Research Article

Spectroscopic and Biological Studies on Newly Synthesized Cobalt (II) and Nickel (II) Complexes with 2-Acetyl Coumarone Semicarbazone and 2-Acetyl Coumarone Thiosemicarbazone

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Received 13 June 2012; Accepted 1 October 2012

Academic Editor: Filomena Conforti

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Co(II) and Ni(II) complexes of general composition ML_2X_2 ($M = \text{Co(II)}, \text{Ni(II)}$; $X = \text{Cl}^-, \text{NO}_3^-$) were synthesized by the condensation of metal salts with semicarbazone/thiosemicarbazone derived from 2-acetyl coumarone. The ligands and metal complexes were characterized by NMR, elemental analysis, molar conductance, magnetic susceptibility measurements, IR, and atomic absorption spectral studies. On the basis of electronic, molar conductance and infrared spectral studies, the complexes were found to have square planar geometry. The Schiff bases and their metal complexes were tested for their antibacterial and antioxidant activities.

1. Introduction

Research on the coordination chemistry, analytical applications, and biological activities of Schiff base complexes has increased steadily for many years. A large number of Schiff bases and their complexes have been studied for their interesting and important biological properties, for example, antimicrobial (El-Wahab et al. [1]), antiviral (Kolocouris et al. [2]), antifungal (Rodríguez-Argüelles et al. [3]), antitumor (Ainscough et al. [4]), and other biological activities (Bharamagouclar et al. [5]; Zhu et al. [6]; Shalin et al. [7]; Kothari and Sharma [8]) particularly with first row of transition metal complexes. The formation of variety of metal complexes with Schiff base ligands as mentioned in our earlier studies (Chandra and Kumar [9]; Chandra and Kumar [10]; Chandra and Gupta [11]) indicates the spectacular progress in coordination and bioinorganic chemistry. It has been demonstrated through several studies that the biological activity of Schiff's bases is enhanced on chelation with a metal ion (Sengupta et al. [12]). In the view of the facts that the metal complexes are better therapeutic agents (Chandra et al. [13]; Kumar and Chandra [14]) as compared to the Schiff bases, the aim of this study is to synthesize the new class of

metal complexes with newly synthesized Schiff base ligands and different metal salts, to find their biological activity such as antioxidant and antibacterial activities and to observe the impact of complexation on their therapeutic values.

2. Experimental

All the chemicals used in the present work were of high purity, Anala R grade, and procured from Sigma-Aldrich. Metal salts were purchased from E. Merck and used as received. The solvents used were either spectroscopic pure from SRL/BDH or purified by the recommended methods (Vogel [15]).

2.1. Synthesis of 2-Acetyl Coumarone Semicarbazone (SCL). An aqueous solution of semicarbazide HCl (1.11 g, 0.01 mol) was added to an ethanolic solution of 2-acetyl coumarone (1.60 g, 0.01 mol) in the presence of sodium acetate (0.82 g, 0.01 mol). The reaction mixture was stirred vigorously for 2 h. The completion of the reaction was confirmed by the TLC. The yellow product formed was collected by filtration which was washed several times with hot water and dried in vacuum

TABLE 1: Molar conductance and elemental analysis data.

Ligand/complex	Λ_M	Atomic mass	Colour	M.P (°C)	Yield (%)	Elemental analysis data (%) found (calculated)			
						M	C	H	N
SCL	—	217	Yellow	224	72	—	59.83 (60.82)	4.97 (5.10)	19.12 (19.34)
[Co(SCL) ₂](Cl) ₂	152	563	Brown	230	72	10.42 (10.44)	46.92 (46.83)	3.97 (3.93)	14.92 (14.89)
[Co(SCL) ₂](NO ₃) ₂	184	616	Brown	219	71	9.53 (9.55)	43.89 (42.80)	3.62 (3.59)	18.37 (18.15)
[Ni(SCL) ₂](Cl) ₂	158	564	Light brown	226	79	10.40 (10.41)	46.92 (46.85)	3.99 (3.93)	15.18 (14.90)
[Ni(SCL) ₂](NO ₃) ₂	179	617	Light brown	218	73	9.50 (9.51)	43.14 (42.82)	3.64 (3.59)	18.53 (18.16)
TSCL	—	233	light yellow	197	70	—	56.21 (56.63)	4.59 (4.75)	17.81 (18.01)
[Co(TSCL) ₂](Cl) ₂	168	595	Brown	205	74	9.84 (9.88)	45.19 (44.30)	3.97 (3.72)	13.87 (14.09)
[Co(TSCL) ₂](NO ₃) ₂	180	648	Light brown	210	81	9.05 (9.07)	39.98 (40.68)	3.37 (3.41)	17.82 (17.25)
[Ni(TSCL) ₂](Cl) ₂	174	596	Light yellow	199	71	9.84 (9.84)	45.15 (44.32)	3.86 (3.72)	13.89 (14.10)
[Ni(TSCL) ₂](NO ₃) ₂	187	649	Brown	198	78	9.02 (9.04)	40.16 (40.70)	3.84 (3.42)	17.54 (17.26)

Λ_M : molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

over P_4O_{10} . The characterization details are tabulated in Table 1. (See Scheme 1.)

2.2. Synthesis of 2-Acetyl Coumarone Thiosemicarbazone (TSCL). Hot ethanolic solution of 2-acetyl coumarone (1.60 g, 0.01 mol) was mixed with hot ethanolic solution of thiosemicarbazide (0.91 g, 0.01 mol) in the presence of 0.5 mL acetic acid. The contents were refluxed at 70–80°C for about 3–4 h. The completion of the reaction was confirmed by the TLC. The solvent was removed using a rotary evaporator and light yellow coloured solid was obtained. It was washed with cold ethanol and dried under vacuum over P_4O_{10} . The characterization details are tabulated in Table 1. (See Scheme 2.)

2.3. Preparation of Metal Complexes. Hot ethanolic solution of metal salts (1 mmol), for example, nickel chloride hexahydrate (0.238 g), nickel nitrate hexahydrate (0.292 g), cobalt chloride hexahydrate (0.237 g), or cobalt nitrate hexahydrate (0.291 g), was mixed with hot ethanolic solution of the corresponding ligand (2 mmol), for example, SCL (0.434 g) or TSCL (0.466 g). The mixture was refluxed for 4–5 hours at 70–80°C. On cooling the contents, the complex separated out in each case. It was filtered, washed with 50% ethanol, and dried under vacuum over P_4O_{10} . The characterization details are tabulated in Table 1.

2.4. Physical Measurements. The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Metal contents were determined by Atomic Absorption studies. Molar conductance was measured on an ELICO (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. IR spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. The ^1H NMR spectrums were recorded on a Jeol FT-NMR Spectrometer using DMSO as a solvent. Thermogravimetry (TG) and Differential Thermogravimetric (DTA) analysis for the metal complexes were carried out on a Perkin Elmer

(Diamond) TG-DTA spectrometer for the determination of complex entrapped water.

3. Results and Discussion

3.1. Infrared Spectra of SCL. The IR spectrum of ligand SCL (Figure 1) shows bands at 3456 and 3144 cm^{-1} which may be assigned to $[\nu(\text{NH}_2)]$ and $[\nu(\text{NH})]$ groups, respectively. The bands due to $[\nu(\text{C}=\text{O})]$ appeared at 1720 cm^{-1} and the bands at 1562 or 1446 cm^{-1} may be assigned to symmetric or asymmetric $[\nu(\text{C}=\text{N})]$ group (Kothari and Sharma [8]; Chandra and Gupta [11]).

3.2. The ^1H NMR Spectra of SCL. The ^1H NMR spectrum of the ligand SCL (Figure 2) was recorded in DMSO. It shows signals at δ 2.21 ppm (3H, CH_3-C , s), δ 6.52 ppm (2H, NH_2-CO , s), δ 9.62 ppm (1H, $\text{N}-\text{NH}-\text{CO}$, s), δ 7.36 ppm (1H, $\text{Ph}-\text{CH}-\text{C}$, s), δ 7.62 (1H, Ph, d), δ 7.57 ppm (1H, Ph, d), δ 7.32 (1H, Ph, m), and δ 7.25 ppm (1H, Ph, m).

3.3. Infrared Spectra of TSCL. The IR spectrum of the ligand TSCL (Figure 3) shows bands at 3310 and 3148 cm^{-1} which may be assigned to $[\nu(\text{NH}_2)]$ and $[\nu(\text{NH})]$ groups, respectively. The bands due to $[\nu(\text{C}=\text{S})]$ appeared at 1598 cm^{-1} and the bands at 1497 or 1257 cm^{-1} may be assigned to symmetric or asymmetric $[\nu(\text{C}=\text{N})]$ group (Kothari and Sharma [8]; Chandra and Gupta [11]).

3.4. The ^1H NMR Spectra of TSCL. The ^1H NMR spectrum of the ligand TSCL (Figure 4) was recorded in DMSO. It shows signals at δ 2.33 ppm (3H, CH_3-C , s), δ 7.82 ppm (2H, NH_2-CO , s), δ 10.51 ppm (1H, $\text{N}-\text{NH}-\text{CO}$, s), δ 7.56 ppm (1H, $\text{Ph}-\text{CH}-\text{C}$, s), δ 7.65 (1H, Ph, d), δ 7.59 ppm (1H, Ph, d), δ 7.35 (1H, Ph, m), and δ 7.26 ppm (1H, Ph, m).

3.5. Infrared Spectra of Metal Complexes. The assignments of the significant IR spectral bands of the metal complexes are shown in Figures 5, 6, 7, and 8 which clearly show the shifting of the bands corresponding to $\nu(-\text{C}=\text{N})$ and $\nu(-\text{C}=\text{S})$

SCHEME 1

SCHEME 2

FIGURE 1: IR spectra of SCL.

FIGURE 2: NMR spectra of SCL.

FIGURE 3: IR spectra of TSCL.

FIGURE 4: NMR spectra of TSCL.

of C=S group or oxygen of C=O (Kothari and Sharma [8]; Chandra and Gupta [11]).

in thiosemicarbazone or $\nu(-C=O)$ in semicarbazone towards the lower side (around ca. 20–50 cm^{-1}) on complexation. This suggests that both the ligands act as bidentate chelating agents coordinating through nitrogen of C=N group and sulphur

3.6. *The ^1H NMR Spectra of Nickel Complexes.* The ^1H NMR spectra of the nickel complexes were recorded in DMSO. They show shifting of signals corresponding to CH_3 , NH_2 -CO and N-NH-CO coordination as compared to the ^1H NMR spectra of the corresponding ligand. It indicates the

FIGURE 5: IR spectra of $[\text{Co}(\text{SCL})_2](\text{Cl})_2$. FIGURE 7: IR spectra of $[\text{Co}(\text{TSCL})_2](\text{NO}_3)_2$. FIGURE 6: IR spectra of $[\text{Ni}(\text{SCL})_2](\text{Cl})_2$. FIGURE 8: IR spectra of $[\text{Ni}(\text{TSCL})_2](\text{NO}_3)_2$.

TABLE 2: Magnetic moment and electronic spectral data of complexes.

Complex	μ_{eff} (B.M.)	Electronic spectral data	
		ν_1 (cm^{-1}) ϵ ($\text{Lmol}^{-1} \text{cm}^{-1}$)	ν_2 (cm^{-1}) ϵ ($\text{Lmol}^{-1} \text{cm}^{-1}$)
$[\text{Co}(\text{SCL})_2](\text{Cl})_2$	2.04	17267	22800
$[\text{Co}(\text{SCL})_2](\text{NO}_3)_2$	1.93	17648	22523
$[\text{Ni}(\text{SCL})_2](\text{Cl})_2$	Diamagnetic	17856	22270
$[\text{Ni}(\text{SCL})_2](\text{NO}_3)_2$	Diamagnetic	17245	22948
$[\text{Co}(\text{TSCL})_2](\text{Cl})_2$	2.01	17112	22842
$[\text{Co}(\text{TSCL})_2](\text{NO}_3)_2$	1.85	17402	22845
$[\text{Ni}(\text{TSCL})_2](\text{Cl})_2$	Diamagnetic	17813	22613
$[\text{Ni}(\text{TSCL})_2](\text{NO}_3)_2$	Diamagnetic	17534	22400

chelation of the ligand through nitrogen of C=N group and sulphur of C=S group or oxygen of C=O.

3.7. Elemental Analysis Data and Molar Conductance of Metal Complexes. The metal contents (Table 1) were determined by the Atomic Absorption studies as shown in Figures 9 and 10. The C, H, and N contents in the metal complexes were

FIGURE 9: Calibration curve for Co metal complexes for Atomic Absorption studies. The solutions of cobalt complexes (10 ppm), that is, $[\text{Co}(\text{SCL})_2](\text{Cl})_2$, $[\text{Co}(\text{SCL})_2](\text{NO}_3)_2$, $[\text{Co}(\text{TSCL})_2](\text{Cl})_2$, and, $[\text{Co}(\text{TSCL})_2](\text{NO}_3)_2$, show the absorbance of 0.0396, 0.0362, 0.0374, and 0.0344, respectively. % of Cobalt = Absorbance $\times$ 10/Slope (where slope = 0.038).

FIGURE 10: Calibration curve for Ni metal complexes for Atomic Absorption studies. The solutions of nickel complexes (10 ppm), that is, $[\text{Ni}(\text{SCL})_2](\text{Cl})_2$, $[\text{Ni}(\text{SCL})_2](\text{NO}_3)_2$, $[\text{Ni}(\text{TSCL})_2](\text{Cl})_2$, and $[\text{Ni}(\text{TSCL})_2](\text{NO}_3)_2$, show the absorbance of 0.0520, 0.0475, 0.0492, and 0.0451, respectively. % of Nickel = Absorbance $\times$ 10/Slope (where slope = 0.050).

TABLE 3: Influence of ligands and metal complexes on the initiation of lipid peroxidation.

Ligands/complexes	Percent of control
SCL	98
$[\text{Co}(\text{SCL})_2](\text{Cl})_2$	82
$[\text{Co}(\text{SCL})_2](\text{NO}_3)_2$	86
$[\text{Ni}(\text{SCL})_2](\text{Cl})_2$	72
$[\text{Ni}(\text{SCL})_2](\text{NO}_3)_2$	77
TSCL	96
$[\text{Co}(\text{TSCL})_2](\text{Cl})_2$	76
$[\text{Co}(\text{TSCL})_2](\text{NO}_3)_2$	79
$[\text{Ni}(\text{TSCL})_2](\text{Cl})_2$	58
$[\text{Ni}(\text{TSCL})_2](\text{NO}_3)_2$	63

analyzed by the Elemental Analyzer and are tabulated in Table 1. The molar conductance measurements (Table 1) of the complexes in DMSO correspond to 1:2 electrolytic nature (Shakir et al. [16]). On the basis of elemental analysis data and molar conductance of the complexes, the metal complexes may be formulated as $[\text{ML}_2]\text{X}_2$ (where $\text{M} = \text{Co}(\text{II})$, $\text{Ni}(\text{II})$; $\text{X} = \text{Cl}^-$, NO_3^-).

3.8. Magnetic Moment and Electronic Spectral Data of Metal Complexes. At room temperature $\text{Ni}(\text{II})$ complexes show diamagnetic character and $\text{Co}(\text{II})$ complexes show magnetic moment in the range 1.85–2.04 B.M. (Table 2) corresponding to one unpaired electron. These values correspond to low spin configurations of the metal complexes. The electronic spectrum of chloride and nitrate complexes shows electronic spectral bands in the range 17100–17900 cm^{-1} and

22400–22800 cm^{-1} corresponding to the following transitions: $\nu_1: {}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, $\nu_2: {}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ which indicates the square planar geometry of the complexes.

3.9. TG-DTA Data of Metal Complexes. All the metal complexes show major weight loss above 175°C which shows that they are free of any entrapped water. The peaks due to melting of complexes in TG-DTA curve agree well with the melting point of the complexes as determined by the MP apparatus (Make: BUCHI, Model: M-560).

4. Antioxidant Activity

4.1. Assay of Initiation of Lipid Peroxidation. The details of the assay procedure are described in the earlier communication (Raj et al. [17]). The reaction mixture in a final volume of 2 mL consisted of 0.025 M Tris-HCl (pH 7.5), microsomes (1 mg protein) which were taken from the laboratory of Prof. H. G. Raj, Department of Biochemistry, VP Chest Institute and were prepared by adopting the method of Ernster and Nordenbrand [18] (protein was assayed by the method of Lowry et al. [19]), 3 mM ADP, and 0.15 mM FeCl_3 . The tubes were preincubated for 10 min at 37°C followed by the addition of the test compounds added at a concentration of 100 μM in 0.2 mL of DMSO and then again incubated for 10 min at 37°C. The reaction was started by the addition of 0.5 mM NADPH for initiation of enzymatic lipid peroxidation and incubated for different intervals. The reaction was terminated by the addition of 0.2 mL of 50% TCA followed by addition of 0.2 mL of 5 N HCl and 1.6 mL of 30% TBA. The tubes were heated in an oil bath at 95°C for 30 min, cooled, and centrifuged at 3000 rpm. The intensity of the colour of the thiobarbituric acid reactive substance (TBRS) formed was read at 535 nm. The lipid peroxidation was found to be linear up to 15 min under the conditions described here. The results (Table 3) illustrate the influence of ligands and metal complexes on the initiation of lipid peroxidation enzymatically. These results clearly indicate that metal complexes have higher antioxidant activities as compared to the schiff's base ligands. Thiosemicarbazone metal complexes show higher antioxidant activities than semicarbazone metal complexes. Moreover, nickel metal complexes show higher antioxidant activities than cobalt metal complexes.

5. Antibacterial Activity

The antibacterial activities of the metal complexes were determined at different concentrations (30 $\mu\text{g}/\text{disc}$) against different pathogenic bacteria (Table 4) by using disc diffusion technique and the results were compared with standard antibiotic, Kanamycin (30 $\mu\text{g}/\text{disc}$). It was found that the metal complexes were active against all of the test bacteria but the metal complexes $[\text{Co}(\text{TSCL})_2](\text{NO}_3)_2$ and $[\text{Ni}(\text{TSCL})_2](\text{NO}_3)_2$ were most effective against all pathogenic bacteria as shown in Table 4. The zones of inhibition of the complexes were, however, lesser as compared to standard Kanamycin. The metal complexes have higher antibacterial activities as compared to the Schiff's base

TABLE 4: Antibacterial activity of ligands and metal complexes.

Test organism	Diameter of zones of inhibition (mm)									
	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆	M ₇	M ₈	L ₁	L ₂
<i>Escherichia coli</i>	8	7	8	7	13	14	12	15	2	2
<i>Klebsiella species</i>	6	5	5	4	14	16	14	17	4	5
<i>Shigella sonnei</i>	7	4	6	8	12	15	13	14	3	4
<i>Bacillus subtilis</i>	9	6	8	5	12	14	14	16	3	3

M₁: [Co(SCL)₂](Cl)₂; M₂: [Co(SCL)₂](NO₃)₂; M₃: [Ni(SCL)₂](Cl)₂; M₄: [Ni(SCL)₂](NO₃)₂; M₅: [Co(TSCL)₂](Cl)₂; M₆: [Co(TSCL)₂](NO₃)₂; M₇: [Ni(TSCL)₂](Cl)₂; M₈: [Ni(TSCL)₂](NO₃)₂; L₁: SCL; L₂: TSCL.

ligands. Thiosemicarbazone metal complexes show higher activities than semicarbazone metal complexes.

6. Conclusions

The present work describes the facile synthesis of metal complexes with newly synthesized Schiff base ligands and their biological activity. On the basis of elemental analysis data, molar conductance, magnetic susceptibility measurements, IR, and atomic absorption spectral studies, the resulting metal complexes may have square planar geometry and may be formulated as [ML₂]X₂ (where M = Co(II), Ni(II); X = Cl⁻, NO₃⁻). The metal complexes show higher antioxidant and antibacterial activities as compared to the ligands. The nickel complexes derived from 2-acetyl coumarone thiosemicarbazone show remarkable antioxidant and antibacterial activities.

Acknowledgments

The authors are thankful to the Principal, Zakir Husain College, Delhi, and the Principal, Government Science & Commerce College, Benazeer, Bhopal, for providing research facilities.

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