Spectrochimica Acta Part A 76 (2010) 22–28

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, characterization and physiochemical information, along with antimicrobial studies of some metal complexes derived from an ON donor semicarbazone ligand

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ARTICLE INFO

Article history:
Received 6 October 2009
Received in revised form 21 February 2010
Accepted 26 February 2010

Keywords:
Benzaldehyde
Semicarbazone
^{1}H and ^{13}C NMR
EPR studies
Antimicrobial studies

ABSTRACT

Eight new transition metal complexes of benzaldehyde-*N*(4)–phenylsemicarbazone have been synthesized and characterized by elemental analyses, molar conductance, electronic and infrared spectral studies. In all the complexes, the semicarbazone is coordinated as neutral bidentate ligand. ^{1}H NMR spectrum of $[Zn(HL)_2(OAc)_2]$ shows that there is no enolisation of the ligand in the complex. The magnetic susceptibility measurements indicate that Cr(III), Mn(II), Fe(III), Co(II) and Cu(II) complexes are paramagnetic and Ni(II) is diamagnetic. The EPR spectrum of $[Mn(HL)_2(OAc)_2]$ in DMF solution at 77 K shows hyperfine sextet with low intensity forbidden lines lying between each of the two main hyperfine lines. The g values calculated for the $[Cu(HL)_2SO_4]$ complex in frozen DMF, indicate the presence of unpaired electron in the $d_{x^2-y^2}$ orbital. The metal ligand bonding parameters evaluated showed strong in-plane σ bonding and in-plane π bonding. The ligand and complexes were screened for their possible antimicrobial activities.

1. Introduction

The chemistry of transition metal complexes of the semicarbazone ligands has been receiving considerable attention because of their biological relevance [1–7]. Semicarbazones are compounds with versatile structural features and can coordinate to the metal either as a neutral ligand or as a deprotonated anion. Semicarbazones exist in two tautomeric forms, keto (A) and enol (B) (Scheme 1). The coordination possibilities in semicarbazones are increased if the substituents of the aldehyde or ketone include additional donor atoms. The π-delocalization and the configurational flexibility of their molecular chain can give rise to a great variety of coordination modes [8].

Herein, we report the synthesis, spectral characterization and antimicrobial studies of eight metal complexes of benzaldehyde-*N*(4)–phenylsemicarbazone. The structure of the semicarbazone ligand (HL) is given (Scheme 2).

2. Experimental

2.1. Materials

The solvents used for the synthesis of semicarbazone complexes were purchased from Merck and used without further purification. *N*(4)-Phenylsemicarbazide (Sigma–Aldrich), benzaldehyde (Merck) were of reagent grade and were used as received. Spectrograde solvents were used for spectral recording.

2.2. Synthesis of the semicarbazone (HL)

A methanolic solution of *N*(4)-phenylsemicarbazide (0.151 g, 1 mmol) was refluxed with benzaldehyde (1 mmol) in methanol containing three to four drops of dilute acetic acid for 3 h (Scheme 3). On slow evaporation, colorless crystals of the compound separated out. It was filtered, washed with ether and dried over P_4O_{10} *in vacuo*. The compound was recrystallized from methanol (m.p. 176 °C, yield 75%). The elemental analysis data (Table 1) are consistent with the formula of the compound. The IR, UV–vis., ^{1}H and ^{13}C NMR data of the compound are discussed along with the complexes.

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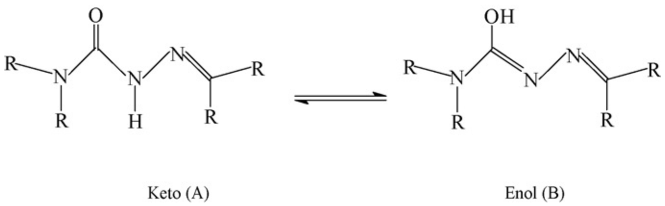
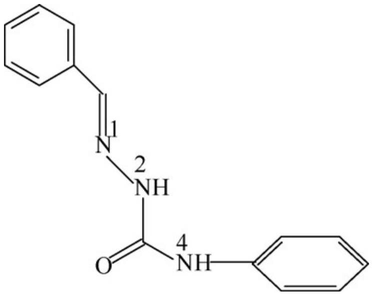
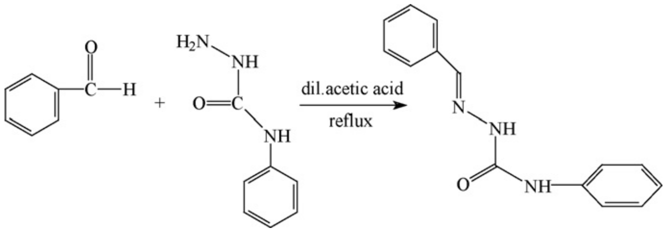
doi:10.1016/j.saa.2010.02.035



Scheme 1.



Scheme 2.



Scheme 3.

2.3. *Synthesis of complexes*

The complexes were prepared by refluxing 1 mmol each of appropriate salt with 2 mmol of HL in methanol for 5 h. On slow evaporation, the compounds formed were filtered, washed with methanol and dried *in vacuo* over P_4O_{10}.

2.4. *Physical measurements*

Analysis of carbon, hydrogen and nitrogen content of the semicarbazone and its complexes were carried out on a Vario EL-III CHN Elemental Analyzer at the SAIF, Cochin University of Science and Technology, India. Infrared spectra were recorded on a PerkinElmer Infrared Spectrometer using KBr pellets in the range 4000–400 cm^{-1}. Electronic spectra were recorded in methanol on a Shimadzu UV-2450 UV-visible Spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded using Bruker DRX – 500 NMR Spectrometer, with $CDCl_3$ as solvent and TMS as the standard at NIIST, Thiruvananthapuram, India. The magnetic susceptibility measurements were carried out at the Indian Institute of Technology, Roorkee, at room temperature in the polycrystalline state on a PAR model 155 Vibrating Sample Magnetometer at 5 kOe field strength. EPR spectra of complexes in solid state at 298 K and in frozen DMF at 77 K were recorded on a Varian E – 112 Spectrometer at X-band, using TCNE as marker with 100 kHz modulation frequency and 9.1 GHz microwave frequency at the SAIF, IIT, Mumbai, India. The molar conductances of the complexes in methanol solutions (10^{-3} M) at room temperature were measured using a Systronics direct reading conductivity meter.

3. Results and discussion

3.1. *Analytical measurements*

The colors, partial elemental analyses, molar conductivities and magnetic susceptibility values are presented in Table 1. The elemental analyses data are consistent with the molecular formula. The complexes are soluble in DMF, $CHCl_3$ and DMSO. The conductivity measurements were made in methanol solutions and all the complexes were found to be non-electrolytes. However, we could not isolate single crystals of suitable quality for X-ray diffraction studies for any of these complexes.

3.2. *Magnetic susceptibilities*

Room temperature magnetic susceptibility studies reveal complexes **1**, **2**, **3**, **4** and **6** to be paramagnetic. In Cr(III) and Mn(II) complexes the magnetic moments are found to be 3.29 and 5.12 B.M., respectively. The room temperature magnetic moment of Mn(II) is consistent with manganese in the +2 oxidation state,

Table 1
Colors, partial elemental analyses, molar conductivities and magnetic moments of benzaldehyde-*N*(4)–phenylsemicarbazone and its metal complexes.

Compound	Color	Composition % found (calc)			λ_m^a	μ_m^b (B.M.)
		Carbon	Hydrogen	Nitrogen		
HL	Colorless	70.24 (70.27)	5.45 (5.48)	17.72 (17.56)		
$[Cr(HL)(OAc)_3]$ (**1**)	Pale blue	51.24 (51.28)	4.74 (4.74)	8.96 (8.97)	10.1	3.29
$[Mn(HL)_2(OAc)_2]$ (**2**)	Brown	58.99 (59.01)	3.34 (3.38)	12.88 (12.91)	10.6	5.12
$[Fe_2(HL)_4(SO_4)_3]$ (**3**)	Brown	49.53 (49.56)	3.85 (3.87)	12.68 (12.39)	8.3	3.42
$[Co(HL)(OAc)_2]$ (**4**)	Pale green	51.89 (51.93)	4.63 (4.61)	10.03 (10.09)	13.3	2.04
$[Ni(HL)(NO_3)_2]$ (**5**)	Brown	39.80 (39.85)	3.07 (3.11)	16.63 (16.60)	6.1	Diamagnetic
$[Cu(HL)_2SO_4]$ (**6**)	Brown	52.63 (52.69)	4.81 (4.11)	13.09 (13.17)	11.3	1.82
$[Zn(HL)_2(OAc)_2]$ (**7**)	Pale yellow	58.01 (58.05)	4.13 (4.58)	12.11 (12.69)	3.4	Diamagnetic
$[Cd(HL)_2(NO_3)_2]$ (**8**)	Colorless	46.91 (47.04)	3.74 (3.67)	15.53 (15.68)	9.3	Diamagnetic

[a] Molar conductivity, 10^{-3} M methanol at 298 K.
[b] Magnetic susceptibility per metal atom.