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In memoriam prof. dr. Ioan A. Silberg

SYNTHESIS AND CHARACTERIZATION OF SOME MIXED LIGAND ZINC(II) COMPLEXES OF THEOPHYLLINE

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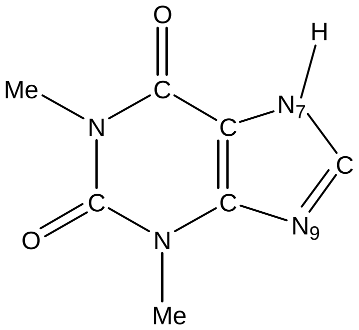
ABSTRACT. The synthesis, spectral and thermal properties of four mixed ligand complexes of Zn(II) with deprotonated theophylline (th) are reported: $[Zn(th)_2(ba)_2]\cdot 2H_2O$ (1), $[Zn(th)_2(dmen)]\cdot H_2O$ (2), $[Zn(th)_2(ea)_2]\cdot H_2O$ (3) and $[Zn(th)_2(pa)_2]\cdot H_2O$ (4) (ba = benzylamine; dmen = N,N-dimethyldiaminoethane; ea = 2-aminoethanol; pa = 3-aminopropanol). The FTIR spectra of complexes indicate that theophylline acts as a monodentate ligand and coordinates *via* the N(7) nitrogen atom.

Keywords*: 2-aminoethanol, 3-aminopropanol, benzylamine, N,N-dimethyldiaminoethane, theophylline, mixed ligand complexes*

INTRODUCTION

Transition metal complexes of theophylline (Scheme 1) are of considerable interest because they may serve as model compounds for the interaction between metal ions and oxopurine bases of nucleic acids. According to previous studies, theophylline coordinates as a monodentate ligand in neutral media *via* N(9), while in basic media it coordinates *via* N(7) [1–5].



Scheme 1

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In some cases theophylline acts as a bidentate ligand, forming N(7)/O(6) chelates [6, 7]. In our research on coordination compounds with theophylline and various amines, we have reported the synthesis and characterization of some new mixed ligand complexes of Cu(II), Co(II) and Ni(II) containing the theophyllinato anion and 2-aminoethanol or benzylamine as co-ligands [8–11]. Here we report the synthesis of four new systems, corresponding to the general formula: $[Zn(th)_2L_n]\cdot xH_2O$, where L: benzylamine (ba) (n=2, x=2), N,N-dimethyldiaminoethane (dmen) (n=1, x=1), 2-aminoethanol (ea) (n=2, x=1), 3-aminopropanol (pa) (n=2, x=1). The complexes were investigated and characterized by FTIR spectroscopy and thermoanalysis.

EXPERIMENTAL PART

The Zn(II)-complexes were prepared in alkaline aqueous solution as previously reported [2, 8]. FTIR spectra were recorded on a Jasco FTIR 600 spectrophotometer in the 4000–400 cm^{-1} range, using KBr pellets. Thermal decomposition was investigated with a 103 MOM Radelkis Derivatograph, by using sample of 100 ± 2 mg and α-Al_2O_3 as reference (for complexes **1** and **4**) and with an Universal V2.3C TA Instruments, by using sample of 10–12 mg (for complex **3**), respectively, at a heating rate of 10℃ min^{-1}. The composition of complexes was determined by elemental analysis (C, H, N).

Synthesis of $[Zn(th)_2(ba)_2]\cdot 2H_2O$ (1). To a suspension of theophylline (0.4 g, 2.02 mmol) in water (15 cm^3), benzylamine (0.5 cm^3) was added. The resulted clear solution was mixed with a second solution of $ZnAc_2\cdot 2H_2O$ (0.2195 g, 1 mmol) in a benzylamine–water mixture (1 cm^3 of benzylamine in 5 cm^3 of water). The reaction mixture was heated at 50℃ for 30 min, under stirring and stored at room temperature over night. The resulted white polycrystalline powder was collected by filtration, washed with aqueous benzylamine (5%) and dried. M.W.: 673.69, Yield: 81.8%, M.P.: >320 ℃ (dec.).

Complexes **2–4**, *i.e.* **$[Zn(th)_2(dmen)]\cdot H_2O$ (2), $[Zn(th)_2(ea)_2]\cdot H_2O$ (3), $[Zn(th)_2(pa)_2]\cdot H_2O$ (4),** were prepared by the described procedure, using the appropriate amine or aminoalcohol. Complexes **3** and **4** precipitated after two weeks as crystalline powder.

The main data of complexes **2–4** are presented in Table 1.

Table 1.

Analytical data of complexes **2**–**4**

Complexes	M.W.	M.P. (°C)	Yield [%]	Elemental analysis [%] Found (calc.)		
				C	**H**	**N**
$[Zn(th)_2(dmen)]\cdot H_2O$ $ZnC_{18}H_{28}N_{10}O_5$ **2**	529.87	295–325 (dec.)	80	42.05 (40.80)	4.65 (5.33)	26.83 (26.43)
$[Zn(th)_2(ea)_2]\cdot H_2O$ $ZnC_{18}H_{30}N_{10}O_7$ **3**	563.88	278	70	37.65 (38.34)	5.59 (5.36)	24.57 (24.84)
$[Zn(th)_2(pa)_2]\cdot H_2O$ $ZnC_{20}H_{34}N_{10}O_7$ **4**	591.94	258–259 (dec.)	68	40.85 (40.58)	5.70 (5.79)	23.46 (23.66)

RESULTS AND DISCUSSION

FTIR spectra

The characteristic vibration bands of the ligands and complexes with their assignments are given in Table 2.

Table 2.

FTIR vibrations (cm^{-1}) of the ligands and complexes **1**–**4**

Ligand/complex	ν(OH)	ν(NH)	ν(C=O)	ν(C=N)
Theophylline (th)	–	3120m	1714s 1667s	1566s
Ethanolamine (ea)	3642s	3331m 3286m	–	–
Propanolamine (pa)	3636s	3351m 3286m	–	–
$[Zn(th)_2(ba)_2]\cdot 2H_2O$ **1**	3420b	3256m	1687s 1645s	1530s
$[Zn(th)_2(dmen)]\cdot H_2O$ **2**	3529m 3446b	3329m	1693s 1645s	1531m
$[Zn(th)_2(ea)_2]\cdot H_2O$ **3**	3421b	3291m	1695s 1638s	1530s
$[Zn(th)_2(pa)_2]\cdot H_2O$ **4**	3446b	3286m	1694s 1640s	1530s

Abbreviations: b - broad, m - medium, s – strong

FTIR spectra of the complexes exhibit obvious differences to the spectrum of theophylline. The two strong bands in the IR spectrum of theophylline, which are assigned to the stretching vibration of the carbonyl groups, are shifted after coordination toward lower wavenumbers, due to the deprotonation of theophylline and the participation of C(6)=O and C(2)=O groups to intra- or intermolecular hydrogen bonds [8–10]. In complexes, the C=N ring vibrations of theophylline are shifted toward lower values, suggesting that the ligand coordinates *via* the imidazole nitrogen atoms. The carbonyl C(2)=O stretching vibration at 1645 cm^{-1} suggests that the carbonyl group does not interact with the water molecules of the framework [9].

There are significant changes in the bands assigned to N–H vibrations, as a consequence of the deprotonation of theophylline at N(7) atom and coordination of the amine type ligands. In the spectra of complexes with a primary amine ligand the symmetric and antisymmetric stretching vibrations of the coordinated NH_2 groups can be assigned in the 3329–3256 cm^{-1} region. In spectrum of **2**, the symmetric and antisymmetric vibrations are overlapped and the symmetric vibration is reduced to a shoulder, recorded at 3309 cm^{-1}. The ν_{CH} vibrations of benzylamine are observed at 2954 cm^{-1} for the aliphatic CH_2 and at 3027–3066 cm^{-1} for the aromatic CH. The ν_{CH} vibrations of coordinated N,N-dimethyldiaminoethane are recorded as a broad band centered at 2953 cm^{-1}. The corresponding aliphatic CH_2 vibrations of alcoholamine are registered at 2962 cm^{-1} for complex **3** and at 2953 cm^{-1} for complex **4**.

The strong broad bands of complexes **3** and **4**, recorded at 3600–3400 cm^{-1}, may be assigned to different hydrogen bonds [11–14]. The water content of complexes with aminoalcohols was also confirmed by thermogravimetry.

The FTIR spectra of complexes **1**–**4** suggest that theophylline acts as a monodentate ligand and coordinates the metal ion *via* the N(7) atom.

Thermal analysis

The investigated complexes undergo a gradual decomposition during heating in flowing air atmosphere. The thermogravimetric curves of complexe with benzylamine (**1)** and of complexes with bidentate ligands (**2–4)** are very different.

The thermogravimetric curve of complex **1** indicates a stepwise decomposition. In the first step, two molecules of water are eliminated in the temperature range of 100–140℃ (experimental weight loss 7%, calculated 5.3%), suggesting that both molecules are bonded similarly. The next step, which occurs in the temperature range 240–350℃, corresponds to the elimination of two molecules of benzylamine, such as in the case of the related Cu(II) complex [10]. Above 350℃, the thermal decomposition is similar to that of $[Zn(th)_2(NH_3)_2]$ [15], with the release and pyrolysis of two theophyllinato moieties. The DTG curve shows that the two theophylline molecules are eliminated in the range of 350–420℃ and 420–540℃, respectively. The last two decomposition steps are exothermic, showing maxima at 560 and 660℃, while the final decomposition product is ZnO (exp. solid residue 13%; calc. 12%).

The water molecule of complex **3** is eliminated at 85℃ (exp. weight loss 4%, calc. 3.1%) and demonstrates that the respective water is not involved in coordination. Above 200℃, two ethanolamine molecules are evolved in two separate steps, recorded in the range 215–250℃ (exp. weight loss 11 %, calc. 10.8 %) and 285–310℃, respectively. The high decomposition temperatures suggest a bidentate binding mode of ethanolamine [6, 7]. Further weight loss corresponds to the release and pyrolysis of theophyllinato moieties. The final decomposition product is ZnO (exp. solid residue 14%, calc. 14.4%), in good agreement with the results of Zelenák for similar complexes [15].

The same decomposition pattern was observed for complex **4**.

CONCLUSIONS

FTIR spectra and thermal data of complexes **1** and **2** suggest a tetrahedral, while in the case of **3** and **4** an octahedral coordination of the metal ions with bidentate bonding of aminoalcohol ligands. The theophylline coordinates *via* the N(7) nitrogen.

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