

TEMPLATE CONDENSATION REACTIONS¹

X. Cr(III) AND Co(III) COMPLEXES WITH A MACROCYCLIC LIGAND RESULTING IN THE CONDENSATION OF BARBITURIC ACID AND ETHYLENEDIAMINE

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New complexes of Cr(III) and Co(III) with general formula $[ML(H_2O)_2]Cl_3 \cdot mH_2O$ (where L is the Schiff base resulting in [3+3] condensation of barbituric acid (BA) with ethylenediamine (en), (1) M=Cr, m=3; (2) M=Co, m=6) have been synthesized and characterized. The bonding and stereochemistry of the complexes have been characterised by IR, EPR and electronic spectroscopy, magnetic susceptibility at room temperature and conductivity measurements.

Introduction

Our continuing interest in the template condensation reactions led us to explore the possibility of obtaining ligands by incorporating hydroypyrimidine residues. Thus, as we reported [2], the condensation reaction between 5,5'-diethylbarbituric acid with ethylenediamine in presence of Cr(III) and Co(III) result in the formation complexes with the Schiff base resulting in the template condensation of the organic reagents.

We report here new complexes with general formula $[ML(H_2O)_2]Cl_3 \cdot mH_2O$ (L= Schiff base resulting in [3+3] condensation of barbituric acid with ethylenediamine, (1) M=Cr, m=3; (2) M=Co, m=6). The complexes were formulated as mononuclear species on the basis of analytical, spectral and magnetical 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 *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 ($g=2.0036$).

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The conductivities of 10^{-3} M DMSO solutions of the compounds were measured with a Radelkis OK-120/1 (Hungary) conductivity bridge, at room temperature.

The chemical analysis was performed by usual micromethods. Metal salts (Merck) were of analytical grade. The complexes $[\text{Cren}_3]\text{Cl}_3\cdot\text{H}_2\text{O}$ and $[\text{Coen}_3]\text{Cl}_3\cdot 3\text{H}_2\text{O}$ have been recrystallised from water before use.

Preparation of the complexes

Compound $[\text{CrL}(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 3\text{H}_2\text{O}$ (**1**): To a solution of $[\text{Cren}_3]\text{Cl}_2\cdot\text{H}_2\text{O}$ (0.713g, 2 mmoles) in ethanol (50 cm^3) was added barbituric acid (0.768g, 6mmoles); the reaction mixture was then refluxed 4h until results a sparingly soluble, yellow-brownish coloured product. The compound was filtered and washed several times with a small volume of cold ethanol and air dried. Analysis found: Cr, 7.8; N, 23.6; Cl, 16.0 %; requires for $\text{CrC}_{18}\text{Cl}_3\text{H}_{34}\text{N}_{12}\text{O}_5$: Cr, 7.4; N, 23.8; Cl, 15.1 %; $\Lambda_{\text{M}}(\text{DMSO}) = 109\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 25°C .

Compound $[\text{CoL}(\text{H}_2\text{O})_2]\text{Cl}_3\cdot 6\text{H}_2\text{O}$ (**1**): To a solution of $[\text{Coen}_3]\text{Cl}_2\cdot 3\text{H}_2\text{O}$ (0.80g, 2 mmoles) in ethanol (50 cm^3) was added barbituric acid (0.768g, 6mmoles); the reaction mixture was then refluxed 4h until results a sparingly soluble, yellow coloured product. The compound was filtered and washed several times with a small volume of cold ethanol and air dried. Analysis found: Co, 7.3; N, 22.0; Cl, 14.1 %; requires for $\text{CoC}_{18}\text{Cl}_3\text{H}_{40}\text{N}_{12}\text{O}_8$: Co, 7.7; N, 21.9; Cl, 13.9 %; $\Lambda_{\text{M}}(\text{DMSO}) = 113\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ at 25°C .

Results and Discussion

In this paper, we report the preparation and the physico-chemical characterisation of two new complexes with general formula $[\text{ML}(\text{H}_2\text{O})_2]\text{Cl}_3\cdot m\text{H}_2\text{O}$ (L= Schiff base resulting in [3+3] condensation of barbituric acid with ethylenediamine, (**1**) $\text{M}=\text{Cr}$, $m=3$; (**2**) $\text{M}=\text{Co}$, $m=6$). The conductivity measurements in DMSO have indicated that complexes behave as 1:3 electrolytes in this solvent³.

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 can be made on the basis of spectral data, are as 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 [4] in the complexes spectra and the appearance of the new bands at 1620 and 1610 cm^{-1} that could be assigned to $\nu(\text{C}=\text{N})$ vibration mode [5] reveals the fact that the condensation reaction have been made and that in this reaction are involves all NH_2 function of amine;
- (iii) the evidence of the bands characteristic of the amidic group [6,7] between $1700\text{-}1710\text{ cm}^{-1}$ (A I) and $1290\text{-}1300\text{ cm}^{-1}$ (A III) suggests that the condensation doesn't involve all carbonylic function of barbituric acid;
- (iv) 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, the additional bands at 870 and 650 cm^{-1} indicate that water molecules are coordinated [8];

- (v) in the 400-500 cm^{-1} range appear bands that could be assigned to $\nu(\text{M-O})$ and respectively $\nu(\text{M-N})$ stretching vibrations [8].

Table1. Absorption maxima (cm^{-1}) and assignments for barbituric acid (BA) and complexes (1) and (2)

BA	(1)	(2)	Assignments
–	3450bm	3500bm	$\nu(\text{OH})$
3220s	3220s 3100m	3220s 3090s	$\nu(\text{NH})$
2920m	2920m	2920m	$\nu_{\text{ass}}(\text{CH}_2)$
2810m	2840m	2835m	$\nu_{\text{sym}}(\text{CH}_2)$
1675vs	1700s	1710vs	$\nu(\text{C=O})$ (A I)
–	1620s	1610m	$\nu(\text{C=N})$
1280m	1300s	1290m	$\nu(\text{C-N}) + \delta(\text{NH})$ (A III)
–	1260m	1250s	$\nu(\text{C-N})$
–	870w	865w	$\rho_r(\text{OH})$
–	775m	790m	$\rho(\text{CH}_2)_2$
–	650w	650w	$\rho_w(\text{OH})$
–	450w 420w	440w 410w	$\nu(\text{M-O}) + \nu(\text{M-N})$

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

The electronic spectral data reveals an octahedral stereochemistry in complexes [9]. Thus the band at 212750 cm^{-1} was assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ transition for Cr(III) ($3d^3$). The electronic spectrum of Co(III) complex (2) shows a band at 20410 cm^{-1} assigned to the ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$ transition.

The EPR spectrum of compound (1) shows a wide and isotrope signal ($g_r=1.99$, $a_r=43$ mT) characteristic for Cr(III) ion in a distorted octahedral geometry [10].

The room-temperature effective magnetic moments for complex (1) of 3.84 μ_B are close to the spin only value being in agreement with a mononuclear and distorted octahedral complex [11] and the complex (2) is diamagnetically.

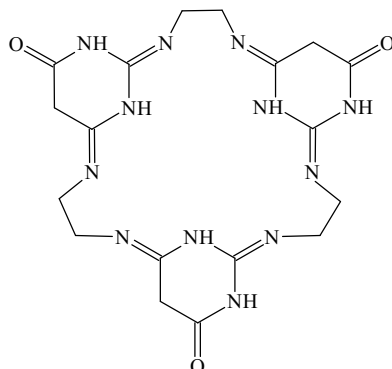


Fig. 1: The Schiff base resulting in [3+3] condensation of barbituric acid with ethylenediamine (L)

Conclusions

Two new Cr(III) and Co(III) complexes have been synthesised in [3+3] condensation reaction of barbituric acid with ethylenediamine.

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

The all complexes adopt a distorted octahedral stereochemistry.

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