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Studies on coordination Compounds of Co(II), Cu(II), Ni(II), Cd(II), Zn(II) 3d-Transition Metal Ions with Acylthiosemicarbazide

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Abstract

The synthesis of some coordination compounds of N^1-[4-(4-brgmophenylsulfonyl) benzoyll-N^4-(4-methylphenyl) thiosemicarbazide (BrATS) with $CuC1_2$, Cu $(CH_3COO)_2$, $Cu(SCN)_2$, $Co(CH_3COO)_2$, $Ni(CH_3COO)_2$, $Cd(CH_3COO)_2$ and $ZnC1_2$ are described. The characterization of the complexes has been performed with the help of various physicoOchemical techniques viz., IR, EPR, electronic spectroscopy, magnetic moments, thermogravimetric analysis, molar conductance and elemental analysis; Experimental data confirm the molar combination ratio M:L =1:1 or 1:2 for the synthesized complexes. Room temperature ESR spectra of Cu(II) complexes yield (g) values characteristic of distorted octahedral and square-planar geometry.

Keywords: Acylthiosemicarbazide, Co(H), Ni(II), Cd(H), Zn(II) Complexes, ESR spectra

Introduction

The coordination compounds of the metallic ions with the 1,4-substituted thiosemcarbazides constitute an interesting study both from the point of view of the adopted structure, as for the most important practical applications in various fields, from technical to medical. It was proven that these complex combinations have several biological properties i.e., antibacterial [1], antifungal [2] and antitumour [3]. Acylthiosemicarbazibe contains oxygen, sulphur and nitrogen as potential donor atoms and is liable to form deprotonated complexes by loss of hydrazinic proton via enolization /thiolization. The acylthiosemicarbazide can also act as neutral ligand via oxygen or sulphur atoms (Fig.1).

A special attention was given to the complex formation of to copper, due to both its bactericide and bacteriostatic properties of the ligand, as well as to the very familiar role of the Cu(II) ion in biological systems [4].

In this paper, the synthesis and characterization of Co(II), Cu(II), Ni(II), Cd(II) and Zn (II) complexes with the ligand N^1-[4-(4-bromophenylsulfonyl)benzoyl]-N^4-(4-methylphenyl) thiosemicarbazide (BrATs) is presented in Fig. 2.

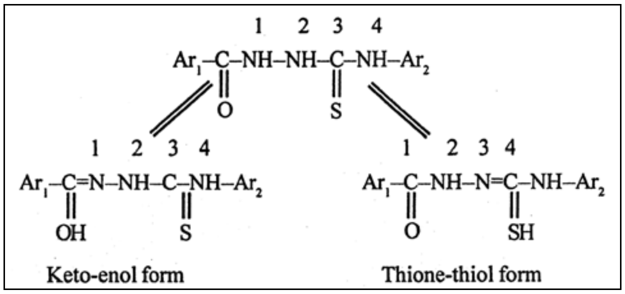


Fig 1: Tautomeric forms for acylthiosemicarbazide

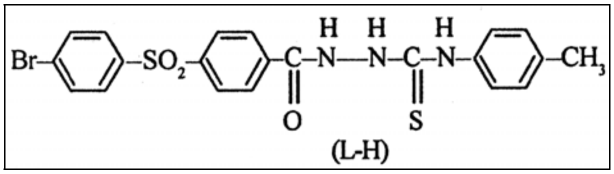


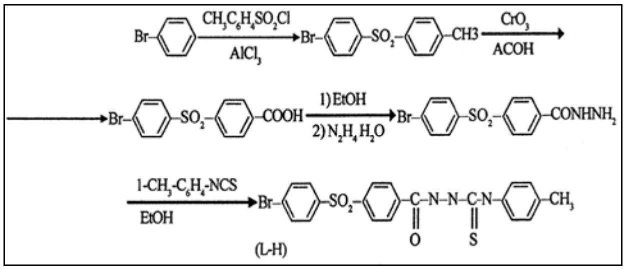
Fig 2: Struicture of the ligand

Experimental

The reagents used were of commercial products (Merck or Chimopar Bucharest). Chemical elemental analyses were done with Carlo-Erba La-118 microdosimeter, for C, N, S and an AAs-IN Cart-Zeiss-Jena spectrometer for metallic ions. Molar conductivities of the complexes were measured in DMSO (3×10^{-3} M), at room temperature using OK-102/1 Radelkis conductivity instrument. Electronic spectra were recorded using a Jasco V-550 spectrophotometer, in diffuse reflectance mode, using MgO dilution matrices. IR spectra (KBr Pellets) were recorded in the 4000-400 cm^{-1} region with BioRad FTS135, spectrophotometer. Therma analysis has been carried out with a TGA V5.1A DuPont 2000 derivatograph. ESR spectra were registered on a ART-6-IFIN type spectrophotometer, equipped with a field modulation unit at 100 kHz. The measurements were done in the X band on micro-crystalline powder at room temperature using DPPH as standard. The melting points were determinate with Boetius apparatus and are uncorrected.

n**Synthesis of ligand:** The BrATS(L-H) was synthesized by

Synthesis of ligand: The BrATS(L-H) was synthesized by following the method described in literature [5] (Scheme-I):



Scheme-I: Synthesis of ligand

Colour : Light-yellow, Yield: 92%, m.p.: 192-194 °C, m.f. $C_{21}H_{17}N_3O_3S_2Br$.

Synthesis of the metal complexes: An enthanolic solution of metallic ion salt (1m mol in 5 mL ethanol) was mixed with stirring with a hot clear solution of the ligand (BrATS) (0.504g, 1m mol) in ethanol (20 mL). After refluxing the solution for 1-2 h, the obtained precipitate was filtered under vacuum, washed successively with water, hot ethanol, cold ethanol and diethyl lether and finally dried under vacuum, For the synthesis of Co(II), Ni(II), Cd(II) complexes were used acetate salts, for Zn(II) complex, chloride salt and for Cu(II) complexes were used chloride, acetate and thiocyanate salts (in this case the salt of the metallic ion*was dissolved in 5.mL NH3 25%).

The values of the molar conductivities of the synthesized combinations and some physical properties of the complexes are reported in Table–I.

Table I: Analytical and Physical Data of the Synthesized Complexes

Compound	Colour	Yield (%)	A ($\Omega^{-1}Cm^2$ mol^{-1})
$[Cu(L–H)_2(H_2O)_2]$	Green	79	3.07
$[Cu(L–H)_2(AcO)_2(H_2O)_4]$	Dark Green	78	2.74
$[Cu(L–H)(SNC)(H_2O)]$	Green	65	2.20
[Co(L–H)(AoC)]	Yellow Green	83	3.70
[Ni(L–H)(AoC)]	Kaki	88	3.17
[Cd(L–H)(AoC)]	Yellow White	69	4.70
$[Zn(L–H)_2]$	Yellow	81	5.23

The data for the elemental analysis for the complex combinations thus obtained confirm the molar ratio M:L =1:1 or 1:2. All the solid complexes are stable in air, are soluble in DMF and DNSO, but insoluble in other organic solvents. The molar conductivity of the complexes in 10^{-3} M DMSO were found to be 2.74–5.23$\Omega^{-1}cm^2mol^{-1}$ and suggesting their non-electrolytic nature [6].

Results and Discussion

The thermal analyses for compounds 1-7 are similar. The elimination of ligands takes place in the 240-610^{0}C range, in two consecutive, sometimes cumulated, steps. For the complexes of Cu(II) the lattice water is eliminated in the domain 110–250 ^{0}C. The data obtained from the IR spectra, both for the ligand as well as for the obtained complexes are presented in Table-2

Table-2: IR spectral (cm^{-1}) bands of the ligand and its metal complexes

Compound	$v(N^4H)$	$v(N^2H)$	$v(N^1H)$	$v(N^1–N^2)$	v(C=O)	v(C–O)	v(C–S) v(C=S) + v(C=M)	v(C=N)	v(C–S)	$v(SO_2)$
BrATS(L–H)	3439	3326	3291	1010	1680	–	751 1257	–	–	1156
$[Cu(L–H)_2(H_2O)_2]$	3450	3271	–	1010	–	1428	758 1246	1610	–	1158
$[Cu(L–H)_2(AcO)_2(H_2O)_4]$	3453	3284	–	1010	1526	1425	756 1224	1598	–	1162
$[Cu(L–H)(SNC)(H_2O)]$	3440	3265	–	1011	–	1429	757 1248	1604	–	1162
[Co(L–H)(AoC)]	3457	3280	–	1009	1513	1419	752 1223	1600	–	1156
[Ni(L–H)(AoC)]	3457	3271	–	1010	1543	1430	759 1228	1600	–	1159
[Cd(L–H)(AoC)]	3557	3283	–	1010	1514	1428	754 1224	1570	–	1158
$[Zn(L–H)_2]$	3478	–	3172	1009	1590	–	–	1572	674	1150

In the IR spectra of the ligand there were identified the absorption bands v(C-O) at 1680 cm^{-1}, v(C=S) at 751 cm^{-1}(C=s)+v(C=N) at 1257 cm^{-1}, $v(N^1H)$ at 3291 cm^{-1} as well as a series of bands characteristic to the benzene nuclei from the ligand structure.

In the IR spectrum of the complex $[Cu(L–H)_2(H_2O)]$ is observed the shift of the 1680 cm^{-1} frequency attributed to the v(C=O) vibration, the disappearance of the band from 3291 cm^{-1} attributed to the $v(N^1H)$ vibration, due to the deprotonation by complexation and the occurrence in the spectra of the complex combinations of a relatively intense band at ca. 1610 cm^{-1}, due to the stretching modes of the C=N bond. The occurrence of these frequencies indicates the bidentate mono-negative coordination of the ligand.

For the complex $[Cu_2(LH)_2(AcO)_2(H_2O)_4]$ in the IR spectrum there occur two extra bans at 1526 and 1425 cm^{-1} characteristic for v(C=O) and v(C–O), the difference between the two frequencies, Δ, being of ~101 cm^{-1}, indicating the bridge coordination of the acetate ion [7].

In the spectrum of the complex [Cu(L-H)(SCN)(1420)] there occur two absorption bands at 681 and 432 cm^{-1}. specific to the coordination of the ligand to the metallic ion by the sulphur atom of the SCN^{-1} group.

In the spectrum of the complexes [Co(L-H)(AcO)], [Ni(L-H)(AcO)], [Cd(L-H) (AcO)] are found the absorption bands specific to the groups C=O and C–O, v(C=O) 1513 cm^{-1}, v(C-O)1419 cm^{-1} for [Co(L-H)(AcO)]; v(C=O) 1543 cm^{-1}, v(C–O) 1430 cm^{-1} for [Ni(L-H) (AcO)] and v(C=O) 1514

cm^{-1}, ν(C-O)1428 cm^{-1} for [Cd(L-H)(AcO)], indication the bidentate coordination of the acetate group.

For the complex $[Zn(L\text{-}H)_2]$ in the IR spectrum it is noticed the disappearance of the vibration frequency ν(N^2H) and shift towards lower wave numbers of the vibration frequency specific to the group C=O at 1590 cm^{-1}, as well as the shifting of the vibration frequency ν(C=S) and of the associated band ν(C=S) + ν(C=N). In the IR spectrum of this complex there occurs a band specific to the vibration frequency ν(C=N) at 1572 cm^{-1} and one characteristic for the vibration frequency ν(C-S) at 674 cm^{-1}. The occurrence of these frequencies indicates the mono negative bidentate coordination of the ligand by the sulphur atom and the nitrogen atom N^1. The coordination manner of the ligands to the metallic ion was appreciated in agreement with the literature information [8–10].

From the study of the electronic spectra of the complexes with Zn(II) and Cd(II) in the visible field, it is not observed the occurrence of an absorption band. This is a characteristic of the complexes of the metallic ions d^{10}, explained by the ligands field theory. The absorption bands that occur in the UV field are specific for the electronic transitions intra-ligand of the type n–π*, –* with a bathochrome movement from the absorption bands of the free ligand (Table-3).

In the electronic spectrum of the complex $[Cu(L\text{–}H)_2(H_2O)_2]$ there are observed two absorption bands at 14705 and 11210 cm^{-1}, assigned to the transitions $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$, respectively, which indicates an octahedral geometry[11]. The value of the magnetic moment of 2.16 BM is specific for one unpaired electron. The relatively high value of the magnetic moment, found for this complex, indicates also an orbital contribution at the momentum of spin, specific for an octahedral arrangement. The electronic spectra of $[Cu_2(L\text{-}H)_2(AcO)_2(H_2O)_4]$ exhibit three bands observed at 11240, 13157 and 15503 cm^{-1} which may be assigned to $d_{x^2-y^2} \rightarrow d_{z^2}, d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xz,yz}$ transition, respectively, due to the distorted octahedral (D4h) geometry around Cu(II). For this complex it is observed that μeff <2 (1.22BM) which indicates an anti-rerromagnetic interaction between the 2 copper centers. The UV-Vis spectrum of $[Cu(L\text{–}H)(SCN)(H_2O)]$ diplays a broad band at 14256 cm^{-1} and a well-defined shoulder around 21915 cm^{-1} attributable to $d_{x^2-y^2}$ d_{xy} and $d_{x^2-y^2}$ $d_{xy,yz}$, transitions which strongly favour square-planar geometry around the central metal ion.

From the values of the d-d transitions, assigned based on literature data [12], in the case [Co(L-H)(AcO)], it may be appreciated that the metallic ion (Co(II) forms with L-H a distorted tetrahedral complex combination. This statement is confirmed as well by the value of the magnetic momentum (4.56 BM), proving the correctness of the assignment of the absorption bands from the electronic spectrum of this combination.

Table-3: Reflection spectra for the ligand and complexes

Compound	Frequencies	Assigning		Geometry	μeff (BM)
BrATS(L–H)	2770 39370	n π	π*, π*	–	–
[Cd(L–H)(AcO)]	26385 36764	n π	π*, π*	Distorted Tetrahedral	–
$[Zn(L\text{–}H)_2]$	25503 31948	n π	π*, π*	Distorted Tetrahedral	–
$[Cu(L\text{–}H)_2(H_2O)_2]$	11120 14705	$d_{x^2-y^2}$ $d_{x^2-y^2}$	d_{z^2} d_{xy}	Octhedral	2.16
$[Cu_2(L\text{–}H)_2(AcO)_2(H_2O)_4]$	11240 13157 1503	$d_{x^2-y^2}$ $d_{x^2-y^2}$ $d_{x^2-y^2}$	d_{z^2} d_{xy} $d_{xy}d_{yz}$	Distorted Octhedral	1.22
$[Cu(L\text{–}H)(SCN)(H_2O)]$	14265 21915	$d_{x^2-y^2}$ $d_{x^2-y^2}$	d_{xy} $d_{xy}d_{yz}$	Square–planar	1.52
[Cd(L–H)(AoC)]	10128 16310	$^4A_2$ $^4A_2$	$^2T_1(F)$ $^2T_1(P)$	Distorted Tetrahedral	4.56
[Ni(L–H)(AcO)]	14556 23980	$d_{x^2-y^2}$ $d_{x^2-y^2}$	d_{xy} $d_{xy}d_{yz}$	Square–planar	Dimagnetic

The complex [Ni(L-H)(AcO)] has a square-planar geometry, proven by the absorption band in visible from 23880 cm^{-1}, assigned to the transition $d_{x^2-y^2}$ $d_{xz,yz}$. Also, in the electronic spectrum of this complex combination it is observed as well an absorption band at 14556 cm^{-1}, assigned to the transition $d_{x^2-y^2}$ d_{xy}, which confirms the square-planar geometry [13]. The magnetic susceptibility determinations effected for this complex combination show its diamagnetic character, being an additional proof that the adopted geometry is square-planar (Table-3).

The EPR spectral data for the coordination compounds of the Cu(II) ion, $[Cu(L\text{-}H)_2(H_2O)_2]$, $[Cu_2(L\text{-}H)_2(AcO)_2(H_2O)_4]$ and $[Cu(L\text{-}H)(SCN)(H_2O)]$, respectively, indicate values of the tensor {g} that confirm the nature of the ground state, $d_{x^2-y^2}$. The ESR spectra were done on crystalline powder at room temperature and in Table-4 are presented the values of the {g} parameters.

Table 4: Values of the {g} parameters for the Cu(II) combinations

Compound	g_{iso}	G_{II}	g?	G
$[Cu(L\text{–}H)_2(H_2O)_2]$	2.17	–	–	–
$[Cu_2(L\text{–}H)_2(AcO)_2(H_2O)_4]$	–	2.15	2.07	2.14
$[Cu(L\text{–}H)(SNC)(H_2O)]$	–	2.40	2.09	4.44

For the coordination compound [$Cu(L\text{-}H)_2(H_2O)_2$], the spectrum presents one signal relatively isotropic, which confirms once again the octahedral geometry of the Cu(II) ion.

The ESR spectra for copper compound [$Cu_2(L\text{-}H)_2(AcO)_2(H_2O)_4$] give the following values: G_{II} = 2.15 and $G_{4\%}$ = 2.07. Because geometrical parameter G<R, it is taken into consideration the existence for some exchange interactions between the two copper centers or super-exchange interactions by, the acetate group, in a distorted octahedral (D_{4h}) geometry [14].

In square-planar [$Cu(L\text{-}H)(SCN)(H_2O)$], the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving 2B1g as the ground state with gn>g4%>2. From the observed values it is clear that g_{II} = 2.40 > $g_{4\%}$ = 2.09 > 2 and the ESR parameters of the complex coincide well with related systems which suggest that the complex has square-planar geometry and the system is axially symmetric. According to Hathaway [15], if the value of G is larger than four, exchange interaction is negligible because the local axes are misaligned. For this compound, the value is 4.44, which suggests that the local tetragonal axis is aligned parallel or slightly misaligned and consistent with $d_{x^2-y^2}$ ground state.

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