

Synthesis and Characterization of Transition Metal(II) Complexes with Heterocyclic Thioamides

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Some new complexes of Fe(II), Ni(II), Zn(II), Cd(II) and Hg(II) have been synthesized with bidentate cyclic ligand with donor atom N and S of the dibenzofuran series. The complexes were characterized by chemical analyses like UV, visible, IR, EPR and NMR spectral analyses alongwith conductivity and magnetic susceptibility measurement. Sulfur and nitrogen atoms of ligands are involved in the coordination to the metal ions(II).

Key Words: Dibenzofuran, Thioamide heterocyclic ligands and Schiff base.

INTRODUCTION

During the last few years, the coordination chemistry has been enriched considerably due to the synthesis and characterization of a large number of four coordinated square-planar complexes of transition elements in which the metal ion is coordinated by sulfur. In some previous work¹⁻⁴ a theoretical consideration on behaviours of sulfur as a donor atom have been presented. It results from papers that the behaviour of donor atoms, including sulfur exhibit vacant *d*-orbitals, able to accept "*d*" electrons of the metal ions and forming *d*_π-*d*_π bonds. Particular attention has been paid to the complex compounds formed by transition metals with thioamides that act as bidentate ligands using both sulfur and nitrogen as donor atoms⁵⁻⁹.

The purpose of the present work is study on the structure of some new complexes of metal ions with *d*⁶⁻¹⁰ electronic configuration. Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with heterocyclic ligands containing donor atoms nitrogen and sulfur, the thioamide 3-(2'-thiofuoroilamino) dibenzofuran (TFADBF)¹⁰ by taking into account that the results of elements analysis, UV-VIS, IR, EPR and NMR spectral analyses alongwith conductivity and magnetic susceptibility measurements are in agreement with the proposed structure of the complexes.

EXPERIMENTAL

All chemicals used were AR grade: FeSO₄·(NH₄)₂SO₄·6H₂O(BDH), CoCl₂·6H₂O (Merck), NiCl₂·6H₂O (Merck),

CuCl₂·2H₂O (Merck) ZnCl₂ (BDH), CdCl₂(BDH), HgCl₂ (Merck) and TFADBF (double recrystallized).

Preparation of the complexes: 0.02 M thioamide 3-(2'-thiofuoroilamino)dibenzofuran (TFADBF) in ethanol solution was added (drop wise with continuous stirring) to an aqueous ethanolic solution of the corresponding metal salt (0.02 M) in a 1:2 molar ratio. The mixture was gently stirred for 1 h and then left at room temperature for 3 h. The precipitated metal complexes were filtered and recrystallized using ethanol and ether mixture. Finally, the pure product was isolated from the reaction flask, washed with ethanol and then with dried ether and finally dried under reduced pressure.

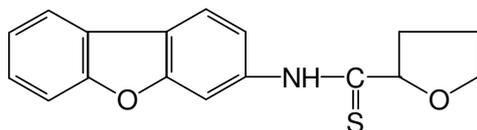
Physical measurements: The IR spectra were recorded on a Perkin-Elmer FT-1600 Hewlett Packard instruments in dry KBr pellets, the electronic spectra were obtained in 10⁻³ M acetone solution with a Unicam UV-2300 spectrophotometer. X-Band EPR spectra were recorded in powder form at the room temperature under Art-5 EPR spectrometer. The modulation of magnetic field being 100 KHz using Mn²⁺ as an internal standard. Both ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-300 B.B. The molar conductivities were measured by using OK-102 conductivity meter at 25 °C. The magnetic susceptibility measurements were performed on a Gouy balance at room temperature.

RESULTS AND DISCUSSION

The complexes obtained were microcrystalline coloured powders, whose melting points are higher than that of the pure thioamide. They are stable at room temperature and their molar

conductivities showed that all the complexes are non-electrolyte with $\lambda = 0.88 - 1.97 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ in DMF (10^{-4}M) solution at room temperature analytical and physico-chemical data of these complexes are given in Table-1.

A comparative interpretation of the IR spectral data (Table-2) suggests that TFADBF act as a bidentate ligand in the investigated complex compound using both sulfur and nitrogen as donor atoms.



TFADBF

Proposed structure of synthesized ligand

The ligand bands at 3220, 3060 and 1600 cm^{-1} characteristic for $\gamma(\text{NH}_2)$ and $\delta(\text{NH}_2)$ appear in complexes at lower frequencies and more flattened. These changes indicate the coordination of the nitrogen with the metal ions. The position of thioamide band I [$\nu(\text{CN}) + \delta(\text{CH})$] at 1460 cm^{-1} in the spectrum of the ligand is not shifted appreciably in the spectra of the complexes, while the position of thioamide band II [$\nu(\text{CN}) + \delta(\text{C-H}) + \nu(\text{C=S})$] of the ligand at 1360 cm^{-1} suffered a considerable shift towards higher wave number side in the complexes at 1410-1390 cm^{-1} .

The thioamide band III [$\nu(\text{CN}) + \nu(\text{C=S})$] at 1210 cm^{-1} in the spectra of the complexes and the thioamide band IV assigned for [$\nu_s(\text{C=S}) + \nu_{as}(\text{C=S})$] at 740 cm^{-1} in the spectrum of the ligand is shifted to the lower wave number side in its complexes. These changes confirmed that the sulfur participates in bonding to the metal ions¹¹. The metal complexes are also characterized by the appearance of some new bands

of medium and low intensity at 460-420 cm^{-1} which can be assigned to $\nu(\text{M-N})$ stretching frequencies¹². A band due to the coordinated water appears in the spectrum of the Fe(II) complexes around 890 and 3500 cm^{-1} .

The magnetic moment value of $[\text{Fe}(\text{TFADBF})\text{Cl}_2(\text{H}_2\text{O})_2]$ is 4.86 BM which indicates that the complexes is spin-free and it has octahedral geometry. The electronic spectrum shows a broad absorption band at 602 nm which may be assigned to the ${}^5\text{T}_{2g} \rightarrow {}^5\text{T}_{eg}$ transition.

For $[\text{Co}(\text{TFADBF})\text{Cl}_2]$, the magnetic moment value is 2.20 BM and its electronic spectrum displays two bands at 594 and 464 nm which may be assigned to the transitions ${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{A}_{1g} \rightarrow {}^2\text{E}_g$, respectively in a square planar configuration¹³.

As far as $[\text{Ni}(\text{TFADBF})\text{Cl}_2]$ is concerned it appears to be diamagnetic and its electronic spectrum exhibits four bands at 471, 330, 299 and 262 nm. The first and the second band are of low intensity, being purely $d-d$ transitions assigned to ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$ and ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$ transitions, respectively. The third band is developed by a strong charge transfer transition while the fourth one is due the inter ligand interactions $\pi \rightarrow \pi^*$. These results also suggests a square planar configuration around the transition metal ion¹⁴.

The room temperature magnetic moment value is 1.92 BM for $[\text{Cu}(\text{TFADBF})\text{Cl}_2]$ indicating the presence of one free electron. The electronic spectrum displays three spectral bands at 691, 485 and 378 nm. The first band corresponds to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition and the third band being assigned to a charge transfer transition. All these observations lead to the conclusion that the geometry is also square planar. The compound $[\text{Cu}(\text{TFADBF})\text{Cl}_2]$ offers a very intense EPR spectrum with an anisotropic parameters $g^{\parallel} = 2.2404$ and $g^{\perp} = 2.0704$ in agreement with the d^9 electronic configuration for Cu(II) in this square-planar complex compound¹⁵.

The absorption bands appearing in the UV-domain are considered to be the characteristic of the ligand. The assignment

TABLE-1
ANALYTICAL AND PHYSICO-CHEMICAL DATA OF COMPLEXES

Compound	Colour	m.p. ($^{\circ}\text{C}$)	Molar cond. ^a ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (BM)	Metal (%) found/(calcd.)
$[\text{FeLCl}_2(\text{H}_2\text{O})_2]$	Red	168	1.97	4.86	12.75 (12.52)
$[\text{CoLCl}_2]$	Red	182	0.88	2.20	13.58 (13.93)
$[\text{NiLCl}_2]$	Brown	154	1.29	Diamagnetic	13.41 (13.88)
(CuLCl_2)	Orange	139	1.54	1.92	14.69 (14.85)
$[\text{ZnLCl}_2]$	Yellow	148	1.93	Diamagnetic	15.07 (15.33)
$[\text{CdLCl}_2]$	Brown	163	1.08	Diamagnetic	23.73 (23.60)
$[\text{HgLCl}_2]$	Yellow	175	1.32	Diamagnetic	35.84 (35.52)

TABLE-2
IR BANDS (cm^{-1}) OF TFADBF

TFADFA	$\text{FeLCl}_2(\text{H}_2\text{O})_2$	CoLCl_2	NiLCl_2	CuLCl_2	ZnLCl_2	CdLCl_2	HgLCl_2	Assignments
—	3448	—	—	—	—	—	—	$\nu(\text{OH})$ water
3220	3218	3204	3200	3208	3210	3200	3206	$\nu(\text{NH}_2)$
3060	3055	3010	3000	3028	2997	2980	3012	$\nu(\text{N-H})$
2900	2880	2875	2890	2888	2847	2852	2896	$\nu(\text{C-H})$
1600	1580	1605	1598	1610	1607	1590	1604	$\delta(\text{NH}_2)$
1460	1475	1468	1466	1472	1462	1470	1460	Thioamide band I
1360	1390	1405	1398	1395	1400	1410	1408	Thioamide band II
1210	1200	1205	1200	1215	1200	1202	1204	Thioamide band III
—	800	—	—	—	—	—	—	Coordinated water
740	720	722	715	710	718	722	708	Thioamide band IV
—	465	475	468	470	458	463	472	$\nu(\text{M-N})$

of $n \rightarrow \pi$ and $\pi \rightarrow \pi^*$ transitions as being due to the (C=S) bond was made based on Sandstrom's investigations¹⁶.

The UV electronic spectra of [Zn(TFADBF)Cl₂], [Cd(TFADBF)Cl₂] and [Hg(TFADBF)Cl₂] show the occurrence of an Cl₂ absorption characteristics of $\pi \rightarrow \pi^*$ transitions shifted by hypsochromic effect.

The ¹³C NMR spectrum of the free ligand shows a signal at $\delta = 195.2$ ppm due to the carbon atom from the C=S group. In the spectra of its complex compounds with Zn(II), Cd(II) and Hg(II), the signal appears at lower values of the magnetic field (189-191 ppm) proving the involvement of the sulfur atom in the coordination. The ¹H NMR spectrum shows a signal at $\delta = 12.24$ ppm corresponding to the proton in the imino (-NH) group. It appears that δ at 0.2-0.7 ppm shifted in the spectra of the complex compounds, indicate the involvement of nitrogen atoms in the coordination. Therefore, the coordinative δ -bands are due to the sulfur and nitrogen atoms in the thioamidic group.

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