes were more ordered systems than the reactants. The results of antimicrobial activity revealed that all the metal-complexes showed an inhibition capacity slightly higher than the ligand, but much less than the standard drug.

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ИЗВОД

СПЕКТРОСКОПСКА, ТЕРМИЧКА И АНТИБАКТЕРИЈСКА ПРОУЧАВАЊА Mn(II) И Co(II) КОМПЛЕКСА ИЗВЕДЕНИХ ИЗ ТИОСЕМИКАРБАЗОНА

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Синтетисани су комплекси Mn(II) и Co(II) општег састава $[M(L)_2X_2]$ (где је L = 2-пиридинкарбоксиалдехид тиосемикарбазона, M = Mn(II) и Co(II), X = Cl^- и NO_3^-). Сви метални комплекси су окарактерисани елементалном анализом, моларном проводљивошћу, мерењем магнетне сусцептибилности, масеним, IR, EPR, електронским спектралним проучавањима и термогравиметријском анализом (TG). На основу спектралних изучавања предложена је октаедарска геометрија за све комплексе. Термичка проучавања једињења сугеришу да су комплекси стабилнији од слободног лиганда. Ово је подржано проучавањем кинетичниких параметара применом Horowitz–Metzger (H–M) и Coats–Redfern (C–R) једначина. Антибактеријске особине лиганда и његових металних комплекса су такође изучаване и примећено је да су компкелси моћнији бактерициди него слободни лиганд.

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