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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

THERMAL, MAGNETIC, FTIR AND XRD STUDY OF NEW Co(II) AND Ni(II) THEOPHYLLINATO COMPLEXES WITH BENZYLAMINE OR ETHANOLAMINE

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Abstract

Four new theophyllinato (**th**) complexes of Co(II) and Ni(II) were synthesized containing ethanolamine (2-aminoethanol, **ea**) or benzylamine (**ba**). Comprehensive FTIR spectroscopic, powder XRD, magnetic and thermal studies on these mixed ligand complexes have been carried out to get structural information. The almost identical FTIR spectra and XRD patterns of Co and Ni compounds with same composition have indicated that $Co(th)_2(ba)_2{\cdot}2H_2O$ (**1**) and $Ni(th)_2(ba)_2{\cdot}2H_2O$ (**2**) or $Co(th)_2(ea)_2$ (**3**) and $Ni(th)_2(ea)_2$ (**4**) have very similar structure pair wise. The infrared spectra and X-ray diffraction patterns of thermally dehydrated **1** and **2** containing benzylamine have allowed only to suggest that the co-ordination number around the metal centres is four, while the high thermal stability of complexes **3** and **4** have indicated that they contain two of bidentate ethanolamine molecules in octahedral co-ordination. A big difference observed between the magnetic moments of Co compounds **1** and **3** have proven that the inner co-ordination sphere of complexes with benzylamine (**1** and **2**) is tetrahedral, whilst that with ethanolamine (**3** and **4**) is basically octahedral, independent of the cation centres (Co or Ni).

Keywords: 2-aminoethanol, benzylamine, magnetic moment, mixed ligand complexes, structure, TG, theophylline

Introduction

Various theophylline containing metal complexes were synthesized as model compounds to study possible metal guanine interactions in genetic processes of DNA [1–3]. According to single crystal data the theophylline moieties are in

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most cases bounded to the metal cation through their N(7) nitrogen atom even in deprotonated form [4–10]. Several mixed ligand complexes of Cu(II), Zn(II), and Cd(II) containing both theophyllinate anion and ammonia or primary amines were prepared by Birdsall *et al.* [11–13]. Unfortunately, no structural data are available for these complexes obtained from alkaline aqueous solutions. Nevertheless some structures of di- and triamine containing theophyllinato complexes have already been reported. Ethylenediaminebis(theophyllinato)zinc(II) showed tetrahedral co-ordination [14], the bis(theophyllinato)diethylenetriaminecopper(II) dihydrate was found to be pentacoordinated [15], while two theophyllinatochlorobis(ethylenediamine)cobalt(III) salts have basically octahedral arrangements [16–17]. In the case of (SPY-5-12)-(2-aminoethanol-N)-(2-aminoethanol-N,O)bis(theophyllinato)copper(II) dihydrate it has been found that ethanolamine behaves as both monodentate and bidentate ligand within the same distorted square pyramidal or pseudo octahedral co-ordination [18].

Here we report synthesis and characterisation of four new mixed ligand theophyllinato complexes of Co(II) and Ni(II) with benzylamine and 2-aminoethanol (**1–4**). In lack of appropriate single crystals, we have carried out FTIR, powder XRD, thermoanalytical and magnetic studies to obtain information on their structure.

Experimental

Thermogravimetric, magnetic, FTIR, and XRD studies

Thermal behaviour of complexes **1–4** was studied in a DuPont 990 Thermal Analytical System equipped with thermobalance model 951. Sample size of 5–10 mg and heating rate of 10°C min^{-1} was used. The measurements were carried out in dynamic air atmosphere with a flow rate of 10 l h^{-1}.

The temperature dependence of the magnetic susceptibility of all the complexes was measured by the Faraday method between 95–300 K on a Bruker magnetic susceptibility meter using $CuSO_4{\cdot}5H_2O$ as calibrant.

FTIR spectroscopy was used to study complexes **1–4** and their intermediates formed during thermal decomposition. The FTIR spectra were obtained in the 400–4000 cm^{-1} range with a Perkin Elmer IR System 2000 instrument by the KBr pellet technique.

The X-ray powder patterns for the complexes and their intermediate and final products were recorded by a FPM HZG-4 diffractometer using CuK_α radiation with Ni filter.

Elemental analysis

The composition of **1–4** was checked by analysis of their C, H and N contents. Analysis of **1** and **2** was carried out at the Institute of Chemistry, Cluj-Napoca, Romania, while that of **3** and **4** by the Microanalytical Laboratory, Eötvös Loránd University of Budapest, Hungary.

Synthesis of Co(th)$_2$(ba)$_2$·2H$_2$O (**1**) *and Ni(th)$_2$(ba)$_2$·2H$_2$O* (**2**) *(th - theophyllinate anion; ba - benzylamine)*

Theophylline (0.4 g, 2.02 mmol) was dissolved in a mixture of 20 cm^3 water and 0.5 cm^3 benzylamine, while 0.8 mmol $Co(CH_3CO_2)_2 \cdot 4H_2O$ or $Ni(CH_3CO_2)_2 \cdot 4H_2O$ was also dissolved in 20 cm^3 water to which a large excess of benzylamine was added till clear solution was obtained. The two solutions were mixed and the mixture was stirred for 30 min. Then the precipitates were filtered, washed with aqueous solution of benzylamine (5%) and dried in a desiccator over $CaCl_2$ in vacuum. The elemental analysis of $Co(C_7H_7N_4O_2)_2(C_7H_9N)_2 \cdot 2H_2O$ (1) gave C 50.83, H 5.34, N 20.77%, (calculated C 50.37, H 5.44, N 20.98%). For $Ni(C_7H_7N_4O_2)_2(C_7H_9N)_2 \cdot 2H_2O$ (2) we obtained C 50.37, H 5.71, N 21.02%, (calculated C 50.40, H 5.44, N 20.99%). Co complex **1** is obtained as a very light pink powder, while Ni complex **2** as very light blue one.

Synthesis of Co(th)$_2$(ea)$_2$ (**3**) *and Ni(th)$_2$(ea)$_2$* (**4**)*, (ea - ethanolamine)*

These complexes were synthesized in a similar way, except that 1 mmol of $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ and an excess amount of ethanolamine (2-aminoethanol) were used as corresponding starting materials. According to the thermogravimetric measurements the air-dried **3** and **4** contained 0.77 and 0.61 water molecules per, complex unit as adsorbed moisture, respectively. For $Co(C_7H_7N_4O_2)_2(C_2H_7NO)_2 \cdot 0.77H_2O$ (**3**) the elemental composition was found to be C 38.46, H 5.48, N 24.51% (calculated C 39.08, H 5.38, N 25.32%), while for $Ni(C_7H_7N_4O_2)_2(C_2H_7NO)_2 \cdot 0.61H_2O$ (**4**) we obtained C 39.17, H 5.28, N 24.69% (calculated C 39.30, H 5.35, N 25.46%). Co compound **3** is obtained as a light pink powder, while Ni compound **4** as light cyan one.

Results and discussion

FTIR and XRD similarities

The FTIR spectra and XRD patterns of the obtained complexes with the same ligands are strikingly similar. The FTIR spectra of the corresponding Co and Ni compounds (**1** and **2**, or **3** and **4**) are hardly distinguishable (Fig. 1). Furthermore, the XRD peak positions of the pairs with same ligand composition are also very close to each other (Figs 2 and 3). That is, the structural details of the related Co and Ni compounds (**1** and **2**, or **3** and **4**) must be very similar.

All FTIR spectra show lower frequencies of the two theophyllinate $\nu_{C=O}$ stretching vibrations (1682 and 1620 cm^{-1} in **1** and **2**, 1687 and 1640 cm^{-1} in **3** and **4**) than those of in free theophylline (1716 and 1667 cm^{-1}) and in chelated neutral theophylline (between 1702–1715 and 1662–1681 cm^{-1}) [1, 2]. These shifts are mainly due to the deprotonation of theophylline at N7 nitrogen, which is the expected donor atom in the metal complexes at the same time. It should be noted that in this range the NH_2 bending vibrations of coordinated primary amine ligands can also occur.

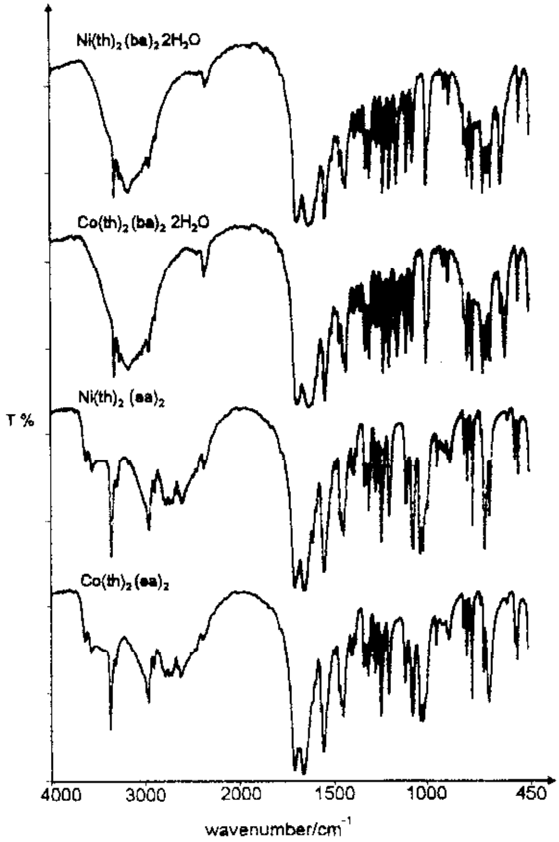

Fig. 1 FTIR spectra of **1** [$Co(th)_2(ba)_2\cdot 2H_2O$], **2** [$Ni(th)_2(ba)_2\cdot 2H_2O$], **3** [$Co(th)_2(ea)_2$], and **4** [$Ni(th)_2(ea)_2$]

The symmetric and asymmetric stretching vibration of NH_2 groups of the primary amine ligands occurred at 3318 and 3265–3266 cm^{-1} in complexes **1** and **2** containing benzylamine, and at 3340 and 3285–3288 cm^{-1} in complexes **3** and **4** containing ethanolamine (Fig. 1). The corresponding ν_{CH} vibration of amines occurred at 2954–2956 cm^{-1} (aliphatic CH_2), at 3027 and 3066 cm^{-1} (aromatic CH stretching) of benzylamine in **1** and **2**; or at 2943–2945 cm^{-1} and 2960–2962 cm^{-1} (aliphatic CH_2) of etanolamine in **3** and **4**.

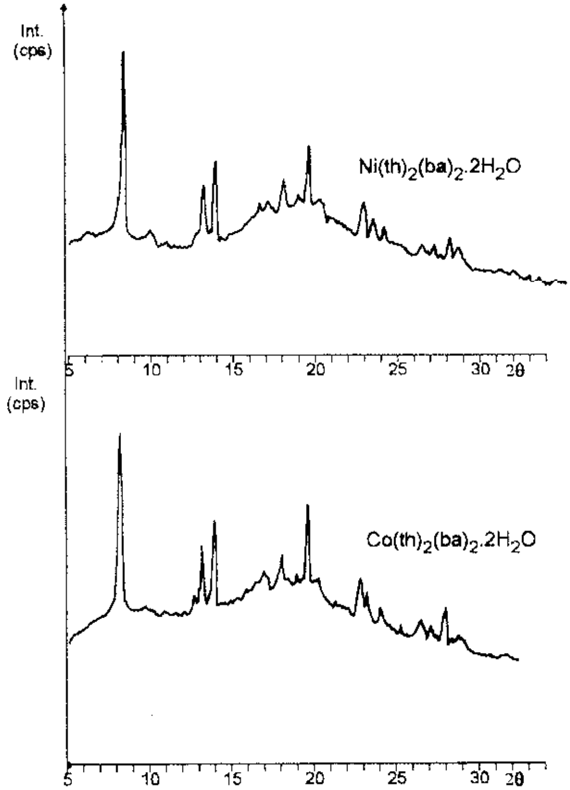

Fig. 2 XRD patterns of **1** [$Co(th)_2(ba)_2 \cdot 2H_2O$] and **2** [$Ni(th)_2(ba)_2 \cdot 2H_2O$]

Both of the NH_2 groups are expected to be coordinated to the metal centre. Their position in the co-ordination sphere must be equivalent, for no further splitting of the ν_{NH} doublet was observed, whilst the presence of mono- and bidentate ethanolamine caused a split in the case of (SPY-5-12)-(2-aminoethanol-N)-(2-aminoethanol-N,O)bis(theophyllinato)copper(II) dihydrate [18].

In N(7)-bonded theophyllinate complexes, the carbonyl group C(6)–O(6) forms usually interligand hydrogen bonds with other chelating ligands containing hydrogen bond donor groups, e.g. amino groups [15]. As additional NH_2 absorption or hydrogen bonds were absent from the spectra of **1** and **2**, there is no indication of interligand interaction there.

The presence of two water molecules in complex **1** and **2** is observed in the spectra (Fig. 1, the upper two spectra) as a broad band centred at 3166 and 3168 cm^{-1}, respectively. The significant shift (about 460 cm^{-1}) of the OH vibration mode in comparison with those of free water indicates a strong binding of water in complexes **1** and **2**. This can be explained by strong interligand hydro-

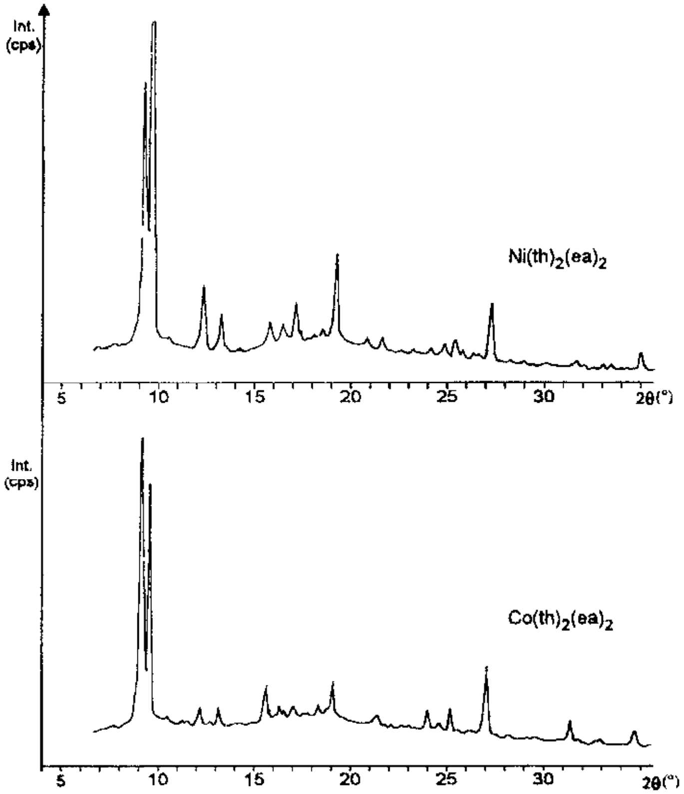

Fig. 3 XRD patterns of **3** [Co(th)$_2$(ea)$_2$] and **4** [Ni(th)$_2$(ea)$_2$]

gen bonds between carbonyl group C(2)–O(2) of theophyllinate anion and water. It is based also on the fact that after the release of two molecules of water from **1** at 127°C, the carbonyl C(2)–O(2) stretching frequency is shifted from 1620 to 1644 cm^{-1}, which is characteristic of a non-bonded carbonyl group of theophylline framework.

In the spectra of complexes **3** and **4**, containing ethanolamine ligand, in addition to the earlier mentioned NH$_2$ vibrations, two sharp peaks at 3615 and 3553 cm^{-1} were observed and assigned to OH group of ethanolamine ligands. The former band is caused by vibration of a non-bonded OH group, the latter one by bonded OH group. The whole absorption spectra of **3** and **4** remained the same if the samples had been dried at 200°C, i.e., the above absorption peaks are due to the alcoholic OH groups of ethanolamine. The above mentioned stretching frequencies suggest that ethanolamine ligands can be positioned different ways. Different binding modes of the 2-aminoethanol ligand were also observed in an analogue Cu complex [18].

Thermal decomposition, structural indications

Each compound undergoes a complex gradual decomposition during heating in flowing air atmosphere. The thermogravimetric curves (Figs 4 and 5) show more or less similar features within the pairs of same ligands, but that of the pairs with benzylamine and etanolamine are definitely different from each other.

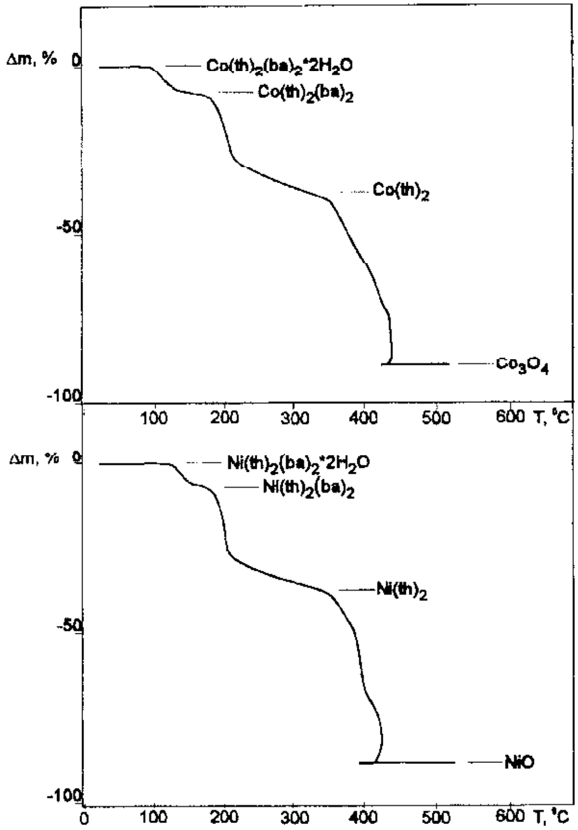

Fig. 4 Thermogravimetric curve of **1** [$Co(th)_2(ba)_2 \cdot 2H_2O$] and **2** [$Ni(th)_2(ba)_2 \cdot 2H_2O$] in an air flow of 10 l h^{-1}, heating rate 10°C min^{-1}, initial mass 5.58 and 5.73 mg, respectively

In the case of complexes **1** and **2** containing benzylamine, in the first step two molecules of water evolved (theoretical mass loss is 5.4% for both complexes). 6.5% mass loss of Co compound **1** was observed between 85 and 125°C, and 6% mass loss of Ni compound **2** between 100 and 150°C (Fig. 4). The next weight loss step up to 340°C corresponds to the release of two molecules of benzylamine (theoretical mass loss is 32.1% for both complexes) in both cases. Above 350°C a degradation of theophyllinato ligands began.

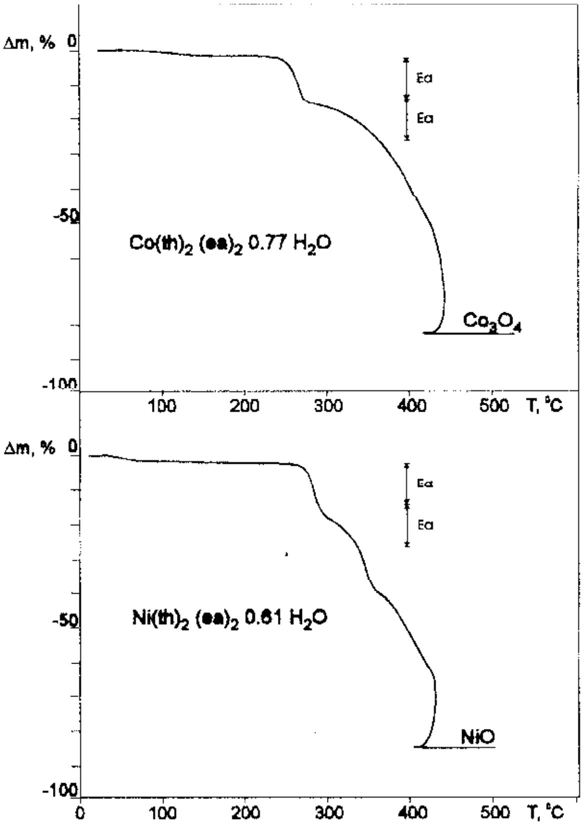

Fig. 5 Thermogravimetric curve of **3** [Co(th)$_2$(ea)$_2$] and **4** [Ni(th)$_2$(ea)$_2$], measured in an air flow of 10 l h^{-1}, heating rate 10°C min^{-1}, initial mass 5.56 and 6.46 mg, respectively

A thermally dehydrated residue of Co compound **1** obtained at 125°C showed a slightly changed FTIR spectrum and its XRD pattern indicated some amorphisation and a destruction of the crystal lattice as a result of dehydration. That is, the dehydration destroyed the original structure, and the crystal structure did not remain the same as in the original Co(th)$_2$(ba)$_2$·2H$_2$O (**1**). If the two water molecules released were coordinated to the Co(II) cation beyond the two theophyllinate anions and two benzylamine molecules as fifth and sixth ligands in an octahedral arrangement, or they took part in structure building hydrogen bonds such a collapse of structure would be expected.

In contrary, the decomposed samples of **2** obtained even at 190°C, well after the total dehydration of **2**, showed unchanged FTIR spectra and the same XRD patterns as those of the original Ni(th)$_2$(ba)$_2$·2H$_2$O (**2**) itself. If the water molecules were not coordinated directly to the Ni centre in the tetrahedral arrangement then such a conservation of the original lattice structure might be possible.

Because of the observed strong structural relation between **1** and **2**, we expect a tetrahedral arrangement round both the Ni and Co cation, based on the above considerations on the crystal lattice decomposition. To get more reliable information and draw a final conclusion on their structure a comparative study of magnetic behaviour and moments was needed (see below).

In the cases of complexes **3** and **4** containing ethanolamine, 1.5–2 % mass loss strongly adsorbed water was removed first, then the compounds were stable up to 250 and 275°C (Fig. 5), respectively. No signal of structural change was observed by FTIR and XRD below these temperatures, where evolution of the two ethanolamine ligands started. These high temperatures of beginning decomposition may be explained by bidentate nature of the 2-aminoethanol ligands. For the Cu compound having the same ligands, the monodentate ethanolamine was released at 180°C, while the bidentate one evolved only above 200°C [18]. Based on the assumption of two bidentate ethanolamine ligands an octahedral inner coordination sphere can be assumed for both **3** and **4**. Nevertheless more decisive magnetic studies of these complexes were required to prove their octahedral configuration.

The step corresponding to the evolution of two aminoalcohol ligands (theoretical mass loss 21.2%) is partially overlapping with the degradation processes of the theophyllinate ligands for both compounds.

At the last stage, each compound (**1**–**4**) showed an oxidative decomposition in air above 400°C. In each case it was accompanied by a sudden and large exothermic heat evolution as a result of burning, or even a mild explosion of the organic decomposition products and the simultaneous air-oxidation of the nascence metal residues. The local temperature has increased even around the sample where the temperature measuring thermocouple is placed. Thus the thermocouple

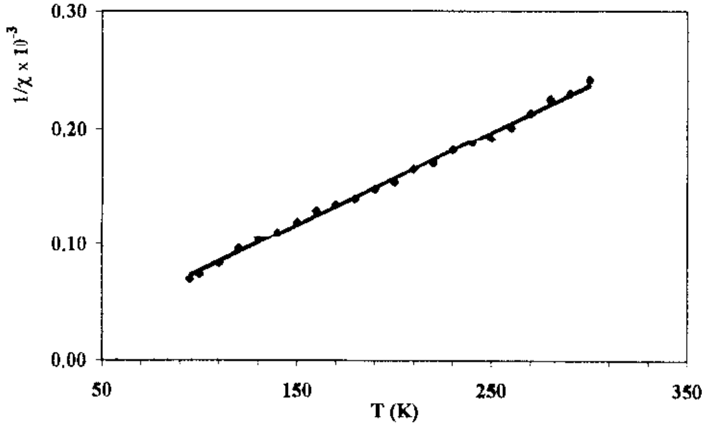

Fig. 6 Reciprocal magnetic susceptibility values of **2** $[Ni(th)_2(ba)_2 \cdot 2H_2O]$ as function of absolute temperature

measured higher temperature than the programmed one. After a maximum the temperature was decreased by the purge gas till the temperature met the increasing programmed temperature itself. The sharp rise and slow drop in the sample temperature recorded on the x axes has caused an unusual shape of the thermogravimetric curves above 400°C. The residues of **1** and **3** showed Co_3O_4 (JCPDS card No. 42-1467), while that of **2** and **4** contained NiO (JCPDS card No. 22-1189).

Magnetic susceptibilities and moments, structure

All of the complexes are found to be paramagnetic. Their reciprocal molar susceptibility values are linearly dependent on temperature in accordance with the Curie law (Fig. 6). This indicates that no metal-metal interaction occurs in the complexes, i. e. metal centres are far enough from each other in the solid matrix.

Table 1 Magnetic moments of complexes **1–4**

Complex	μ_{eff}(B.M.)
$Co(th)_2(ba)_2{\cdot}2H_2O$ (**1**)	4.39
$Ni(th)_2(ba)_2{\cdot}2H_2O$ (**2**)	3.18
$Co(th)_2(ea)_2$ (**3**)	5.07
$Ni(th)_2(ea)_2$ (**4**)	3.19

The magnetic moments of the complexes, calculated via Eq. (1), are presented in Table 1.

$$\mu_{eff} = 2.828(T\chi_{mol})^{1/2} \tag{1}$$

The obtained magnetic moments show that the investigated compounds are high-spin complexes of Co(II) or Ni(II) with 3 or 2 unpaired electrons, respectively.

For a high spin octahedral Co complex a magnetic moment of about 5.2 or somewhat lower is expected [19]. Deviations from the octahedral symmetry decrease the μ_{eff} value. The expected μ_{eff} value for tetrahedral complexes lie between 4.4 and 4.8 B.M. According to this consideration and taking into account the measured magnetic moments, we can conclude that $Co(th)_2(ba)_2{\cdot}2H_2O$ (**1**) has a tetrahedral structure, while $Co(th)_2(ea)_2$ (**3**) has a distorted octahedral geometry.

In general, different μ_{eff} values could be expected for octahedral, square planar or tetrahedral stereochemistry of Ni(II) complexes. The square planar nickel complexes are diamagnetic (μ_{eff}=0). In case of an octahedral complex, the expected magnetic moment is about 10% higher than the spin only value (μ=2.83). For a tetrahedral complex of Ni a μ_{eff} value between 3.2 and 4.0 is expected. The observed values, μ_{eff}=3.18 of **2** and μ_{eff}=3.19 of **4** are at the border of tetrahedral and octahedral case. A tetrahedron or a very distorted octahedron could be suggested for both 2 and 4.

The difference of the magnetic moments between a tetrahedron and a distorted octahedron is much larger in Co(II) complexes than in Ni(II) complexes. So, the structural difference between the investigated theophyllinato-complexes containing benzylamine and ethanolamine can be judged on the basis of the Co complexes **1** and **3**. Ethanolamine may act as a bidentate ligand and its O atom is stronger donor atom than the O atom of water. Thus, it is not surprising that in the $Co(th)_2(ea)_2$ (**3**) complex a distorted octahedral co-ordination sphere with bidentate aminoalcohol ligands can be found. On replacing the ethanolamine molecules with benzylamine molecules, a tetrahedral symmetry becomes dominant around the Co^{2+} ion in $Co(th)_2(ba)_2 \cdot 2H_2O$ (**1**). Probably, owing to the aromatic parts of the theophyllinate anions and benzylamine molecules, the water molecules can only be placed relatively far from the Co^{2+} ion in an outer co-ordination sphere of the proposed tetrahedron of **1**.

Because of the observed strong similarities of the FTIR spectra and the XRD patterns of Co and Ni compounds containing the same ligands, we can conclude that $Ni(th)_2(ba)_2 \cdot 2H_2O$ (**2**) has also a tetragonal, while $Ni(th)_2(ea)_2$ (**4**) has a distorted octahedral structure, despite of their very close magnetic moment value measured.

Conclusions

Combination of thermal investigations with FTIR, powder XRD and magnetic studies on the above mixed ligand complexes of Co(II) and Ni(II) (**1**–**4**) resulted in two main conclusions. Firstly, complexes with the same ligand composition have identical crystal structure, regardless of the metal present, as has been proven by FTIR and XRD. Secondly, complexes with benzylamine (**1** and **2**) are found by both thermal and magnetic methods to be tetrahedral, whilst the ones with ethanolamine (**3** and **4**) show octahedral co-ordination, indicating in the latter case at least partially bidentate feature of ethanolamine ligands. Unfortunately, no sufficient information is available to describe the exact spatial configuration of complex **3** and **4**.

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