

SOME d^n METAL COMPLEXES WITH 4,4'-BIPYRIDINE AND TRICHLOROACETATES Preparation, characterization and thermal properties

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Abstract

The new mixed ligand complexes with formulae $\text{Co}(4\text{-bpy})_2\text{L}_2 \cdot 2\text{H}_2\text{O}$ (I), $\text{Cu}(4\text{-bpy})_2\text{L}_2 \cdot \text{H}_2\text{O}$ (II) and $\text{Cd}(4\text{-bpy})\text{L}_2 \cdot \text{H}_2\text{O}$ (III) ($4\text{-bpy}=4,4'$ -bipyridine, $\text{L}=\text{CCl}_3\text{COO}^-$) were prepared. Analysis of the IR spectra indicate that 4-bpy is coordinated with metal ions and carboxylates groups bond as bidentate chelating ligands. The electronic spectra are in accordance with pseudo-octahedral environment around the central metal ion in the Co(II) and Cu(II) complexes. The thermal decomposition of the synthesized complexes was studied in air. A coupled TG-MS system was used to analyse the principal volatile thermal decomposition products of Co(II) and Cu(II) complexes. Corresponding metal oxides were identified as a final product of pyrolysis with intermediate formation of metal chlorides.

Keywords: 4,4'-bipyridine complexes with Cd(II), 4,4'-bipyridine complexes with Co(II), 4,4'-bipyridine complexes with Cu(II), IR-VIS spectra, mass spectra data, thermal decomposition, trichloroacetate

Introduction

Metal complexes with carboxylates and nitrogen ligands were a subject of particular interest considering their biochemical importance. Data concerning complexes of title metals with heterocyclic nitrogen ligands and trichloroacetates (L) are few [1–7]. However, studies on the complexes of Co(II), Cu(II), Cd(II) with bipyridine and trichloroacetates are not yet in literature. Only the complexes of Zn(II) with trichloroacetates and 2,2'-bipyridine or 4,4'-bipyridine (4-bpy) were described in [8]. The thermal decomposition of copper(II) trichloroacetates has also been evidenced [9, 10]. Recently, mixed ligand complexes of Mn(II), Co(II), Ni(II) and Cu(II) with 4-bpy and monochloroacetates were obtained and investigated in our laboratory [11].

The aim of this paper is to study properties of the newly synthesized complexes of Co(II), Cu(II), Cd(II) with 4-bpy and trichloroacetates. These compounds were characterized by elemental analysis, IR, electronic spectra and molar conductivity. The thermal decomposition of prepared complexes was investigated in air. A coupled TG-MS system was used to analyse the principal volatile thermal decomposition products.

Experimental

Materials

4,4'-Bipyridine (*m.p.* 69.9°C) and trichloroacetic acid p.a. were obtained from Aldrich. Methanol (anhydroskan) was purchased from Lab. Scan. Other chemicals were p.a. from POCH, Gliwice. Metal(II) trichloroacetates were prepared in water solution by adding 20 cm³ of 2 M trichloroacetic acid to freshly precipitated metal carbonates in ca. stoichiometric proportion. The metal(II) contents in obtained solutions were determined by standard complexometric titration.

Synthesis of complexes

A solution of 4-bpy (12.8 mmol) in 96% *v/v* ethanol (31.3 cm³) was directly added to the appropriate metal(II) trichloroacetate (4.3 mmol) in 8.7 cm³ of water. After stirring for several minutes the precipitates were filtered off and washed with 40% *v/v* ethanol and then with ethanol and diethyl ether mixture (1:1). The products were air dried at room temperature. Metal analyses in mineralized samples of these complexes were carried out by complexometric method. The contents of C, H and N were determined by elemental analysis with V₂O₅ as oxidizing agent. The analytical results of the investigated compounds are collected in Table 1.

Table 1 Analytical data and solubility, *S* (mol dm⁻³) in water at 21°C of the complexes

No.	Complex (colour)	Analysis: found (calculated)/%				<i>S</i> ·10 ³
		M	C	N	H	
I	Co(4-bpy) ₂ L ₂ ·2H ₂ O	8.36	39.59	7.45	2.58	1.20
	(pink)	(8.05)	(39.38)	(7.65)	(2.75)	
II	Cu(4-bpy) ₂ L ₂ ·H ₂ O	8.90	40.34	8.25	2.63	4.30
	(blue)	(8.84)	(40.11)	(7.80)	(2.52)	
III	Cd(4-bpy)L ₂ ·H ₂ O	19.05	27.68	4.77	1.79	0.44
	(white)	(18.39)	(27.51)	(4.58)	(1.65)	

Measurements

The thermal properties of complexes were studied by TG, DTG and DTA techniques. Samples of 100 mg were heated in the range 25–1000°C at a heating rate of 10°C min⁻¹. TG, DTG and DTA curves were recorded on derivatograph type Q-1500. α-Al₂O₃ served as reference material. Mass spectrometer was used for the characterization of volatile pyrolysis products of the Co(II) and Cu(II) complexes (with samples of mass ca. 7 mg). The TG-MS system: derivatograph TG/DTA-SETSIS-16/18, mass spectrometer ThermoStar from Balzers, crucible Pt 100 μl. All the thermal investigations were carried out in air. The molar conductivities (Λ_M) of the complexes

were measured on $1.0 \cdot 10^{-3}$ mol dm⁻³ solutions in methanol at 25°C. The other apparatus and experimental conditions were described in earlier papers [12, 13].

Results and discussion

The empirical formulae of the isolated compounds agree with the analytical results and their solubility in water which are given in Table 1. All the complexes were small crystalline solids and air stable at room temperature. The complexes Co(4-bpy)₂L₂·2H₂O and Cd(4-bpy)L₂·H₂O were fairly dissolved in methanol, whereas Cu(4-bpy)₂L₂·H₂O was practically insoluble. The molar conductivities of Co(II) and Cd(II) complexes in methanol (72.2 and 74.2 Ω⁻¹ cm² mol⁻¹, respectively) show behaviour intermediates between those of non-electrolytes and 1:1 electrolytes [14]. Higher than expected Λ_M values are possible due to the displacement of trichloroacetate groups by solvent molecules. Similar behaviour was previously observed in metal complexes with bipyridine and other ligands [11, 15, 16].

Electronic and IR spectra

VIS spectra were obtained in Nujol mulls within the 26 000–12 000 cm⁻¹ region. The assignments of *d-d* transition bands of the solid Co(II) and Cu(II) complexes are based on the works of Lever [17] and Hathaway [18]. The electronic spectra of these complexes are all consistent with a pseudooctahedral configuration with tetragonal distortion. The cobalt(II) complex exhibit broad band at 21 300 cm⁻¹, which corresponds to the transition ⁴T_{1g}(F)→⁴T_{1g}(P). This band is apparently asymmetrical and has a shoulder in the region ca. 19 250 cm⁻¹. The single band observed for Cu(4-bpy)₂L₂·H₂O at 15 750 cm⁻¹ allows us to conclude that all three transitions, i.e. ²B_{1g}→²E_g, ²B_{1g}→²B_{2g}, ²B_{1g}→²A_{1g} lie within one broad envelope. The position, as well as the shape of this band revealed tetragonal distortion of the copper(II) complex from one electron orbital ground state *d*_{x²-y²} [18].

For consistency, only fundamental vibration modes of 4-bpy and OCO groups for obtained complexes are reported in Table 2. The most characteristic ring vibrations ν(CN), ν(CC) and pyridine ‘breathing’ mode are observed in these compounds in the range (cm⁻¹): 1602.7–1608.5, 1533.3–1537.2 and 1006.8–1016.6, respectively. These bands are shifted towards higher frequencies in comparison to free 4-bpy [11, 19, 20]. The observed changes are ascribed to the fact that 4-bpy is coordinated to metal(II).

The absorption bands arising from asymmetric ν_{as}(OCO) and symmetric ν_s(OCO) of OCO groups appear at 1656.7–1695.3 and 1369.4–1396.4 cm⁻¹, respectively. The magnitudes of separation, Δν=ν_{as}-ν_s between the frequencies ν_{as}(OCO) and ν_s(OCO) for the Co(II) and Cd(II) complexes are lower than for the sodium trichloroacetate salt (Table 2). Accordingly, taking into account the Nakamoto criterion [22] and other papers [23–29], the carboxylate group here appears as bidentate chelating ligand. However, ν_{as}(OCO) band of Cd(II) complex is splitted into a poorly resolved doublet. From there, it is probable that non-completely equivalent bonds be-

tween Cd(II) and carboxylate groups of the trichloroacetate ligand are formed [30]. The vibration modes of $\nu_s(\text{OCO})$ for the complex $\text{Cu}(4\text{-bpy})_2\text{L}_2\cdot\text{H}_2\text{O}$ is masked by the absorption of the 4-bpy. Thus, it is difficult to discuss the nature of copper–trichloroacetate bonds. The band of $\nu_{\text{as}}(\text{OCO})$ for $\text{Cu}(4\text{-bpy})_2\text{L}_2\cdot\text{H}_2\text{O}$ occurs at 1681.8 cm^{-1} . According to [31], frequency $\nu_{\text{as}}(\text{OCO})$ is observed at 1691 cm^{-1} in the case of $\text{CuL}_2(\text{py})_4$ ($\text{py}=\text{pyridine}$) probably with bidentate chelating trichloroacetate attached to the copper(II) atom.

A strong and broad band in the water stretching region (ca. $3400\text{--}3500\text{ cm}^{-1}$) and peak (or shoulder) in the water bending region (at ca. 1650 cm^{-1}) were present in IR spectra of the obtained complexes. The water wagging modes appear at ca. $520\text{--}532\text{ cm}^{-1}$ for coordinated water. The $\nu(\text{M}\text{--}\text{O})+\delta(\text{OCO})$ vibrations are observed as weak bands in the interval ca. $473\text{--}492\text{ cm}^{-1}$.

Table 2 Principal IR bands (cm^{-1}) for 4-bpy and OCO group in obtained complexes

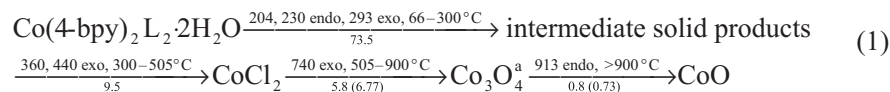
Compound	$\nu(\text{CN})$	$\nu(\text{CC})$	γ	$\nu_{\text{as}}(\text{OCO})$	$\nu_s(\text{OCO})$	$\Delta\nu$
NaCCl_3COO [21]	–	–	–	1677	1353	324
$\text{Co}(4\text{-bpy})_2\text{L}_2\cdot 2\text{H}_2\text{O}$	1608.5	1533.3	1008.7	1695.3	1396.4	299
$\text{Cu}(4\text{-bpy})_2\text{L}_2\cdot\text{H}_2\text{O}$	1600.8	1537.2	1016.6	1681.8	*	–
$\text{Cd}(4\text{-bpy})\text{L}_2\cdot\text{H}_2\text{O}$	1602.7	1533.3	1006.8	1670.2 1656.7 pd	1369.4	287

γ – pyridine ‘breathing’ mode; $\Delta\nu=\nu_{\text{as}}(\text{OCO})-\nu_s(\text{OCO})$; * – overlaid by 4-bpy absorption; pd – poorly resolved doublet

Thermal behaviour

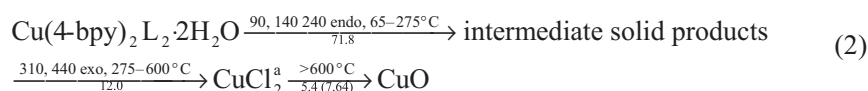
The thermal stability and behaviour of compounds tested during heating in air are described on the basis of thermal analysis and MS results (only for I and II). Co(II) and Cu(II) complexes are stable up to 65°C and only small differences in their thermal behaviour were observed. Probably the processes of the dehydration, the subsequent detachment of organic ligands and their decomposition are weakly separated from one another. The thermal decomposition of Co(II) and Cu(II) compounds is characterized by a sudden mass loss, which begins at ca. 150°C . The temperature of DTG peak minimum was at 260°C . For this reason, the process of isolation and identification of the solid intermediate products could not be carried out in the range $66\text{--}300^\circ\text{C}$ (I) and $65\text{--}275^\circ\text{C}$ (II). Furthermore, slow mass loss is observed. CoO and CuO were identified as final products of decomposition with intermediate formation of metal chlorides. DTA curves present mixtures of several endo- and exothermic peaks. The very strong exothermic maxima with centers at $360, 440^\circ\text{C}$ (I) and $310, 440^\circ\text{C}$ (II), correspond to pyrolysis of ligands.

The thermal decomposition of these complexes can be expressed by the Schemes (1) and (2):



^awith traces of CoO

On Schemes (1)–(3) below of the arrows the mass loss values (%) are shown (found and (calculated)). Below the arrows the temperature ranges of decomposition of compound and peaks of the DTA (°C) are presented.



^awith traces of CuO and Cu

MS data of Co(II) and Cu(II) complexes are very similar. They detected several ions signal intensities. Figure 1 presents the ion current for m/z detected in the mass spectrometer vs. time for complexes $\text{Co(4-bpy)}_2\text{L}_2\cdot 2\text{H}_2\text{O}$ and $\text{Cu(4-bpy)}_2\text{L}_2\cdot \text{H}_2\text{O}$ in

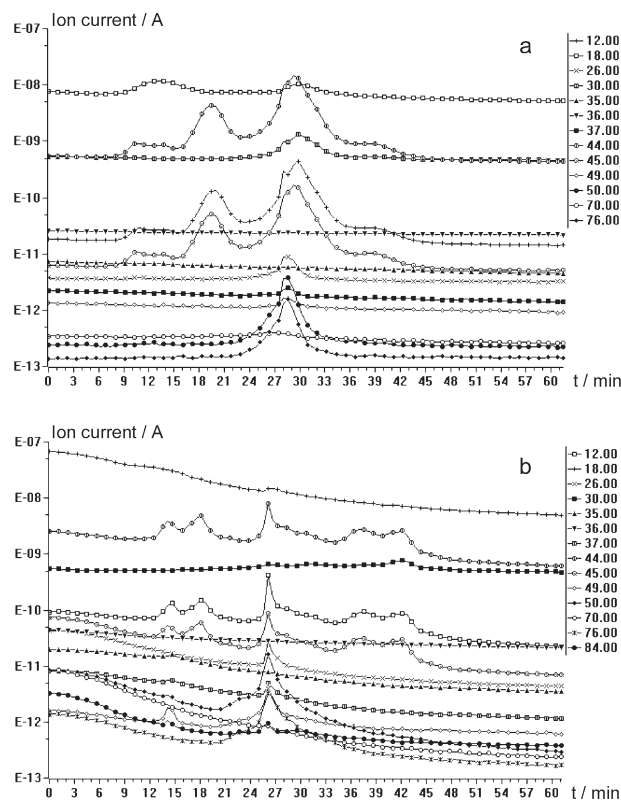


Fig. 1 Ion current for m/z detected in the mass spectrometer vs. time, heating rate $10^\circ\text{C min}^{-1}$. a – $\text{Co(4-bpy)}_2(\text{CCl}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, mass sample of 7.76 mg; b – $\text{Cu(4-bpy)}_2(\text{CCl}_3\text{COO})_2\cdot \text{H}_2\text{O}$, mass sample of 6.93 mg; original record

air. Generally, many signals are observed in the range 195–295°C for complex (I) and 145–265°C in the case (II). In complex (I), the corresponding MS peak for coordination water appeared at 151°C and for H_2O produced during decomposition of organic ligand at 317°C. In complex (II), similar profile of H_2O is observed (peaks at 140 and 282°C). The first maximum in the elimination of CO_2 (and its isotopes) occurs in the case (I) at 211 and second at 310°C. The profiles observed for CO_2 and its isotopes are similar. In contrast to (I) MS results, the ion signal intensities of CO_2 have centers at 159, 196, 279, 390 and 438°C in (II). Probably maximum rate of forming of NO at 315, 410°C for (I) and 278, 329, 438°C for complex (II) (with traces of N_2O_3 at 303 and 279°C in (I) and (II), respectively) are observed. CH_3Cl , traces of HCl , Cl_2 and probably fragment containing halogen with $m/z=49$ (I, II) and 84 (only for II) were produced by heating of Co(II) and Cu(II) complexes. Also peaks for fragments with $m/z=12, 13, 17, 26$ (I, II) were detected. A very low intensity of ion current is observed for $m/z=78$ (probably 4-bpy radical or $CClH_2CHO$) at 299 (I) and 273°C (II). TG coupled with MS data for some decomposition gaseous products are presented in Fig. 2.

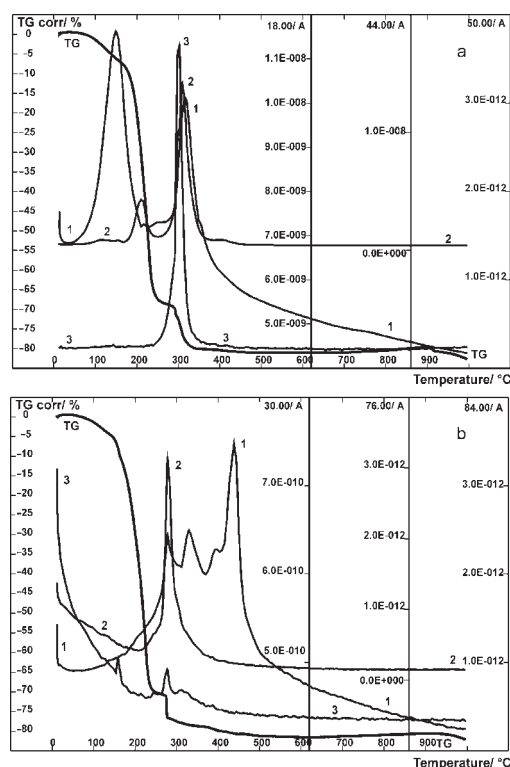


Fig. 2 TG curve of complexes and ion current detected by the MS for mass fragments m/z . $Co(4-bpy)_2(CCl_3COO)_2 \cdot 2H_2O$ (mass sample of 7.76 mg) – m/z : 1 – 18; 2 – 44; 3 – 50 (a); $Cu(4-bpy)_2(CCl_3COO)_2 \cdot H_2O$ (mass sample of 6.93 mg) – m/z : 1 – 30; 2 – 76; 3 – 84 (b); original record

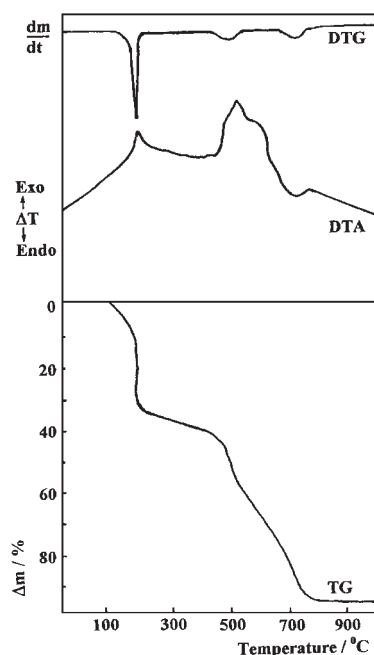
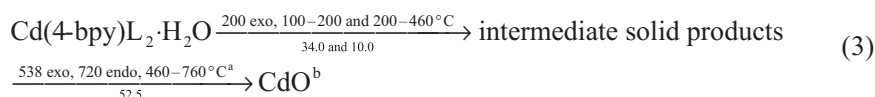


Fig. 3 Thermoanalytical curves of $\text{Cd}(4\text{-bpy})(\text{CCl}_3\text{COO})_2\cdot\text{H}_2\text{O}$; mass sample of 100 mg

The most stable is $\text{Cd}(4\text{-bpy})\text{L}_2\cdot\text{H}_2\text{O}$, it starts decomposition at 100°C . The TG curve shows a very rapid mass loss between $177\text{--}200^\circ\text{C}$ and slower in temperature range $200\text{--}460^\circ\text{C}$. The temperature of DTG peak minimum is at 200°C (Fig. 3). Such a decrease in mass is connected with the elimination of H_2O and a partial decomposition of organic ligand. Further sudden mass loss occurs above $460\text{--}760^\circ\text{C}$ as a result of total decomposition of ligands residue. The volatilization of CdCl_2 also takes place; only ca. 4% of CdO is formed as the final product. The decomposition may be represented as follows



^avolatilization of CdCl_2 and total decomposition of ligands, ^bfound only 4%

The DTA curve presents two exoeffects. A strong broad exothermic peak is observed in the range $460\text{--}610^\circ\text{C}$ with a center at about 538°C . It is connected with the oxidation of organic ligands. The endothermic effects associated with elimination of the ligands and volatilization of CdCl_2 are masked by this broad exothermic peak and only as the shoulders were observed on the DTA curve. The gaseous products of decomposition of $\text{Cd}(4\text{-bpy})\text{L}_2\cdot\text{H}_2\text{O}$ were not investigated.

Conclusions

IR spectra of the obtained complexes are similar. The values of $\Delta v = \nu_{as} - \nu_s$ for complexes correspond to chelating character of carboxylate groups. IR data indicate interaction of the 4,4'-bipyridine nitrogen atom with title metal ions. The electronic spectra of Co(II) and Cu(II) complexes are consistent with a distorted octahedral environment around the metal atom.

Complex of Cd(II) is thermally more stable. The compounds of Co(II) and Cu(II) decompose at the temperature ca. 40°C lower than Cd(II) complex. Also temperatures of the decomposition of Co(4-bpy)(CClH₂COO)₂·2H₂O and Cu(4-bpy)(CClH₂COO)₂·4H₂O [11] are significantly greater than those of Co(4-bpy)₂L₂·2H₂O and Cu(4-bpy)₂L₂·H₂O. Cu(CCl₃COO)₂·4H₂O (in nitrogen [10]) begins losing water at about 65°C, similarly to the obtained complexes of Co(II) and Cu(II). During heating the complexes the decomposition of organic ligand took place. In case of complex (III) also volatilization of CdCl₂ takes place. As the first major gaseous decomposition products H₂O and CO₂ were detected. The temperature of the oxide formation increases in the sequence: CuO < CdO < CoO.

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