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Bis(*N*,*N*-DIETHYLNICOTINAMIDE) *p*-CHLOROBENZOATE COMPLEXES OF Ni(II), Zn(II) AND Cd(II)

Synthesis and characterization

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Three novel mixed ligand complexes of Ni(II), Zn(II) and Cd(II) with *p*-chlorobenzote and N,N-diethylnicotinamide were synthesised and characterized on the basis of elemental analysis, FTIR spectroscopic analysis, solid state UV-Vis spectrometric and magnetic susceptibility data. The thermal behavior of the complexes was studied by simultaneous TG–DTA methods in static air atmosphere and the mass spectra data were recorded.

According to microanalytical results, formulas of complexes are $C_{34}H_{40}N_4O_8ClNi$, $C_{34}H_{40}N_4O_8ClZn$ and $C_{34}H_{44}N_4O_{10}ClCd$. The complexes contain two moles of coordination waters, two moles *p*-chlorobenzoate and two mole N,N-diethylnicotinamide (dena) ligands per formula unit. In these complexes, the *p*-chlorobenzoate and N,N-diethylnicotinamide behave as monodentate ligand through acidic oxygen and nitrogen of pyridine ring. The decomposition pathways and the stability of the complexes are interpreted in the terms of the structural data. The final decomposition products were found to be as metal oxides.

Keywords: *p-chlorobenzoate N,N-diethylnicotinamide, mixed ligand complexes, thermal decomposition, transition metal complexes*

Introduction

The diversity of inorganic compounds and their applications in medicine encompass cancer chemotheraphy, arthritis, antimicrobial agents, metalloenzyme inhibitors, antimanic agents and many others [1]. The carboxylates play an important role in inorganic chemistry, and then again many metal cations in a great number of various biological processes, especially six-membered ring system, are components of several vitamins and drugs [2]. Also some carboxylate compounds (e.g. benzoates) are known to have antibacterial activity. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment for fungal skin diseases [3, 4]. Metal complexes of biologically important ligands are sometimes more effective than the free ligands [5]. It is well documented that heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems being a component of several vitamins and drugs [6–9]. In the coordination compounds of some transition metals of aryl carboxylic acid and derivatives of halogeno, the bonding occurs by acidic –OH group of carboxylic acid as monodentate [10]. According to X-ray structures in literature, halogeno group of aryl carboxylic acid has not participated to coordination and it is to free. The N,N-diethylnicotinamide (dena) ligand has been coordinated by hetero nitrogen atom of pyridine ring. These types of complexes are resembled to in literature [11–17]. It is not surprising; therefore, that many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms. The presence of pyridine ring in numerous naturally abundant compounds, adducts of dena are also scientific interest. Therefore, the structure of dena has been the subject of many studies [18–22]. The thermal decomposition properties of title compounds are compatible with literature [23–29].

In the present paper, we reported the synthesis, spectroscopic and thermal properties of some new mixed-ligand complexes of Ni(II), Zn(II) and Cd(II) containing *p*-chlorobenzoate-N,N-diethylnicotinamide. The structures of the ligands are shown in Fig. 1.

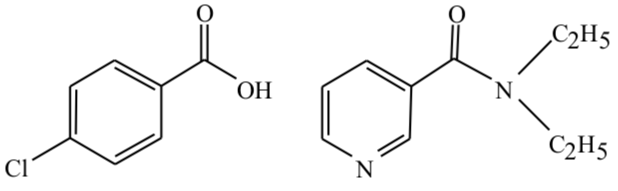

Fig. 1 Structures of the ligands

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Experimental

Materials

All chemicals used were analytical reagent products. $NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot 6H_2O$, $CdSO_4 \cdot 6H_2O$ and *p*-chlorobenzoic acid were obtained from Merck (Darmstadt, Germany). Diethylnicotinamide was purchased from Darmitsa Chemicals Union (Kiev, Ukraine).

Preparation of *p*-chlorobenzoate complexes

At the first step, *p*-chlorobenzoic acid sodium salts were prepared according to the following equation:

$$2p\text{-Clba}+2NaHCO_3 \rightarrow 2Na(p\text{-Clba})+2CO_2+2H_2O$$

where *p*-Clba=p-chlorobenzoic acid.

At the second step, M(II)-*p*-Clba salts were synthesized from Na(*p*-Clba) salt by substitution reaction:

$$2Na(p\text{-Clba})+MSO_4 \cdot 6H_2O \rightarrow$$
$$\rightarrow M(p\text{-Clba})_2 \cdot nH_2O+Na_2SO_4$$

where *M*=Ni(II), Zn(II) and Cd(II).

The compounds of $M(_p\text{-Clba})_2 \cdot nH_2O$ were occurred in aqua media.

Synthesis of mixed-ligand complexes

A solution of dena (2 mmol) in distilled water (30 mL) was added dropwise with stirring to a solution of $M(p\text{-Clba})_2(H_2O)_n$ (1 mmol) in hot distilled water (50 mL). The solutions were heated to 50°C in a temperature-controlled bath and stirred for 4 h and then cooled to room temperature and allowed to stay 10–12 days for crystallization. The crystals formed were filtered and washed with cold water and acetone and dried in vacuo. The mixed-ligand complexes were prepared according to the following equations:

$$M(p\text{-Clba})_2(H_2O)_n+2\text{dena} \rightarrow$$
$$\rightarrow M(p\text{-Clba})_2(\text{dena})_2(H_2O)_n$$

where dena:N,N-diethylnicotinamide.

Methods

Elemental analyses (C, H, N) were performed by standard methods in Tubitak Laboratory (Scientific and Technical Research Council of Turkey). Magnetic susceptibility measurements at room temperatures were determined on a Sherwood Scientific MXI model magnetic balance (Gouy Method) using $Hg[Co(SCN)_4]$. IR spectra were recorded in 4000–400 cm^{-1} region with a Perkin Elmer 1000 FTIR spectrophotometer as KBr pellets.

Thermal analysis curves (TG-DTA) were recorded simultaneously in a static air atmosphere with a Schimadzu DTG 60 thermal analyzer. The samples weighed approximately 10 mg and highly sintered $\alpha\text{-}Al_2O_3$ was used as a reference material. The heating rate was 10°C min^{-1} and the DTG sensitivity is 0.05 mg s^{-1}. Schimadzu UV3600/UV-VIS-NIR model spectrophotometer was used for solid state ultraviolet-visible range studies. Mass spectrum data were recorded Agilent with Technologies 5973 spectrophotometer using DIP-MS method.

Results and discussion

The complexes were synthesized with high purity. The results of the elemental analysis indicated that the complexes contain two moles of *p*-chlorobenzoate, two moles N,N-diethylnicotinamide ligands and two moles of coordinated water per mole formula units. The two moles of hydrate waters is bonded to Cd(II) complex by hydrogen bonds, but Ni(II) and Zn(II) complexes has not any hydrate water. Analytical results, compositions of the complexes and confirmation the proposed formula of the complexes are given in Table 1. In the complexes, octahedral coordination of the Ni(II), Zn(II) and Cd(II) ions are formed by carboxylic acid oxygen atoms from two moles of *p*-chlorobenzoates as monoanonic monodentate ligand and two donor nitrogen atoms from two N,N-diethylnicotinamides and two moles of coordinated waters. The suggested coordination of metal was compatible with literature [15, 22, 23, 30].

Table 1 Analytical data of the metal complexes

Complex	*M*/g mol^{-1}	Yield/%	Found (calcd.)/%		
			C	H	N
$[Ni(p\text{-Clba})_2(\text{dena})_2(H_2O)_2]$ $C_{34}H_{40}N_4O_8ClNi$	762.29	75	53.51 (53.56)	5.09 (5.25)	7.43 (7.35)
$[Zn(p\text{-Clba})_2(\text{dena})_2(H_2O)_2]$ $C_{34}H_{40}N_4O_8ClZn$	768.99	86	52.89 (53.09)	5.01 (5.27)	7.26 (7.20)
$[Cd(p\text{-Clba})_2(\text{dena})_2(H_2O)_2] \cdot 2H_2O$ $C_{34}H_{44}N_4O_{10}ClCd$	852.01	90	47.83 (47.92)	4.85 (5.16)	6.65 (6.58)

[a] decomposition point *p*-chlorobenzic acid (*p*-Clba), N,N-diethylnicotinamid (dena)

Due to the low solubility, solid sample record satisfactory UV-Vis spectra for the complexes was studied. The electronic spectrum of the Ni(II) complex shows absorption bands at about 7500 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{2g}$), 15400 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{1g}$)($^3F$) and 25300 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{1g}$)($^3P$). The Zn(II) and Cd(II) complexes do not show any absorption peak in UV bands. The peaks belonging to the $\pi\rightarrow\pi^*$ transitions are shifted to a longer wavelength as a consequence of coordination when binding with metal, confirming the formation of *p*-Clba–dena metal complexes. The Ni(II) complex is paramagnetic while, Zn(II) and Cd(II) complexes are diamagnetic. These values suggest octahedral coordination around the metal ions.

FTIR spectra

Characteristic FTIR spectrum peaks of the complexes are given in the Table 2. When investigation of FTIR spectra of complexes –OH absorption bands of aqua ligands are presence in the range of 3600–2900 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of water molecules. Pyridine ring vibrations of free diethylnicotinamide at 1580 cm^{-1} shifts to lower frequencies in the spectrum of the metal complexes. These shifts are shown in range of 1420 cm^{-1} for Ni(II), 1415 cm^{-1} for Zn(II) and 1413 cm^{-1} for Cd(II), it may indicate that the pyridine ring is coordinated. Conjugation between the carbonyl group and the amide nitrogen causes small frequency shifts. The strong bands observed at around 1580 cm^{-1} for Ni(II), 1582 cm^{-1} for Zn(II) and 1585 cm^{-1} for Cd(II) are assigned to this mode. The main difference in the spectrum of *p*-chloro-benzoic acid is that the C=O stretching vibration of the carboxyl group at 1730–1708 cm^{-1} is shifted to lower frequency (1623, 1619 and 1620 cm^{-1}, respectively) in all the metal complexes. This may be a consequence of coordination takes place through the carboxyl group by deprotonation of the *p*-Clba molecule during coordination. When the metal-*p*-Clba-dena mixed ligand complexes are produced, the peak of acidic COOH group at 1688 cm^{-1} disappears [16]. At the same time, in the complexes, the $(COO^-)_{as}$ are located at 1548 cm^{-1} for Ni(II), 1550 cm^{-1} for Zn(II) and 1546 cm^{-1} for Cd(II) complexes. $(COO^-)_s$ peaks are observed at 1397 cm^{-1} for Ni(II), 1392 cm^{-1} for Zn(II) and 1391 cm^{-1} for Cd(II) complexes. The splitting of the ν_{as} and ν_s bands of COO^- groups are for Ni(II), Zn(II) and Cd(II) complexes almost identical (151, 158 and 155 cm^{-1}, respectively) and slightly than for the sodium salts of these acids (134 cm^{-1}) [31] that monodentate carboxylate group exists [32]. For monodentate geometry of carboxylate group, the bands of $\nu_{as(COO-)}$ $\nu_{s(COO-)}$ in synthesized complexes are shifted to higher and lower region or $\nu_{as(COO-)\text{prepared complex}}>\nu_{s(COO-)\text{sodium salt}}$. The band of ν_{C-Cl} is almost in the same position in the FTIR spectra of prepared complexes (780 cm^{-1} for Ni(II) and Zn(II), 778 cm^{-1} for Cd(II)) as in the spectrum of sodium salt (780 cm^{-1}). This result is supported since, the *p*-chlorobenzoate ligand do not coordinate to metal atom via halogen group [33]. The low intensity bands in the region of 710–450 cm^{-1} are attributed to M–N for dena ligand and M–O for *p*-Clba vibrations [22, 34–37].

Table 2 Characteristic FTIR peaks of metal complexes

Gruplar	Ni(II)	Zn(II)	Cd(II)
$\nu_{(-OH)H2O}$	3550–2900	3500–3100	3600–2900
$\nu_{(C-H)}$	3056	3067	3090
$\nu_{(C=O)ester}$	1623	1619	1620
$\nu_{(COO-)as}$	1548	1550	1546
$\delta_{(H2O)}$	1472	1470	1465
$\nu_{(COO-)s}$	1397	1392	1391
$\Delta\nu$	151	158	155
$\nu_{(C-O-C)}$	1170	1171	1195
$\nu_{(C-H)CH3}$	1319	1319	1312
$\nu_{(C-N)py}$	1420	1415	1413
$\nu_{(C-N)amid}$	1271	1293	1281
$\nu_{C=O)amid}$	1580	1582	1585
$\nu_{(C-halogen)}$	780	780	778
ν_{Me-N}	646	644	635
ν_{Me-O}	480	470	475

Thermal data

$[Ni(p\text{-}Clba)_2(dena)_2(H_2O)_2]$

TG-DTA curves for the Ni(II) complex are given in Fig. 2. Two moles of coordinated water of this complex are removed in the interval of 100–167°C and at 133°C gives max. DTA peak (exp. 5.23%; calc. 4.73%). After then at this temperature, organic

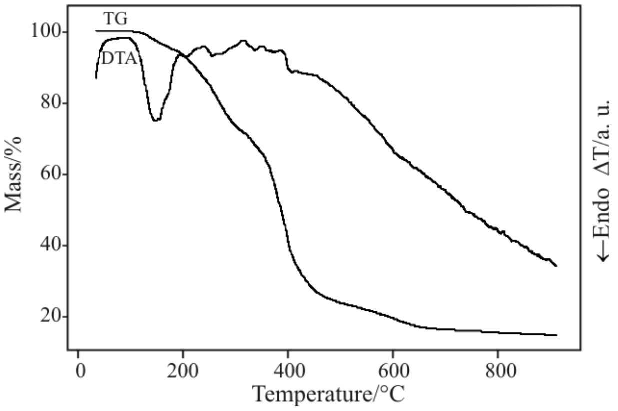

Fig. 2 TG-DTA curve of the $[Ni(p\text{-}Clba)_2(dena)_2(H_2O)_2]$

ligands start to decompose together. The decomposition occurs in the temperature range of 175–605°C at four steps by giving endothermic DTA peaks at 224, 296 and 356°C. At the result of the removing organic ligands, NiO is the residue (exp. 10.55%; calc. 9.84%). The final decomposition product, by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides

[Zn(p-Clba)$_2$(dena)$_2$(H$_2$O)$_2$]

Firstly, dehydration of two moles of crystal water occur at 107 and 150°C in two steps by giving endothermic DTA peak (Fig. 3) (exp. 5.02%; calc. 4.68%). The anhydrous Zn(II) complex is not stable and after the dehydration fortwith organic parts start to decompose in the range of 170–522°C by giving endothermic DTA peaks at 223, 294 350 and 448°C. Lastly, decomposition of the complex, the residue ZnO was identified by IR spectroscopy (exp. 10.11%; calc. 10.47%). The experimental values for the mass loss of the dehydration stage are well consistent with the calculated values.

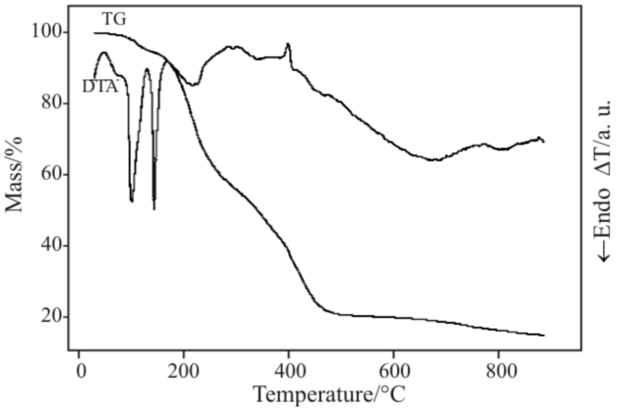

Fig. 3 TG-DTA curve of the [Zn(p-Clba)$_2$(dena)$_2$(H$_2$O)$_2$]

[Cd(p-Clba)$_2$(dena)$_2$(H$_2$O)$_2$]·2H$_2$O

The thermal decomposition of Cd(II) complex starts at the 65–102°C temperature range with the release of the two moles of hydrate waters (exp. 4.23%; calc. 4.21%). The decomposition is occurred one-step by giving endothermic DTA peak at 91°C. The coordinated aqua ligands of Cd(II) complex are dehydrated in the one-step temperature in the interval of 168–197°C giving endothermic DTA peak at 186°C (exp. 4.67%; calc. 4.23%). The decomposition of the complex associated with the complete pyrolysis of the organic part of the compound starts above this temperature. The thermoanalytical responses of the complex is shown in Fig. 4. The organic part of the comlex decomposes with the release of CO$_2$ molecules. The descending continuous TG curve is obtained in the temperature range of 202–697°C (endothermic DTA peaks at 217, 412, 566 and 675°C). The final decomposition product is CdO (exp. 14.150%; calc. 15.27%). Similar decompositions behaviors are shown in literature [15, 23, 27–30, 34].

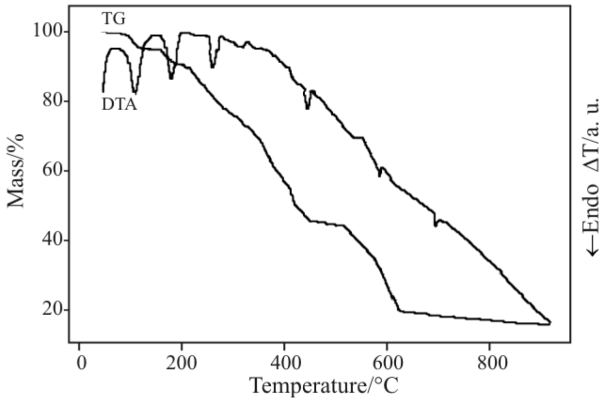

Fig. 4 TG-DTA curve of the [Cd(p-Clba)$_2$(dena)$_2$(H$_2$O)$_2$]·2H$_2$O

Mass spectra

To conclude the thermal decomposition pathway of the [Ni(p-Clba)$_2$(dena)$_2$(H$_2$O)$_2$] complex mass spectrum was recorded (Fig. 5) using direct insertion probe pyrolysis mass spectrometry method. The molecular ion peak is not detected in the recorded mass spectrum. The obtained mass spectrum is relatively complex and exhibits a large number of peaks that extend to m/z value above 750. These peaks belong to decomposition products of complex and ligands.

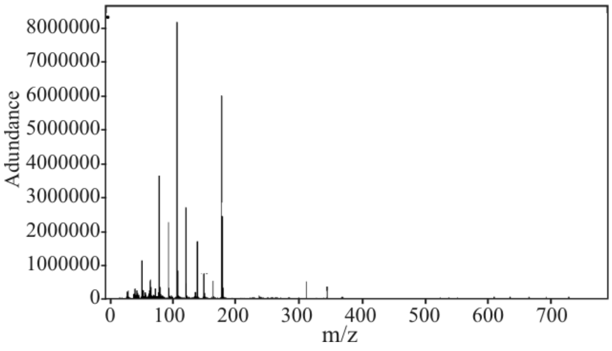

Fig. 5 Mass spectrum of [Ni(p-Clba)$_2$(dena)$_2$(H$_2$O)$_2$] complex

Conclusions

The IR spectra of the intermediate products show similar results. In the complexes, all ligands are coordinated to the metal ion as monodentate and their structures are octahedral that in each complex, two moles aqua, two moles p-chlorobenzoate and two moles dena ligands coordinate to metal ion. The p-chlorobenzoate ligand was bonded to concerned metal atoms via acidic oxygen atom and N,N-diethylnicotinamide via nitrogen atom of pyridine ring. It was found that Cd(II) complexes has two moles of hydrate water molecules, but Ni(II) and Zn(II) complexes have not. This result may be attributed to the diameter of Cd(II) ion. The coordinated aqua ligands remove almost in the same temperature range from all of the metal complexes. The complexes lose crystal water molecules in one-step. There is a study about determination of $[Zn(p\text{-Clba})_2(dena)_2(H_2O)_2]$ structure in [38] supports probable structures proposed of our results.

After the dehydration process, decomposition stages of the anhydrous complexes are related to release N,N-diethylnicotinamide and the partial decomposition of *p*-chlorobenzoate involving the release of CO_2. Previous studies show that the benzoate-metal complexes decompose by releasing of CO_2 [39–43]. The order of complexes according to changing of stabilities are Ni(II)>Zn(II)>Cd(II), anhydrous complexes are limited Zn(II)>Cd(II)>Ni(II). The final decomposition products were concerned as metal oxides in the 700–900°C temperature intervals. The mass spectrum shows that *m/z* molecular ion peaks belong to organic parts of Ni(II) complex. For example; at 177*m*/*z*, 120*m*/*z* may belong to N,N-diethylnicotinamide, benzoate ion respectively.

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