

# TEMPLATE CONDENSATION REACTIONS <sup>1</sup>

## VIII. Cr(III), Ni(II) AND Cu(II) COMPLEXES RESULTING IN THE SYSTEM 5,5'-DIETHYLBARBITURIC ACID - ETHYLENEDIAMINE

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A series of new complexes of Cr(III), Ni(II) and Cu(II) with with general formula  $[ML(NO_3)_2](NO_3)_n \cdot mH_2O$  (where L is the Schiff base resulting in [3+2] condensation of 5,5'-diethylbarbituric acid (DEBA) with ethylenediamine (en), (1) M=Cr, n=1, m=2; (2) M=Ni, n=0, m=2; (3) M=Cu, n=0, m=3) have been synthesised and characterised. The free ligand has been isolated by treatment of Cu(II) complex with potassium cyanide. The bonding and stereochemistry of the complexes have been characterised by IR, EPR and, electronic spectroscopy, magnetic susceptibility at room temperature and conductivity measurements. The results concerning the thermal behaviour of complexes (2) and (3) are presented. The ligand behaves as tetradentate and coordinates through the azomethynic nitrogen atoms and nitrate behaves as monodentate.

### Introduction

The barbituric acid and his derivatives posses interesting biological [2] and coordinative properties, but there are known only few studies on coordination ability of these compounds. Recently, barbituric acid has been used as locking fragment in macrocyclization [3].

Our continuing interest in template condensation reactions led us to explore the possibility to generate ligands incorporating hydropyrimidine residues. Thus, as we reported [4], the [3+3] condensation reaction of 5,5'-diethylbarbituric acid with ethylenediamine in presence of Cr(III) and Co(III) result in the formation of binuclear complexes. In this paper, we have extended the study to complexes of Cr(III), Ni(II) and Cu(II) with the Schiff base resulting in template condensation of 5,5'-diethylbarbituric acid with ethylenediamine. We report here three new complexes with general formula  $[ML(NO_3)_2](NO_3)_n \cdot mH_2O$  (L = Schiff base resulting in [3+2] condensation of 5,5'-diethylbarbituric acid with ethylenediamine ((1) M=Cr, n=1, m=2; (2) M=Ni, n=0, m=2; (3) M=Cu, n=0, m=3). The complexes were formulated as mononuclear 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,

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at room temperature, using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as standard. The *molar magnetic susceptibilities* were calculated and corrected for the atomic diamagnetism. *EPR spectra* were recorded on microcrystalline samples at room temperature with a Varian E-9 spectrometer. The field was calibrated using crystalline diphenylpicrylhydrazyl ( $g=2.0036$ ). The *conductivities* of  $10^{-3}$  M DMF solutions of the compounds were measured with a Radelkis OK-120/1 (Hungary) conductivity bridge, at room temperature. *Thermal decomposition* was studied with a MOM (Budapest) derivatograph, type Paulik-Paulik-Erdey, in a static air atmosphere with a sample weight of 50 mg over the temperature range  $20\div 800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ .

Metal salts (Merck) were of analytical grade. The complexes  $[\text{Ni}(\text{NO}_3)_2]$  and  $[\text{Cu}(\text{NO}_3)_2]$  have been obtained as reported in literature [5, 6]. The chemical analysis was performed by usual micromethods.

### **Preparation of the complexes (1) ÷ (3)**

Compound  $[\text{CrL}(\text{NO}_3)_2](\text{NO}_3)\cdot 2\text{H}_2\text{O}$  (**1**): To a solution of  $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (0.40g, 1 mmole) in ethanol ( $50\text{ cm}^3$ ) was slowly added ethylenediamine (0.13 mL, 2 mmoles) and added 5,5'-diethylbarbituric acid (0.552g, 3mmoles); the reaction mixture was then refluxed 10h until it results a sparingly soluble, green coloured product. The compound was filtered off and washed several times with a small volume of cold ethanol and air dried. *Analysis found*: Cr, 5.2; N, 20.2%; *requires for*  $\text{CrC}_{28}\text{H}_{48}\text{N}_{13}\text{O}_{14}$ : Cr, 5.9; N, 20.8 %;  $\Lambda_{\text{M}}(\text{DMF}) = 140\ \Omega\cdot\text{cm}^2\text{mol}^{-1}$  at  $25^\circ\text{C}$ ;

Compound  $[\text{NiL}(\text{NO}_3)_2]\cdot 2\text{H}_2\text{O}$  (**2**): To a solution of  $[\text{Ni}(\text{NO}_3)_2]$  (0.303g, 1mmole) in ethanol ( $50\text{ cm}^3$ ) was added 5,5'-diethylbarbituric acid (0.552g, 3mmoles); the reaction mixture was then refluxed 8h until it results a sparingly soluble, green coloured product. The compound was filtered off and washed several times with a small volume of cold ethanol and air dried. *Analysis found*: Ni, 7.3; N, 20.3%; *requires for*  $\text{NiC}_{28}\text{H}_{48}\text{N}_{12}\text{O}_{13}$ : Ni, 8.4; Cl, 30.4; N, 8.0 %;  $\Lambda_{\text{M}}(\text{DMF}) = 8\ \Omega\cdot\text{cm}^2\text{mol}^{-1}$  at  $25^\circ\text{C}$

Compound  $[\text{CuL}(\text{NO}_3)_2]\cdot 3\text{H}_2\text{O}$  (**3**): To a solution of  $[\text{Cu}(\text{NO}_3)_2]$  (0.308g, 1mmole) in ethanol ( $50\text{ cm}^3$ ) was added 5,5'-diethylbarbituric acid (0.552g, 3mmoles); the reaction mixture was then refluxed 10h until it results a sparingly soluble product, green coloured. The compound was filtered off and washed several times with a small volume of cold ethanol and air dried. *Analysis found*: Cu, 6.8; N, 22.7%; *requires for*  $\text{CuC}_{28}\text{H}_{50}\text{N}_{12}\text{O}_{14}$ : Cu, 7.5; N, 23.0 %;  $\Lambda_{\text{M}}(\text{DMF}) = 5\ \Omega\cdot\text{cm}^2\text{mol}^{-1}$  at  $25^\circ\text{C}$ .

Compound L: To a solution of  $[\text{CuL}(\text{NO}_3)_2]\cdot 3\text{H}_2\text{O}$  (0.841g, 1mmole) in ethanol ( $100\text{ cm}^3$ ) was added potassium cyanide (0.25g, 4mmoles); the reaction mixture was then refluxed 4h until it results a sparingly soluble product. The compound was filtered off and washed several times with a small volume of cold ethanol and air-dried. *Analysis found*: C, 56.7%; N, 23.7%; *requires for*  $\text{C}_{16}\text{H}_{26}\text{N}_{12}\text{O}_{14}$ : C, 56.0%; N, 23.3 %.

## Results and Discussion

In this paper, we report the preparation and physico-chemical characterisation of three new complexes (1)÷(3) of Cr(III), Ni(II) and Cu(II) with the Schiff base (L) resulting in [3+2] condensation of 5,5'-diethylbarbituric acid with ethylenediamine. The free ligand was isolated by reaction of  $[\text{CuL}(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$  with potassium cyanide in ethanol.

By thermogravimetric analysis it was proved that all the water present in the molecule of the complexes (2) and (3) was lost in a single step in range 20÷145 °C, with the following weight loss: 4.8/4.4 (found/calcd.) for (2) and 6.7/6.4 (found/calcd.) for (3). This fact proves that the water molecules are equivalent and that only lattice water is present in these compounds. The oxidative degradation of this compound and nitrate decomposition was made in four steps in range 250÷750 °C with metal oxide as final residue.

The conductivity measurements in DMF have indicated that complex (1) behaves as 1:1 electrolyte and complexes (2) and (3) behave as nonelectrolytes in this solvent [7].

The most important IR absorption bands for the 5,5'-diethylbarbituric acid (DEBA) and for the isolated complexes (1) ÷ (3) are given in the Table 1.

**Table 1. Absorption maxima ( $\text{cm}^{-1}$ ) and assignments for 5,5'-diethylbarbituric acid (DEBA) and complexes (1) ÷ (3)**

DEBA	(1)	(2)	(3)	Assignments
–	3400bm	3500bm	3400bm	$\nu(\text{OH})$
3220s 3100s	3240m 3125m	3230s 3120s	3240s 3100s	$\nu(\text{NH})$
2960m	2920m	2920m	2940m	$\nu_{\text{ass}}(\text{CH}_2)$
2880m	2840m	2835m	2840m	$\nu_{\text{sym}}(\text{CH}_2)$
1760vs 1720vs 1685vs	1700vs	1690vs	1705vs	$\nu(\text{C=O})$ (A I)
–	1620vs 1600vs	1620vs 1590vs	1620m 1590vs	$\nu(\text{C=N})$
–	1510s 1350vs	1500m 1340s	1500m 1340s	$\nu_2(\text{NO}_3)$
1255s	1220m	1210m	1210m	$\nu(\text{C-N}) + \delta(\text{NH})$ (A III)
–	1060m	1050m	1050m	$\nu_1(\text{NO}_3)$
–	800m	780m	780m	$\nu_2(\text{NO}_3)$
700w	725w	730w	730w	$\rho(\text{CH}_2)$
–	680w	650w	660w	$\nu_4(\text{NO}_3)$
–	470w	470w	475w	$\nu(\text{M-O})$
–	435w	410w	430w	$\nu(\text{M-N})$

The spectra of 5,5'-diethylbarbituric acid and complexes **(1)** ÷ **(3)** are very complex. The most important remarks, which are available on the basis of spectral data, are as follows:

- (i) the IR spectra of the three complexes exhibit the same pattern;
- (ii) the absence of the absorption bands assigned to the  $\text{NH}_2$  group stretching mode of ethylenediamine [8] in the complexes spectra and the appearance of the new bands at  $1575\text{-}1620\text{ cm}^{-1}$  that could be assigned to  $\nu(\text{C}=\text{N})$  vibration mode [9] reveals the fact that the condensation reaction involves all  $\text{NH}_2$  function of amine;
- (iii) the evidence of the bands characteristic of the amidic group [10, 11] in the ranges  $1690\text{-}1705\text{ cm}^{-1}$  (A I) and  $1250\text{-}1280\text{ cm}^{-1}$  (A III) suggests that the condensation doesn't involve all carbonylic function of 5,5'-diethylbarbituric acid;
- (iv) the fundamental vibrations associated with nitrate indicate their monodentate nature [12];
- (v) the presence of water molecules in all compounds could be responsible for the appearance of a large medium band in the  $3400\text{-}3500\text{ cm}^{-1}$  range, assigned to  $\nu(\text{OH})$  stretching vibrations [13];
- (vi) in the  $400\text{-}500\text{ cm}^{-1}$  range appear bands that could be assigned to  $\nu(\text{M-O})$  and respectively  $\nu(\text{M-N})$  stretching vibrations [13].

In spectrum of the free ligand, the bands assigned to  $\nu(\text{C}=\text{N})$  vibration mode (at  $1600$  and respectively  $1635\text{ cm}^{-1}$ ) are shifted to higher wavenumbers by comparing spectra of complexes. This could indicate the ligand coordination to metal ion through azomethynic nitrogen.

These modifications indicate that all species contain the Schiff base resulting in [3+2] condensation of 5,5'-diethylbarbituric acid with ethylenediamine (Fig. 1) that acts as tetradentate ligand through the four azomethynic nitrogen. The fifth and sixth coordination sites are occupied by nitrate.

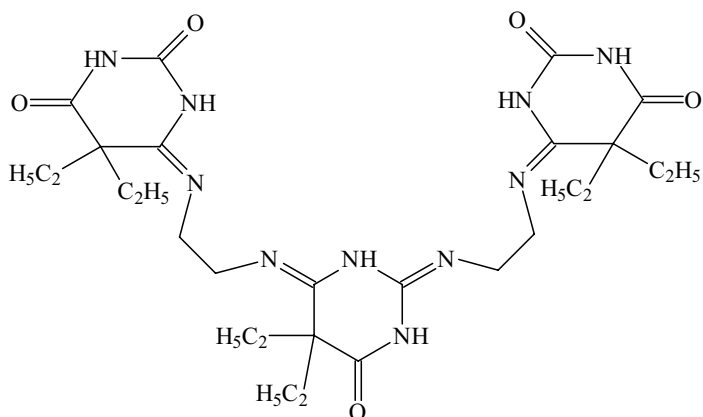


Fig. 1: The Schiff base resulting in [3+2] condensation of 5,5'-diethylbarbituric acid with ethylenediamine (L).

Electronic spectral data of the complexes (1) ÷ (3) are presented in Table 2. The electronic spectral data revealed an octahedral stereochemistry in all complexes [14]. Thus, the band at  $22730\text{ cm}^{-1}$  was assigned to the  $\nu_2$  and the absorption at  $16670\text{ cm}^{-1}$  to  $\nu_1$  transition for Cr(III) ( $3d^3$ ). The solid state d-d spectrum of (2) shows three characteristic bands of Ni(II) in an octahedral environment. The absence of splitting of  $\nu_1$  and  $\nu_2$  in complex indicates *cis*- rather *trans* -  $[\text{Ni(II)N}_4\text{O}_2]$  chromophore.

The electronic spectrum of Cu(II) complex (3) show a broad band centred at  $12580\text{ cm}^{-1}$  and shoulders at low energies.

**Table 2. UV-VIS spectral and magnetic moment data of the complexes (1) ÷ (3)**

Complex	Absorption maxima ( $\text{cm}^{-1}$ )	Assignments	B ( $\text{cm}^{-1}$ )	$\beta$	$\mu(\mu_B)$
[CrL(NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )·2H <sub>2</sub> O (1)	22730	$^4A_2 \rightarrow ^4T_1$	590	0.64	3.84
	16670	$^4A_2 \rightarrow ^4T_2$			
[NiL(NO <sub>3</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O (2)	25640	$^3A_2 \rightarrow ^3T_1$	979	0.94	3.10
	13890	$^3A_2 \rightarrow ^3T_1$			
	(8285)	$^3A_2 \rightarrow ^3T_2$			
	>26300	LMCT			
[CuL(NO <sub>3</sub> ) <sub>2</sub> ]·3H <sub>2</sub> O (3)	12580	$d_{xz}, d_{yz} \rightarrow d_z^2$			2.06
	10990	$d_{xy} \rightarrow d_z^2$			
	10200	$d_{x^2-y^2} \rightarrow d_z^2$			

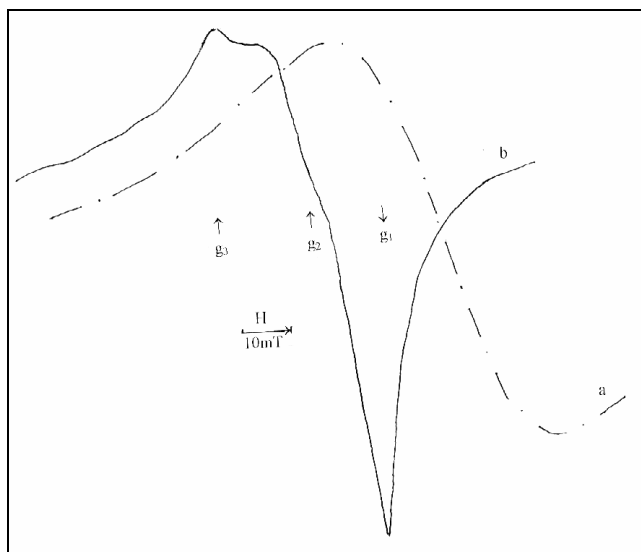


Fig. 2: EPR spectra of  $[\text{CrL}(\text{NO}_3)_2](\text{NO}_3)\cdot 2\text{H}_2\text{O}$  (1) (a) and  $[\text{CuL}(\text{NO}_3)_2]\cdot 3\text{H}_2\text{O}$  (3) (b).

The EPR spectrum of compound (1) shows a wide and isotropic signal ( $g_i=1.994$ ,  $a_i=42.5\text{ mT}$ ) characteristic for this ion in a distorted octahedral geometry [15]. For complex (3), the EPR spectrum (Fig.2) gives three  $g$ -values ( $g_1=2.077$ ,  $g_2=2.142$  and  $g_3=2.266$ ).

Such a spectrum with lowest  $g > 2.04$  can be observed for a Cu(II) ion in an elongated rhombic octahedral stereochemistry with all the axes parallel aligned [15÷17].

The room-temperature effective magnetic moments for complexes (Table 2) are close to the spin only value being in agreement with a mononuclear and distorted octahedral complex [18].

## Conclusions

Three new Cr(III), Ni(II) and Cu(II) complexes have been synthesised in [3+2] condensation reaction of 5,5'-diethylbarbituric acid with ethylenediamine. The free ligand was isolated by treatment of Cu(II) complex with potassium cyanide.

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

All complexes are adopting distorted octahedral stereochemistry. The Schiff base acts as tetradentate through the four-azomethinic nitrogen, the fifth and sixth coordination sites being occupied by nitrate.

## REFERENCES

1. Olar, R., Cristurean, E., Marinescu, D., Badea, M., and Ivan, L., (2000) *Sci. Bull. „Politehnica” University of Bucharest*, Series B **62**(3-4), 62-70.
2. Zotta, V., **Chimie farmaceutica**, (1985) Ed. Medicala, Bucuresti, 305-309.
3. Lampeca, Y. D., Prikhod'ko, A. I., Nazarenko, A.Y. and Rusanov, E. B., (1996) *J. Chem. Soc., Dalton Trans.*, 2017-2019.
4. Cristurean, E., Marinescu, D., Olar, R., Badea, M. and Dumbrava A., (1996) *Anal. Univ. „Ovidius” Constanta, Ser.Ing.*, **VII**, 6-11.
5. \*\*\* (1968) Gmelin's Handbuch der Anorganischen Chemie, Verlag Chemie, 57(C1).
6. Konyama, Y. and Lingafelter, E.C., (1964) *Acta Crystallogr.*, **17**, 1145-1149.
7. Geary, W.J., (1971) *Coord. Chem. Rev.*, **7**, 81-122.
8. Powell, D. B. and Sheppard, N., (1959) *Spectrochim. Acta*, 791-802.
9. Balaban, A.T., Banciu, M. and Pogany, I., (1983) **Aplicatii ale metodelor fizice in chimia organica**, Ed. Stiintifica si enciclopedica, Bucuresti, 13-36.
10. Desseyn, H. O., Herman, M. A., (1967) *Spectrochim. Acta* **23A**, 2457-2463.
11. Paul, R. C., Moudgil, A. K., Chadha, S. L. and Vasisht, S.K., (1978) *Ind. J. Chem.*, **8**, 1017-1023.
12. Hathaway, B. J., (1988) **Oxyanions in Comprehensive coordination chemistry**, vol 2, Elsevier, Amsterdam, London, New York, 413-434.
13. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, (1986) Wiley, New York, 227-231, 201-206.
14. Lever, A.B.P., (1984) **Inorganic Electronic Spectroscopy**, Elsevier, Amsterdam, London, New York, 417-429, 507-543, 554-572.
15. Pedersen, E. and Toftlund, H., (1974) *Inorg. Chem.*, 1603-1608.
16. Smith, T.D. and Pilbrow, J.R., (1979) *Coord. Chem. Rev.*, **13**, 173-207.
17. Hathaway, B.J. and Billing, D.E., (1970) *Coord. Chem. Rev.*, **5**, 143-167.
18. Brezeanu, M., Patron, L. and Andruh, M., (1986) **Combinatii complexe polinucleare**, Ed. Academiei RSR, Bucuresti, , 42-65.