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TRANSITION METAL COMPLEXES OF HETEROCYCLIC LIGANDS. PART VI. COMPLEXES OF 5- HYDROXY – 6- MERCAPTO-BENZO[a]PHENAZINE WITH Co(II), Ni(II), Cu(II), Zn (II) AND Cd(II)

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ABSTRACT

The paper reports the conclusions about the structure of five new complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the heterocyclic ligand, 5- hydroxy –6- mercapto – benzo[a] phenazine (H_2L). These were obtained by elemental analysis, IR, UV-VIS and EPR spectral analysis, conductivity and magnetic susceptibility measurements and thermal analysis. Bacteriological studies revealed that the ligand and the complexes possess moderate antimicrobial activity.

KEYWORDS : heterocyclic ligand; antibacterial activity; thermal decomposition; activated energies; transition metal complexes

RESUMO

Foi determinada a estrutura de cinco complexos novos do ligante heterocíclico 5-hidroxi-6-mercapto-benzo(a)fenazina (H_2L) com Co(II), Ni(II), Zn(II), Cu(II) e Cd(II). Foram usadas técnicas de análise elementar, infravermelho, ultravioleta-visível, RPE, condutividade, susceptibilidade magnética e análise térmica. Estudos bacteriológicos indicaram que o ligante e os complexos possuem atividade antimicrobial.

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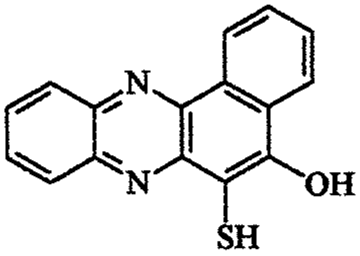
INTRODUCTION

Metallic complexes of heterocyclic ligands are of considerable interest from the structural point of view and, also, as a consequence of their applications *e.g.* in analytical chemistry, in polymer industry and, specially, in medical-biological systems, where their bacteriostatic and cytostatic properties are useful [1].

In continuation of our earlier studies on the study of such complexes [2], we report here the synthesis and characterization of the products obtained by the reaction of 5- hydroxy –6- mercapto – benzo[a]phenazine (H_2L) [3], with Co(II), Ni(II), Cu(II), Zn (II) and Cd(II).



H_2L

The bacteriostatic activity of the ligand and its complexes was determined against selected bacteria.

EXPERIMENTAL PROCEDURE

All chemical used were of analytical grade: $Co(OAc)_2 \cdot 4H_2O$ (Merck, p.a.); $Ni(OAc)_2 \cdot 4H_2O$ (Merck, p.a.); $Cu(OAc)_2 \cdot H_2O$ (Merck, p.a.); $Zn(OAc)_2 \cdot 2H_2O$ (Merck, p.a.) and $Cd(OAc)_2$ (Merck, p.a.).

The ligand was doubly recrystallized from ethanol.

The IR spectra were recorded on a BIO RAD FTS 135 instrument in anhydrous KBr pellets in the range 400-4000 cm^{-1}. An Unicam UV2-300 spectrometer was used to obtain electronic spectra. The molar conductivities were determined using an OK - 102 Radelkis conductivity meter. The magnetic susceptibility measurement was made with a Faraday balance at room temperature. The thermogravimetric curves were traced with derivatograph MOM 1500-D (10°C/min). The EPR spectrum was registered on a Art –5 – Ifin Bucharest spectrometer, that operates in the X band, the modulation of magnetic field being 100 kHz, using Mn^{2+} as an internal standard.

The complexes were prepared by mixing ethanolic solutions of metal acetate with 5-hydroxy –6- mercapto – benzo[a]phenazine in a 1:1 molar ratio and an adequate pH. The resulting solution was gently refluxed for one hour at 100°C. The reaction mixture was left at room temperature for six hours. Then, the corresponding metal complexes precipited. They were filtered, washed with ethanol and dried in an oven at 100-110°C.

RESULTS AND DISCUSSIONS

The complexes obtained were microcrystalline colored powders. They are stable at room temperature and their solubilities in common inorganic and organic solvents are medium.

The elemental analysis data for C, H, N and S showed that the complexes prepared are of the type $[M(HL)_2] \cdot EtOH$ where M=Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and HL=the mono-anion of the ligand. The molar electric conductivities are in the range λ=10.0-15.2 Ω^{-1} cm^2mol^{-1} in DMF (10^{-3}M) solutions at room temperature, which means that all the complexes are non-electrolytes.

The important bands (cm^{-1}) observed in the infrared spectra of the ligand and the metal complexes were as follows:the ligand shows absorption band at 3400 cm^{-1} characteristic for ν_{OH} which appears in complexes at lower frequencies (3435-3440 cm^{-1}). This decrease indicates the coordination of the oxygen atom with the metal ion. The absorption band observed at 2550 cm^{-1} in the spectrum of the ligand due to ν_{SH}, disappeared in the complexes, indicating the deprotonation of thiol group and coordination of the sulphur atom with the metal ion. Another significant change in the IR spectra of metal complexes was the appearance of $\nu_{C\text{-}OH}$ band between 1125-1130 cm^{-1} as compared to 1140 in the ligand, thus showing a shift towards lower region by 10-15 cm^{-1}. This decrease indicated the existence of hydroxyl group and the coordination of oxygen atom. The metal complexes were also characterized by the appearance of some new bands of medium and low intensity at 440-450 cm^{-1}, which could be assigned to $\nu_{M\text{-}O}$ stretching frequencies. The absorption band observed at 685 cm^{-1} in the spectrum of ligand appeared at 655-662cm^{-1}, thus showing a shift towards lower regions. This band was characteristic of $\nu_{C\text{-}S}$, and its shift supported the coordination of sulphur atom.

In conclusion, 5-hydroxy-6-mercapto-benzo[a]phenazine acts as a monoanionic bidentate ligand in the complex compounds investigated.

The information referring to the geometry of the complexes was obtained from the electronic spectra in solution and from values of the magnetic moments.

The UV spectrum of the ligand reveals two bands assigned to the transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. These transitions were also found in the spectra of the complexes but shifted to lower frequencies ($\Delta\nu$=1500-3000 cm^{-1}), confirming the coordination of the ligand to the metal ions.

The magnetic moment value of the Co (II) complex is 3.08 MB. Its electronic spectrum displays two bands at 16400 and 21200 cm^{-1}, which may be assigned to $^2A_{1g} \rightarrow {}^2B_{2g}$ and $^2A_{1g} \rightarrow {}^2E_g$ transitions, respectively, in a square-planar configuration around Co(II)[4].

The Ni(II) complex is diamagnetic. The electronic spectrum of this chelate exhibited two bands at 18700 (ν_1), 20900 (ν_2), which are assigned to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively. These transitions are characteristic of compounds with a square - planar geometry for the Ni (II) ion[5].

The magnetic moment for the Cu(II) complex is 1.83 B.M. (close to the spin - only value of d^9 ion). The electronic spectrum displays two weak and broad bands around 21700 and 16800 cm^{-1} which may be assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively in a square- planar symmetry[4].

The EPR spectrum of the compound $[Cu(HL)_2] \cdot EtOH$ presents values for the anisotropic parameters as follows: $g_{\parallel}$=2.2014 and $g_{\perp}$=2.0102. Because $g_{\parallel} > g_{\perp}$ the line shape suggests a tetragonal geometry specific for Cu(II) in a square planar configuration[6].

The Zn (II) and Cd (II) complexes are diamagnetic. The electronic spectra exhibit two peaks in the UV domain due to $L \rightarrow L^*$ transitions only.

Thermal analyses were carried out for the Co(II), Ni(II) and Cu(II) complexes and the results are presented in Table 1. The agreement between experimental and theoretical mass loss for each of the complexes is within experimental error (±2%) and confirms the formula of the complexes.

Table 1. Thermal analysis data for the complexes.

Step	T_i (°C)	T_f (°C)	T^a (°C)	Δm^b (%)	T_V^c (°C)
$[Co(HL)_2]\cdot EtOH$					
1	58.3	102	78.5(+)	6.9	78.5
2	102	185.6	175(+)	22.76	125
3	185.6	340	260.8(-)	52.17	254.6
4	340	480.8	-	37.63	-
5	480.8	580.2	506.6(-)	50.48	506.6
6	580.2	665.3	-	51.2	-
7	665.3	780	-	56	-
8	780	995	-	67.2	-
$[Ni(HL)_2]\cdot EtOH$					
1	70.8	90.7	78.5(-)	6.83	78.5
2	90.7	175.7	-	7.12	-
3	175.7	240	240(+)	8.21	-
4	240	325	306.6(-)	12.83	300.4
5	325	373.4	370(-)	20.12	370
6	430	890	-	61.6	454.4
$[Cu(HL)_2]\cdot EtOH$					
1	73.5	82.8	78.5(+)	6.51	78.5
2	82.8	182.3	170(+)	32.15	154.08
3	182.3	240	-	34.42	233.6
4	240	313.6	-	36.17	299.2
5	313.6	479.4	320.6(+)	46.35	-
6	479.4	673.8	-	66.21	538.3
7	673.8	980	748.3(-)	73	-

[a] Endothermic (+) or exothermic (-) process
[b] Total mass losses
[c] The temperature when the speed of decomposition is maximum

The thermogravimetric curves proved again the existence of one molecule of ethanol in the structure of the complexes. The loss of this molecule takes place at 78.5°C which means that the ethanol is not chemically bound.

The mass losses of the TG and DTG curves indicate that the ligand is lost in two steps as a radical which is then stabilized through dimerization. Confirmation of this process has been obtained for case of the Ni(II) complex at room temperature by IR analysis of the evolved heterocycles of the cooled melt initially obtained at about 300°C, by collection.

The two steps in which are lost the two molecules of ligand have maximum of temperatures which are specified for each complex. In table 2 are presented these temperatures ΔT_1 and ΔT_2 and the activated energies of the thermal decomposition [7].

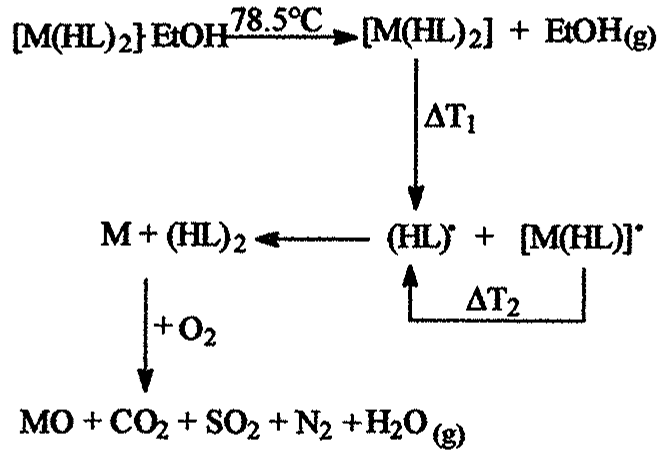
The activation energies have comparable values for the three complexes, but the temperatures are different, which means that the strength metal – ligand is not the same in these complexes. The bond is stronger in nickel complex (ΔT_1=300.4°C) but in radical complex $[Ni(HL)]^\bullet$, the breaking of the metal – ligand bond is achieved easier (ΔT_2=370°C) than in the case of $[Co(HL)]^\bullet$ and $[Cu(HL)]^\bullet$ complexes (ΔT_2=538.3°C, ΔT_2=500.6°C, respectively).

Table 2. The maximum of the temperatures ΔT_1 and ΔT_2 and the activation energies.

Complex	ΔT_1 (°C)	E'_a (kJ/mol)	ΔT_2 (°C)	E''_a (kJ/mol)
$[Co(HL)_2]\cdot EtOH$	125	98.12	506.6	50.2
$[Ni(HL)_2]\cdot EtOH$	300.4	94.24	370	40.96
$[Cu(HL)_2]\cdot EtOH$	154.08	87.97	538.3	42.19

The chemical analysis of the black final residue in each case, gave no indication of carbon, nitrogen, sulphur and hydrogen being present in the composition, and it was mainly identified as MO (where M=Co(II), Ni(II) and Cu(II)).

The general mechanism proposed for the thermal decomposition of the three complexes is one radicalic:



Base on the above observations, a structure in which metal ions in the complexes prepared with the sulphur and oxygen donating ligand have coordination number equal to 4, may be proposed.

Bacteriological Studies

Antibacterial activity of the ligand and its complexes was studied against S. aureus and E. coli by employing the diffusion method using streptomycin as control [8]. The ligand does not exhibit any remarkable activity (zone of inhibition < 8mm) while the complexes showed moderate activities (zone of inhibition 10-20 mm). The antibacterial activity was found to increase in the order: Ni>Co>Cu.

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