TEMPLATE CONDENSATION REACTIONS [1]
IX. COMPLEX COMPOUNDS OF Cu(II) AND Ni(II) WITH A MACROCYCLIC LIGAND RESULTING IN THE CONDENSATION REACTION OF ETHYLENEDIAMINE AND PROGESTERONE

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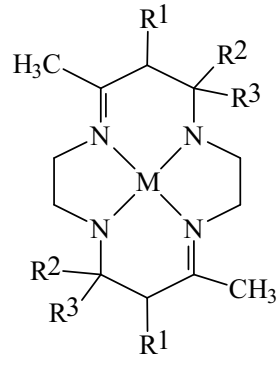
This paper deals data regarding the synthesis and the characterisation of two new complex compounds with the general formula $[MA](ClO_4)_2$ (where M is Ni(II) and respectively Cu(II) ion and A is the macrocyclic ligand resulted by the condensation reaction of progesterone with ethylenediamine). The complexes were formulated according to the chemical analysis, electronic and infrared spectra.

Introduction

This paper continues to reveal the compounds obtained by template condensation reactions [2÷7].

It has been proved that the reactions of the unsaturated α,β-ketones with 1,2-diaminoethane in the presence of metallic ions or an acid proton provide a convenient way to obtain tetraaza macrocyclic compounds with the general structure (**1**) [8].



(**1**)

In order to obtain new complexes with macrocyclic ligands, we have studied the condensation reaction of progesterone and $[Men_2]X_2$ (M: Ni(II) and Cu(II)).

This study gave us the possibility to isolate two new compounds with the general formula $[MA](ClO_4)_2$, where A is the macrocyclic ligand formed by the progesterone and ethylenediamine condensation.

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These compounds were formulated on the basis of chemical analysis, electronic and infrared spectra.

Experimental

Syntheses

1. [NiA]$(ClO_4)_2$. 0.25 g (1 mmole) [Nien$_2$Cl$_2$] was dissolved in 20 ml ethanol; separately, 0.63 g (2 mmoles) progesterone was dissolved in 20 ml ethanol. The mixture of the solutions was refluxed on a steam bath during 100 h. In order to precipitate the new compound, we added $NaClO_4$ and cyclohexane. The microcrystalline, light brown coloured, sparingly soluble product was filtered off in vacuum and washed with ethanol. *Chemical analysis. Found:* Ni 5.73; C 56.23; N 5.98%. *$NiC_{46}H_{72}O_{10}N_4Cl_2$ requires*: Ni 6.05; C 56.92; N 5.77%.

2. [CuA]$(ClO_4)_2$. 0.3 g (1 mmole) [Cuen$_2$]$(NO_3)_2$ and 0.63 g progesterone were dissolved separately, each in 20 ml ethanol. Following the same procedure as in the previous synthesis, it was obtained a reddish-brown microcrystalline, sparingly soluble product. *Chemical analysis. Found:* Cu 6.42; C 56.21; N 5,59%. *$CuC_{46}H_{72}O_{10}N_4Cl_2$ requires*: Cu 6.51; C 56.64; N 5.74%.

Chemical analyses were performed using the well-known micromethods.

The diffuse reflectance spectra were recorded in the range 350÷800 nm on a VSU2-P Zeiss Jena spectrophotometer, using MgO as standard.

The IR - spectra were recorded in the range 400÷4000 cm^{-1} with a UR29 Zeiss Jena spectrophotometer, using KBr pellets.

Results and Discussion

This paper deals with the possibility of condensation between the unsaturated α,β-ketones and the coordinated ethylenediamine.

It is well known that, usually, an unsaturated α,β-ketone reacts with a complex compound, which contains dynamic ligands, as the Scheme 1 shows.

Having in view these data, in the systems $[Men_2]^{2+}$ - $C_{21}H_{30}O_2$ (progesterone) the syntheses have been developed in the molar ratio 1:2.

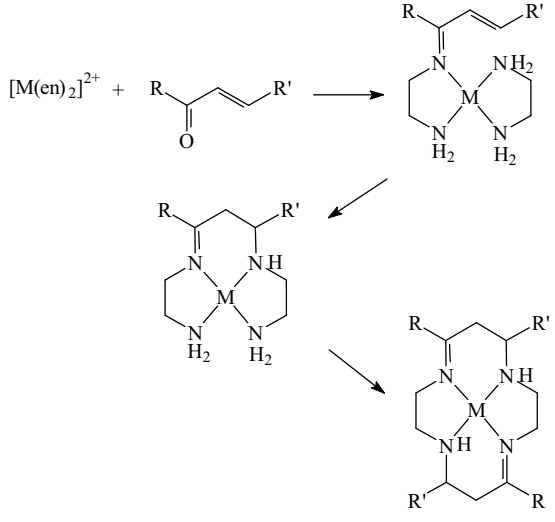
The new complexes were isolated as sparingly soluble, brown coloured products from the reaction medium, using sodium perchlorate and cyclohexane as precipitating agents.

On the basis of chemical analysis, the minimal formula correspond to:

$$[NiA](ClO_4)_2 \quad (2)$$

$$[CuA](ClO_4)_2 \quad (3)$$

where A is the macrocyclic ligand formed by the progesterone and ethylenediamine condensation.



Scheme 1.

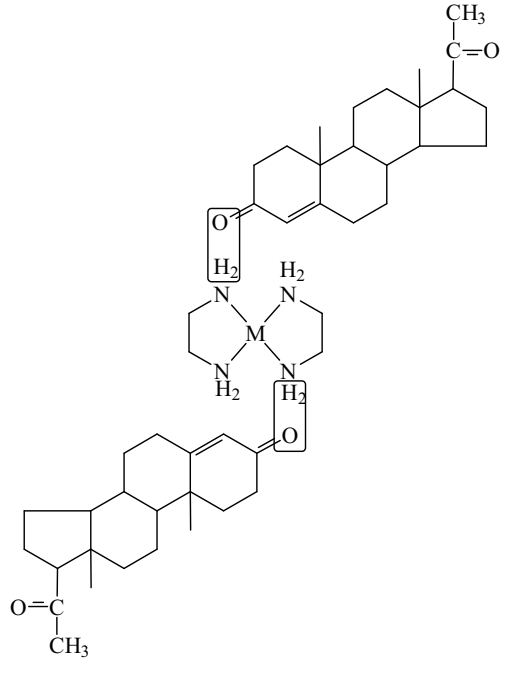
Infrared spectra. The IR-spectra of progesterone and complexes recorded within the 400÷4000 cm^{-1} range offer information about the nature of ligands and also about the nature of the donor atoms, according to the literature data [9, 10].

Table 1. Infrared spectra (cm^{-1})

$C_{21}H_{30}O_2$	$[NiA](ClO_4)_2$	$[CuA](ClO_4)_2$	Assignments
–	460 w	420 w	ν(M–N)
–	605 vs	600 i	$\nu_4(ClO_4)$
1045 w	1050 m	1070 m	$\rho(CH_3)$
–	1100 vs	1110 vs	$\nu_3(ClO_4)$
1150 s	1160 s	1150 s	ν(C–C) + δ(C–C)
1360 m	1360 m	1370 m	$\delta_s(CH_3)$
1460 m	1460 w	1460 w	$\delta_{as}(CH_3)$
1600 vs	–	–	ν(C=C) (unsaturated α,β–ketones)
1675 vs	–	–	ν(C=O) (unsaturated α,β–ketones)
1715 s	1720 m	1720 m	ν(C=O)
–	1740 m	1745 m	ν(C=N)
2870 m	2850 w	2860 w	$\nu_s(CH_3)$
2960 m	2940 w	2920 w	$\nu_{as}(CH_3)$
–	3380 m	3360 m	ν_s(NH)

The most important remarks that can be made of these spectra (Table 1) are the following:

- both of the complexes spectra contain almost all characteristic bands of progesterone, which proves that progesterone acts as ligand.
- yet, two of the characteristic bands are missing:
  - the band characteristic to the valence vibration ν(C=O) for unsaturated α,β-ketones disappeared and its place is taken by the band characteristic to the stretching vibration ν(C=N); this is also a proof that the condensation took place;
  - the second missing band is the one characteristic to the valence vibration ν(C=C), instead it appears the band characteristic to the secondary amine valence vibration ν(NH);
- in the 400÷500 cm^{-1} range there are absorption bands of weak intensity which can be assigned to the stretching vibration of M-N bond;
- both spectra of complexes contain the bands characteristic for the uncoordinated perchlorate ion.



Thus, the infrared spectra of these complexes suggest that the condensation between the carbonyl group of progesterone and ethylenediamine took place.

The intermediates resulted still have the primary amino- groups, which can bind to the unsaturated ketone by the β atom carbon of this. Finally, will result the complexes compounds with macrocyclic ligands.

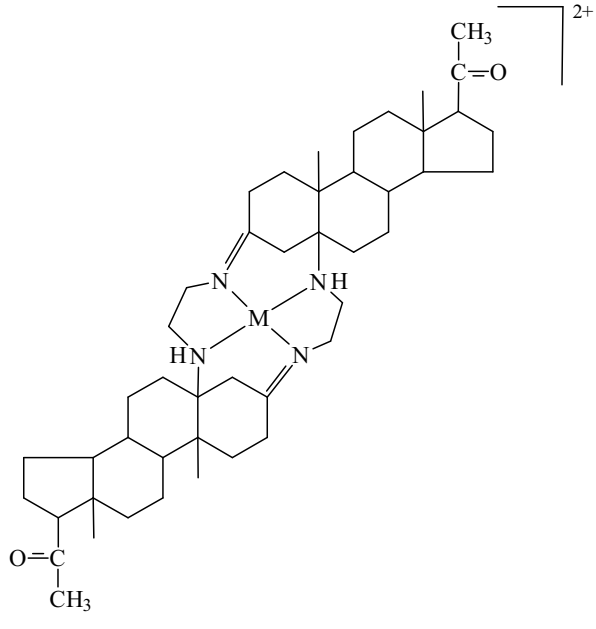
Electronic spectra. The examination of the diffuse reflectance spectra recorded within the 350÷800 nm range, offers the following informations about stereochemistry and coordination number of the complexes (Table 2), according to the literature data [11]:

Table 2. Electronic spectra $\bar{\nu}$ (cm^{-1})

Complex	Absorption maxima	Assignments
$[NiA](ClO_4)_2$	25770	CT
	20500	$^1A_{1g} \rightarrow {}^1E_g$
	18870	$^1A_{1g} \rightarrow {}^1A_{2g}$
	16400	$^1A_{1g} \rightarrow {}^1B_{1g}$
$[CuA](ClO_4)_2$	26300	CT
	22700	$^2B_{1g} \rightarrow {}^2A_{2g}$
	16400	$^2B_{1g} \rightarrow {}^2E_g$
	12500	$^2B_{1g} \rightarrow {}^2B_{2g}$

– for nickel complex (**1**) there were observed three bands in the 480÷700 cm^{-1} range, which were assigned according to a square-planar stereochemistry of the $3d^8$ Ni(II) ion. This is also in conformity with the reddish-brown colour of the combination;

– the Cu(II) complex (**2**) spectrum is dissimilar with the known square-planar compounds spectra.



As it results by correlating the data of chemical analysis, IR- and electronic spectra, the proposed formula of the new complexes are the following:

Conclusions

1. There were synthesised two new complexes with a macrocyclic ligand obtained by the condensation reaction of progesterone with ethylenediamine.
2. These new compounds are very important especially because their similar structure with the natural compounds.
3. These complexes were characterised on the basis of the chemical analysis, IR and electronic spectra.

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