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Synthesis and Spectroscopic Studies of the Nicotinamide Adducts of Cobalt(II), Nickel(II) and Zinc(II) Chlorides

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Nicotinamide (na) adducts of Co(II), Ni(II) and Zn(II) chlorides are synthesized and characterized by thermoanalytical methods (TG, DTG, DTA), FT IR (4000–400 cm^{-1}) and UV/Vis spectroscopy. Structural similarity is inferred between the octahedral Co and Ni compounds of type $[M(na)_2(H_2O)_4]Cl_2$. The tetrahedral Zn complex $[Zn(na)_2Cl_2]$ presents a different structure. The coordination of the metal ions in the Co and Ni adducts modelled by semiempirical theoretical methods compares well with the structural data for $[Ni(na)_2(H_2O)_4](NO_3)_2\cdot 2H_2O$.

Key words: FT IR, UV/Vis spectra, nicotinamide adducts, synthesis, semiempirical calculations

During the recent years, there has been significant interest in the coordination chemistry, the structural properties and the reactivity of metal complexes of nicotinamide (na) [1–4], mostly owing to its function as electron acceptor in some enzymatic reactions [5]. A number of nicotinamide complexes and salts, therefore, have been both structurally and spectroscopically investigated. Recently, the crystal structure of a nicotinamide adduct of Ni(II) nitrate, $[Ni(H_2O)_4(na)_2](NO_3)_2\cdot 2H_2O$ [6], as well as some investigations on $Zn(na)_2Cl_2$ and $ZnX_2\cdot 1{-}2(na)\cdot nH_2O$ (X = $CH_2BrCH_2CH_2COO^-$, $CH_3CH_2CHBrCOO^-$) complexes were reported [7,8]. Nevertheless, aside from the synthesis (starting from $Zn(CH_2ClCH_2CH_2COO)_2$) and some thermal information on $Zn(na)_2Cl_2$ [7], we have found no data on metal(II) chloride nicotinamide complexes.

In the present paper an alternative synthesis of Zn(II) nicotinamide chloride is reported, and for the first time, synthesis and various data for novel nicotinamide adducts of Co(II) and Ni(II) chlorides are presented.

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EXPERIMENTAL

Reagents and instruments: Nicotinamide, $CoCl_2$, $NiCl_2$ and $ZnCl_2$ were purchased from Merck. The reagents were applied without further purification. All solutions were prepared in deionized triply-distilled water just before use.

Thermal (TG, DTG, DTA) analyses were performed with a Rigaku TG8110 thermal analyser in static air atmosphere (Pt crucibles, heating rate 10 °C/min, sample mass about 10 mg). Elemental (H, N) analyses were carried out at TÜBİTAK Marmara Research Centre (Gebze). The FT IR spectra were recorded using pressed KBr pellets with a Perkin-Elmer System 2000 interferometer, and a P/N 21525 variable temperature cell (Graseby Specac) with KBr windows. Electronic spectra were recorded on Unicam V2-100 UV/Vis spectrophotometer in the 800–200 nm range at 1 cm cell length. The spectra of mixtures with ambient mole ratio of both metal chloride and nicotinamide aqueous solutions were recorded, following the changes in absorbance at the wavelength of maximum absorption. The modelling package Chem 3D Pro [9] was used for semi empirical geometry optimizations and generation of the model figures.

Synthesis: The compounds were prepared by addition of nicotinamide to warm stirred aqueous solutions of the respective metal (II) chlorides in the stoichiometric ratio. After cooling of the solutions, pale pink well-shaped crystals of the cobalt compound, pale green crystals of the nickel compound and colourless crystals of the zinc compound were obtained. The compounds are soluble in water. The crystals were filtered, washed with acetone and dried at room temperature.

RESULTS AND DISCUSSION

Thermal analysis: The thermal data for the complexes are presented in Table 1. Formulae $M(na)_2(H_2O)_4Cl_2$ (M = Co and Ni) and $Zn(na)_2Cl_2$ can be deduced from the mass losses, giving good agreement between the observed and the calculated values. The above formulae are supported by elemental analysis. The empirical formulae of the Co and Ni compounds, therefore, with respect to the crystal water are different with that of the octahedral (na) adduct of Ni nitrate [6]. The decomposition of the Co and Ni adducts starts far below 100°C with endothermic dehydration. The unhydrous Co complex exists up to about 210°C, when one nicotinamide molecule sublimes, while the Ni compound immediately looses one nicotinamide ligand. This process proceeds in as well-defined step, accompanied by a DTA peak, exothermic at 245°C for Co and endothermic at 238°C for Ni. The residue adopts complex decomposition pathway, accompanied with strong exothermic effects (main peaks at 390 and 425°C for the Co and Ni complexes, respectively), finally leading to Co_3O_4 (converted to CoO at 909°C) and NiO.

As expected, the anhydrous Zn complex with the onset of decomposition at 302°C is notably more stable. The compound undergoes melting at 221°C prior to the thermolysis. Single (na) molecule is released during an endothermic process (DTA peak at 313°C), followed by a group of exothermic redox processes. ZnO is obtained as a final product.

Fourier-transform infrared spectra: The 4000–400 cm^{-1} region in the FT IR spectra of the adducts is presented in Fig. 1. From the overall spectral appearance it is immediately inferred about pronounced structural similarity between the Co and Ni complexes, and a distinctively different structure of the Zn compound. All internal benzenoid modes of nicotinamide are closely reproduced in the spectra of the Co and

Ni adducts, as expected for an aromatic *N*-donor base [10], indicating structural similarity if not equivalence among the nicotinamide ligands in the respective structures. In the same time, apparently larger complexity and pronounced doubling of the nicotinamide ring bands in the spectrum of the Zn adduct might be taken as indication for the existence of at least two crystallographically non-equivalent types of (na) molecules in the respective structure. Since the benzenoid (na) modes are largely coupled, they can be hardly employed for structural analysis; thus, only some characteristic IR features will be discussed below. Two strong, overlapped and apparently complex bands are present between 3700 and 2860 cm^{-1}, where bands due to XH (X = O, N) stretchings are expected (Fig. 1). The band frequencies of the XH stretchings (3383/3194 cm^{-1}, 3364/3170 cm^{-1} and 3377/3198 cm^{-1} for Co, Ni and Zn compounds, respectively) imply that the XH groups in the studied complexes participate in hydrogen bonds of medium strength. The appearance of the XH stretching region is regularly influenced by vibrational interactions; hence, no precise comment on the number of the XH oscillators can be given. In the absence of overlapping OH stretches, *two* strong ν(NH) bands in the spectrum of the Zn adduct are well resolved (in addition to those from the ν(CH) and non-fundamental modes), again implying presence of at least two nicotinamide ligands in its structure, one of them being involved in somewhat stronger N–H···A (A = acceptor) hydrogen bonding. The chloride ions are the most likely acceptors to be found in the lattice. The additional high-frequency band in the spectrum of the Zn complex (Fig. 1) at 3568 cm^{-1} is probably not a fundamental, but rather an inherently weak band intensified upon the overlap with the ν(NH) bands.

Table 1. Thermal data for the nicotinamide adducts of Co(II), Ni(II) and Zn(II) chlorides.

Stage	Temp. range/°C	DTA peaks/°C[a]	Mass loss %		Leaving species
			Calculated	Experimental	
$[Co(na)_2(H_2O)_4]Cl_2$		(calc.%/obs.%) H: 4.52/4.29, N: 12.55/14.70			
1	25–114	89(–)	16.15	16.36	$4H_2O$
2	210–247	245(+)	27.37	29.50	1na
3	247–420	390(+) (complex)	38.58	41.25	undefined
$[Ni(na)_2(H_2O)_4]Cl_2$		(calc.%/obs.%) H: 4.52/4.02, N: 12.56/14.90			
1	36–163	144(–)	15.06	16.16	$4H_2O$
2	163–251	238(–)	27.39	28.45	1na
3	252–967	425(+) (complex)	40.80	39.35	undefined
$[Zn(na)_2Cl_2]$		(calc.%/obs.%) H: 3.18/2.82, N: 14.72/12.08			
1	302–360	313(–)	32.09	35.00	1na
2	372–648	482(+), 504(+), 613(+)	46.52	44.84	undefined

[a] Symbols denote: (–) – endothermic, (+) – exothermic.

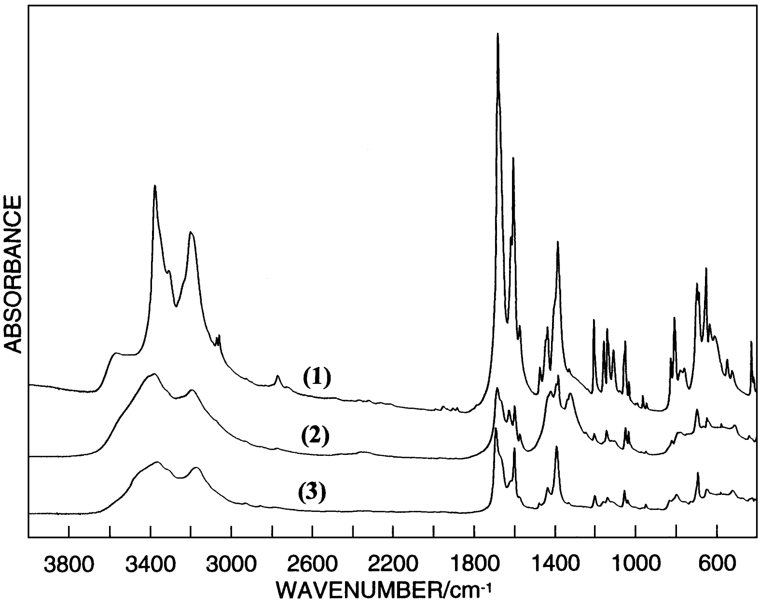

Figure 1. The 4000–400 cm^{-1} region in the FT IR spectra of nicotinamide adducts of Zn(II) (1), Co(II) (2) and Ni(II) (3) chlorides.

The ν(CO) mode (usually referred to as amide I) in the spectra of the studied complexes appears as a strong band at 1687 (Co), 1693 (Ni) and 1680 cm^{-1} (Zn) with shoulder on its lower-frequency side (at about 1670 cm^{-1}). The present variation in the ν(CO) frequency might be a result of combined factors such as the degree of conjugation of the carbonyl group with the benzene ring or influence of intermolecular interactions. It is known that the hydrogen bonding influences heavily the length and the force constant of the CO group, and thus the respective stretching frequency. This might be the reason for the larger red-shift of the ν(CO) mode in the spectrum of the Zn complex. The mode known as amide II was identified as somewhat less intense bands at 1600 (Co), 1603 (Ni) and 1606 cm^{-1} (Zn).

Electronic spectra: The λ_{max} and 10 Dq values of d–d transitions, displayed by the complexes, are listed in Table 2. The higher energy $\pi \rightarrow \pi^*$ transitions (*ca.* 40000 cm^{-1}), which are not significantly altered on complex formation are not given in Table 2. The values of the 10 Dq parameter were found using the Tanabe and Sugano diagrams [11]. The d–d transitions correspond to the relevant coordination geometry of the metal ions. The Ni adduct absorbs below and above 15000 cm^{-1}, indicating that it contains 6-coordinate distorted octahedral Ni(II) center [12]. The band at 19 880 cm^{-1}, attributable to the $^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_2) transition, is consistent with an octahedral stereochemistry around Co(II) ion in the Co complex [13]. Furthermore, the spectra of all complexes exhibit an intense band in 33333–37000 cm^{-1} region, which might be due to charge transfer processes or the $n \rightarrow \pi^*$ transitions associated with the pyridyl and the amino group of (na). Also contributing to the intensity and complexity of the spectra in the region above 30000 cm^{-1} of the complexes can be the Cl → metal(II) bands [14]. The colourless Zn compound did not absorb in the UV/Vis region.

Table 2. Electronic spectra of the studied nicotinamide complexes of Co(II), Ni(II) and Zn(II) chlorides.

Complex	λ_{max}/(nm)^a	10 Dq / (cm^{-1})	Assignment of d-d transitions
$[Co(na)_2(H_2O)_4]Cl_2$	503	19880	$^4T_{1g}$ (F) → $^4T_{1g}$ (P) (ν_2)
$[Ni(na)_2(H_2O)_4]Cl_2$	715	14184	$^3A_{2g}$ → ^1E_g
	385	25974	$^3A_{2g}$ → $^1T_{1g}$ (P)
$[Zn(na)_2Cl_2]$	–	–	–

[a] The values were obtained for the mixtures with ambient mole ratio of both metal(II) chlorides and nicotinamide aqueous solutions.

Theoretical calculations: On the basis of the above analyses, the existence of hexacoordinated $[M(na)_2(H_2O)_4]^{2+}$ (M = Co, Ni) ions and tetracoordinated $[Zn(na)_2Cl_2]$ molecules in the studied compounds was supposed. Models of these species were built with Chem3D [9] and their geometry was optimized by the Allinger's MM2 force field [15] and the parameters for non-MM2 atoms implemented in the program. For the metals, the available atom types accounting for the respective coordination geometries were used.

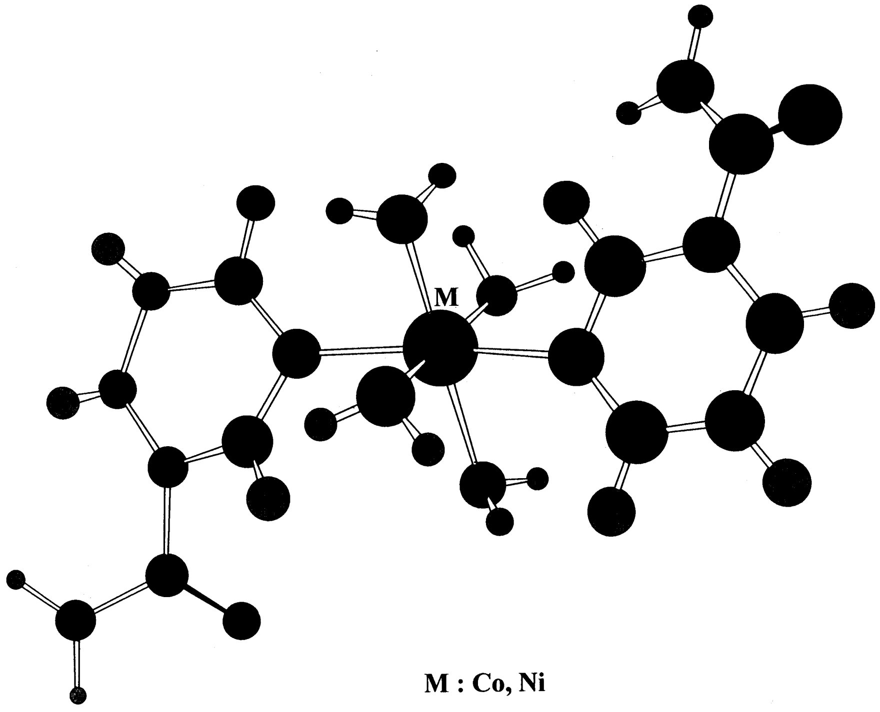

Figure 2. The model molecular structure of the $[M(na)_2(H_2O)_4]^{2+}$ ions in the Co(II) and Ni(II) nicotinamide chloride.

The Co and Ni complex ions resulted in centrosymmetric octahedral geometries (Fig. 2). The four water oxygen atoms of two structural types are placed in the equatorial plane, while the two structurally equivalent nicotinamide molecules with their pyridine nitrogen atoms approach from the apexes. In the model, the amide group is not coplanar with the pyridine ring, being rotated for about 60°. Nevertheless, the planarity within the pyridine ring and the amide groups is essentially preserved. Predicted Co–N(na) distances (about 2 Å) are somewhat shorter than the mean Co–pyridine distance (2.182(23) Å) obtained from the survey of octahedral Co(II) pyridine complexes in the Cambridge Structural Database [16]. The calculated Co–O_W distances (1.8–2 Å) agree well with the expected values for pyridine compounds (2.086(32) Å [16]).

For the Zn adduct, a structure with molecular symmetry C_1 was obtained (Fig. 3), comprising two structurally different (na) ligands for each structural type of formula unit in the cell. The (na) pyridine rings should be nearly coplanar with each other, but the amide groups are again slightly rotated in respect to the respective aromatic planes. The Zn–N(na) bonds should amount to around 1.9 Å. The two chlorine atoms with an Cl–N–Cl angle of 90° are about 2.3 Å away from the Zn atom, which matches very well the statistical value (2.267(20) Å) for tetrahedral Zn(II) chlorides [16].

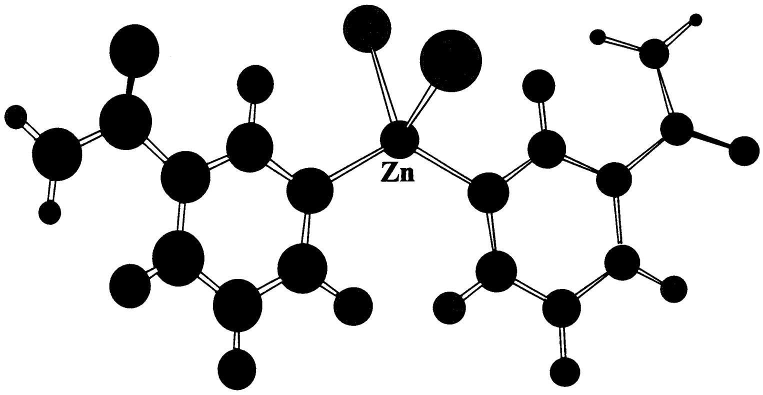

Figure 3. The model molecular structure of the $[Zn(na)_2Cl_2]$ formula unit in Zn(II) nicotinamide chloride.

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