TEMPLATE CONDENSATION REACTIONS [1]
XI. Fe(II) AND Ni(II) COMPLEXES RESULTING IN THE SYSTEM BARBITURIC ACID - ETHYLENEDIAMINE

Elena Cristurean, Dana Marinescu, Rodica Olar *,
Mihaela Badea, Viviana Radulescu, Carmencita Ciomaga

abstract: New complexes with the general formula $[M_2LX_2]X_2 \cdot mH_2O$ (where L is the Schiff base resulting in [3+3] condensation of barbituric acid (BA) with ethylenediamine (en), (**1**) M=Fe, X= 1/2SO_4, m=2; (**2**) M=Ni, X= Cl, m=12) have been synthesised and characterised The bonding and stereochemistry of the complexes have been characterised by IR and electronic spectroscopy, magnetic data at room temperature and conductivity measurements.

Introduction

In the last years, a lot of work has been done on the synthesis of complexes with hydroxypyrimidine derivatives [2, 3]. Such compounds have polifunctional ligands that combine good coordination properties and hydrogen-bonding sites. It has been shown that barbituric acid can be implicated in condensation reaction that leads to complexes with saturated macrocyclic ligands [4-6]. As we reported [1], the condensation reaction of barbituric acid with ethylenediamine in presence of Cr (III) and Co (III) results in the formation of mononuclear complexes. In this paper, we have extended the study to complexes of Fe(II) and Ni(II) with the Schiff base resulting in template condensation of barbituric acid with ethylenediamine. The new complexes have the general formula $[M_2LX_2]X_2 \cdot mH_2O$ (L = Schiff base resulting in [3+3] condensation of barbituric acid with ethylenediamine ((**1**) M=Fe, X= 1/2SO_4, m=2; (**2**) M=Ni, X= Cl, m=12). The compounds were formulated as binuclear species on the basis of analytical, spectral and magnetic data.

Experimental

IR spectra were recorded in KBr pellets with an UR 20 Zeiss Jena instrument; *electronic spectra* were obtained by diffuse reflectance technique, using MgO as standard, with a VSU-2P Zeiss Jena instrument. *Magnetic measurements* were done by Faraday's method, at room temperature, using $Hg[Co(NCS)_4]$ as standard. *The conductivities* of 10^{-3} M DMSO or MeOH solutions of the compounds were measured with a Radelkis OK-120/1 (Hungary) conductivity bridge, at room temperature.

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* Department of Inorganic Chemistry, University of Bucharest, Dumbrava Rosie, 23, Bucharest, Romania

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Metal salts (Merck) were of analytical grade. The chemical analysis was performed by usual micromethods.

Preparation of the complexes

Compound $[Fe_2L(SO_4)_2]\cdot 2H_2O$ (**1**): To a solution of $FeSO_4\cdot 7H_2O$ (0.556 g, 2mmoles) in ethanol (100 cm^3) was slowly added ethylenediamine (0.2 mL, 3 mmoles) and barbituric acid (0.384 g, 3 mmoles); the reaction mixture was then refluxed 2 h until it results a sparingly soluble product, brown coloured. The compound was filtered off and washed several times with a small volume of cold ethanol and air dried. *Analysis found*: Fe, 14.2; N, 21.0; S, 8.1 %; *requires for* $Fe_2C_{18}H_{28}N_{12}O_9S$: Fe, 14.2; N, 21.0; S, 8.2 %; Λ_M(DMSO) = 10 $\Omega^{-1}cm^2mol^{-1}$ at 25^0C.

Compound $[Ni_2LCl_2]Cl_2\cdot 12H_2O$ (**2**): To a solution of $NiCl_2\cdot 6H_2O$ (0.475g, 2mmoles) in ethanol (100 cm^3) was slowly added ethylenediamine (0.4 mL, 6 mmoles) and barbituric acid (0.768 g, 6 mmoles); the reaction mixture was refluxed 10 h until it results a sparingly soluble product, light green coloured. The compound was filtered off and washed several times with a small volume of cold ethanol and air dried. *Analysis found*: Ni, 12.9; N, 17.9; Cl, 15.7 %; *requires for* $Ni_2C_{18}H_{48}N_{12}O_{15}$: Ni, 12.6; N, 18.0; Cl, 15.2 %; Λ_M(MeOH) = 413 $\Omega^{-1}cm^2mol^{-1}$ at 25^0C.

Results and discussions

In this paper, we report the preparation and physico-chemical characterisation of new complexes of Fe(II) and Ni(II) with the Schiff base (L) resulting in [3+3] condensation of barbituric acid with ethylenediamine. The attempt to isolate the free ligand by reaction of $[Ni_2LCl_2]Cl_2\cdot 12H_2O$ with potassium cyanide in ethanol failed.

The thermal weight loss proved that all the water present in the molecule of the complexes was lost in a single step until 140°C. This fact proves that the water molecules are equivalent and that only lattice water is present in these compounds.

The conductivity measurements in DMSO have indicated that complex (**1**) behaves as nonelectrolyte and complexe (**2**) as 1:2 electrolyte [7].

The most important IR absorption bands for the barbituric acid (BA) and for the isolated complexes (**1**) and (**2**) are given in the Table 1.

The most important remarks, which are available on the basis of spectral data, are as it follows:

(i) the IR spectra of the complexes exhibit the same pattern;

(ii) the absence of the absorption bands assigned to the NH_2 group stretching mode of ethylenediamine [8] in the complexes spectra and the appearance of the new bands at 1590÷1600 cm^{-1} that could be assigned to ν(C=N) vibration mode [9] reveals the fact that the condensation reaction involves all NH_2 function of amine;

(iii) the evidence of the bands characteristic of the amidic group [10, 11] at 1680 cm^{-1} (A I) and 1290÷1300 cm^{-1} (A III);

(iv) the fundamental vibrations associated with sulphate indicate their bidentate nature [12];

(v) the presence of water molecules in all compounds could be responsible for the appearance of a large medium band in the 3400÷3500 cm^{-1} range, assigned to ν(OH) stretching vibrations [13];

(vi) in the 400÷500 cm^{-1} range appear bands that could be assigned to ν(M-O) and respectively ν(M-N) stretching vibration [13].

Table 1. Absorption maxima (cm^{-1}) and assignments for barbituric acid (BA) and complexes (1) and (2)

BA	(**1**)	(**2**)	Assignments
–	3420bm	3420s	ν(OH)
3220s 3100s	3220s 3100m	3240s 3100s	ν(NH)
2920m	2920m	2920m	$\nu_{ass}(CH_2)$
2810m	2840m	2835m	$\nu_{sym}(CH_2)$
1685vs	1680s	1680s	ν(C=O) (A I)
–	1590vs	1600s	ν(C=N)
1280m	1290m	1300m	ν(C–N)+ δ(NH) (A III)
–	1210s 1090vs	–	$\nu_1(SO_4)$
–	785m	760m	$\rho(CH_2)_2$
–	590m	–	$\nu_4(SO_4)$
–	445w 400w	460w 430w	ν(M-O)+ ν(M-N)

These modifications indicate that the two species contain the Schiff base resulting in condensation of barbituric acid with ethylenediamine (Fig. 1).

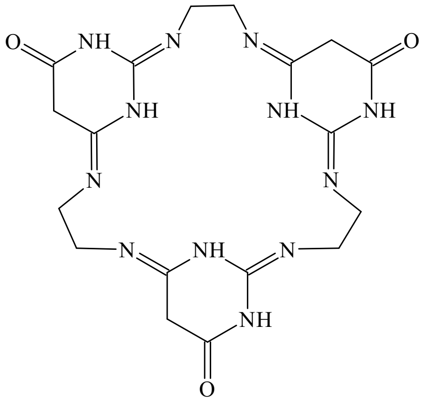

Fig. 1: *The Schiff base resulting in condensation of barbituric acid with ethylenediamine (L)*

Electronic spectral data of the complexes are presented in Table 2. These data revealed an octahedral stereochemistry for both ions [14].

Table 2. UV-vis spectral and magnetic moment data of the complexes (1) and (2)

Complex	Absorption maxima (cm^{-1})	Assignments
$[Fe_2L(SO_4)_2]\cdot 2H_2O$ (**1**)	28570 10750 9175	CTLM $^5T_2 \rightarrow {}^5E$
$[NiLCl_2]Cl_2\cdot 12H_2O$ (**2**)	25000 14490 9524	$^3A_2 \rightarrow {}^3T_1$ $^3A_2 \rightarrow {}^3T_2$ $^3A_2 \rightarrow {}^3T_2$

The band assigned to the spin allowed transition $^5T_2 \rightarrow {}^5E$ for Fe(II) ($3d^5$) is splited in two components due to the Jahn-Teller effect. The solid state d-d spectrum of (**2**) shows three characteristic bands of Ni(II) in an octahedral environment, as is show in Fig. 2. The 10Dq value (9524 cm^{-1}) fall within the range observed for a $[Ni(II)N_4Cl_2]$ chromophore [14]. The shape of spectrum and absence of splitting of ν_1 and ν_2 in complex indicates *cis*- rather *trans* - $[Ni(II)N_4Cl_2]$ chromophore.

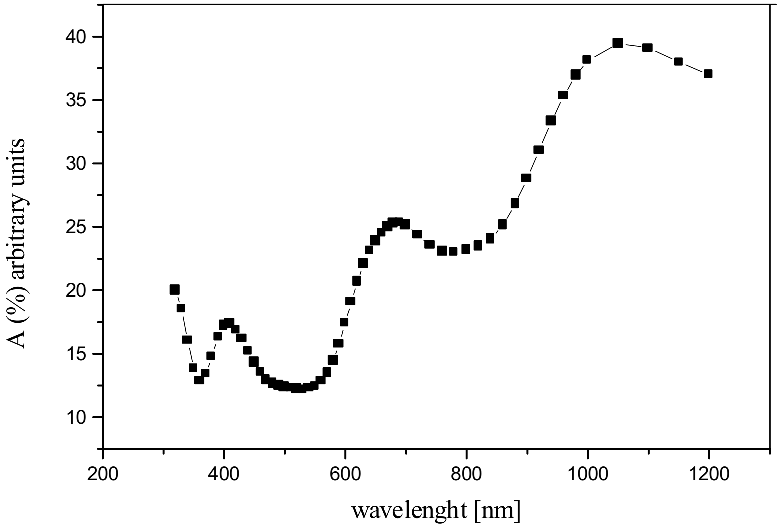

Fig. 2: *Electronic spectrum of the complex (2).*

The room-temperature $(\chi_M T)_{HT}$ experimental values for complexes (Table 3) are slightly lower than the theoretic values suggesting an interaction between paramagnetic centres.

Table 3. Magnetic data for compounds (1) and (2) at room temperature.

Complex	χT	
	calculated	experimental
$[Fe_2L(SO_4)_2]\cdot 2H_2O$ (**1**)	6.00	5.65
$[NiLCl_2]Cl_2\cdot 12H_2O$ (**2**)	2.00	1.82

Conclusions

Three new Fe(II) and Ni(II) complexes have been synthesised in [3+3] condensation reaction of barbituric acid with ethylenediamine.

The complexes were formulated as dinuclear species on the basis of chemical analysis, molar conductivity measurements, electronic and IR spectral data and also magnetic behaviour at room temperature.

All complexes adopt distorted octahedral stereochemistry.

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