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Thermal properties of Ca(II) and Cd(II) complexes of pyridinedicarboxylates

Correlation with crystal structures

B. Barszcz · J. Masternak · W. Surga

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Abstract The thermal behavior of [Ca(H_2O)$_3$(2,3-pydcH)$_2$]$_n$ (I), [Cd(H_2O)$_3$(2,3-pydc)]$_n$ (II), and [Cd(H_2O)$_6$][Cd(2,3-pydcH)$_3$]$_2$ (III) complexes with pyridine-2,3-dicarboxylic acid was monitored by TG, DTG, and DSC analysis, where 2,3-pydcH—mono deprotonated pyridine-2,3-dicarboxylic acid and 2,3-pydc—doubly deprotonated dicarboxylate anion. Thermal decomposition of these compounds go through one or two dehydratation stages, followed by the loss of organic matter. The final decomposition products are found to be the corresponding metal oxides. The possible scheme of destruction of the complexes have been used to reveal the relationships between stability and molecular structure.

Keywords TG · DTG · Pyridine-2,3-dicarboxylate · Calcium (II) complex · Cadmium (II) complex

Introduction

According to specific physicochemical properties, the individual metals exert differential cellular effects. One of the most important metals, calcium plays a wide range of roles in biological systems: intercellular and intracellular signaling, regulation of enzyme activity, conduction of nerve impulse, and contribution to the structural integrity of the skeleton [1]. Calcium homeostasis is maintained within a narrow range 2.10–2.60 mmol/L by balance between calcium absorption in the intestine, calcium excretion in the urine, and calcification and decalcification of bone [2–4]. Follow-up research into cadmium-related effects, especially at a low level, indicates an increased risk for low bone mass and deterioration of the skeleton [1, 5]. The close ionic radii of calcium and cadmium (0.95 and 1.00 Å) favors the exchange of the metals. Therefore, a comparison of coordination chemistry of calcium and cadmium model complexes ought to provide a solid-based example of how toxic metal ion substitution may perturb the structure of the calcium compound with the same ligand, pyridine-2,3-dicarboxylic acid which is great importance in biochemistry [6]. On the other hand, pyridine-2,3-dicarboxylic acid is remarkably attractive for its flexible and variety coordination modes to construct polymeric architecture. It can act as monodicarboxylate chelating anion, or three-dentate coordinating anion with acid hydrogen on nitrogen and doubly deprotonated, three-dentate dicarboxylate anion (2,3-pydc) and even in Mn(II) complexes as tetra-denatate and penta-dentate ligand [7–16]. Hence, studies on the thermal stability of Ca(II) and Cd(II) complexes with such ligand are of significant interest. Therefore, in this paper, we report thermal behaviors of three complexes, namely [Ca(H_2O)$_3$(2,3-pydcH)$_2$]$_n$ (I), [Cd(H_2O)$_3$(2,3-pydc)]$_n$ (II), and [Cd(H_2O)$_6$][Cd(2,3-pydcH)$_3$]$_2$ (III) in comparison to their crystal structure.

Experimental procedure

Pyridine-2,3-dicarboxylic acid (2,3-pydcH_2) (Aldrich) and the metal salts were obtained from Merck and used without further purification. Ethanol was purchased from P.O.Ch. Gliwice, and water was deionised.

B. Barszcz (✉) · J. Masternak · W. Surga
Institute of Chemistry, Jan Kochanowski University
of Humanities and Science, 15G Świętokrzyska Str.,
25-406 Kielce, Poland
e-mail: Barbara.Barszcz@ujk.kielce.pl

Syntheses of the complexes

The syntheses of $[Ca(H_2O)_3(2,3\text{-pydcH})_2]_n$ (I) and $[Cd(H_2O)_3(2,3\text{-pydc})]_n$ (II) complexes for thermal researches were performed in close analogy to the procedure described in [17] but, as it was not necessary to obtain crystals suitable for X-ray diffraction, the procedure was modified in the following way: a solution of 2,3-pydcH$_2$ (4 mmol) in ethanol/redistilled water (20/20 mL) heated to 353 K was stirred while $CaCO_3$ (2 mmol) in 40 mL redistilled water was added dropwise to the solution. After a few minutes, the resulting mixture was cooled to room temperature. The solution was filtered to remove any undissolved material and left to crystallize at room temperature. The colorless powder was collected by vacuum filtration, washed with mother liquid, and dried in a vacuum box. The products were collected in 69% and 52% yield, respectively. $[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ (III) was obtained in the same manner as described in [17].

Physicochemical techniques

Elemental analyses (C, N, H) were performed on Model 240 Perkin–Elmer CHN Analyzer. The metals after destroying the organic part by treatment with concentrated HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration [18]. IR spectra were recorded with Nicolet FTIR spectrophotometer in the region 4000–400 cm^{-1} using the diffusive reflection method. The thermal decompositions of ~10 mg of the prepared complexes were measured under the static air atmosphere with Mettler-Toledo Star TG/SDTA 851^e thermal analyzer at a heating rate of 5 K/min. For all complexes in the temperature range of 298–1273 K, alumina open crucibles were used. DSC analysis was carried out using DSC Mettler-Toledo instrument in standard closed sample pans, static air atmosphere, and heating rate of 5 K/min.

Results and discussion

Formulae of the complexes

For obtained complexes of Ca^{2+} and Cd^{2+}, the content of metal, C, N, and H was determined and the results are present in Table 1. All of the metal complexes are insoluble in water, alcohol, acetone, and chloroform, all are hydrated and stable in air.

Infrared spectra

The main IR spectral bands of pyridine-2,3-dicarboxylic acid (2,3-pydcH$_2$) and its complexes and their tentative assignments are summarized in Table 2.

The spectra confirm the structural data indicating that the pyridine-2,3-dicarboxylic acid may function as the mono deprotonated-2,3-dicarboxylic acid (2,3-pydcH) (complexes III and I) or as doubly deprotonated

Table 1 Elemental analysis data of Ca(II) and Cd(II) pyridinedicarboxylates

Complex	C/%		N/%		H/%		M/%	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[Ca(H_2O)_3(2,3\text{-pydcH})_2]_n$	39.70	39.47	6.54	6.55	3.05	3.31	9.43	9.09
$[Cd(H_2O)_3(2,3\text{-pydc})]_n$	25.36	25.30	4.22	4.27	2.74	2.72	33.90	33.53
$[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$	34.98	35.09	5.83	5.80	2.51	2.45	23.39	23.67

Table 2 IR spectral data for pyridine-2,3-dicarboxylic acid and its complexes/cm^{-1}

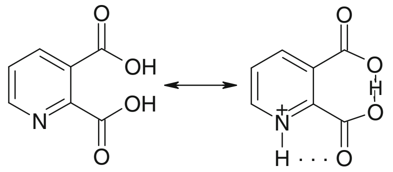
2,3-pydcH$_2$	$[Ca(H_2O)_3(2,3\text{-pydcH})_2]_n$ (I)	$[Cd(H_2O)_3(2,3\text{-pydc})]_n$ (II)	$[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ (III)	Assignments
	3548	3521 vs	3579, 3564vb	$\nu(OH)_{H_2O}$
3443vb	3436		3440vb	$\nu(OH)_{COOH}$
1715	1698		1706	ν(COOH)
	1648, 1362	1679,1664, 1402, 1378	1668, 1365	ν_{as}, $\nu_s(COO^-)$
	$\Delta = 286$	$\Delta = 277$, $\Delta = 286$	$\Delta = 303$	
1602, 1584	1605, 1584	1583, 1545s	1603, 1584	ν(ring)
1474, 1439	1500, 1458	1460, 1441	1444	ν(C=N)
1056, 1040	1091, 1049	1103, 1062	1099, 1052	δ (C–O)

vb, very broad; *vs*, very strong; *s* strong pyridine-2,3-dicarboxylate anion in the structure of II. The absence of strong IR bands around 1700 cm^{-1} in the spectrum of II indicates that all carboxylic groups are deprotonated [19, 20]. The single crystal analysis [17] indicates that all carboxylic groups coordinated with unidentate fashion [21] in all complexes and it correlated with the Δ values, defined by Deacon and Phillips [22] as $\nu_{as}(COO^-)$–$\nu_s(COO^-)$.

Thermal analysis

The crystal structure of ligand (pyridine-2,3-dicarboxylic acid) has been determined by both X-ray analysis [23] and neutron analysis [24]. Pyridine-2,3-dicarboxylic acid (2,3-$pydcH_2$) could exist in solution and solid state as zwitterionic isomer with one acid proton bound to the nitrogen of the pyridine ring and another bound to the oxygen of a carboxylate substituent, or as a non-zwitterionic isomer with acidic protons bound to each of the carboxylate groups (Scheme 1).

Due to clarifying the thermal decomposition of Ca(II) and Cd(II) complexes with the ligand mentioned above, we attached temperature degradation of 2,3-$pydcH_2$ under the same condition (Fig. 1). The compound is thermally stable up to 433 K. Above this temperature, the TG curve exhibits two steps of decomposition. The first significant weight loss of 31.17% corresponding to a loss of one molecule of water and carbon dioxide from carboxylate group in meta-position. Elimination of C_6H_4NO (calcd. 61.0%, found 62.12%) takes place in the second step.



Scheme 1 Non-zwitterionic and zwitterionic isomer of 2,3-$pydcH_2$ in equilibrium

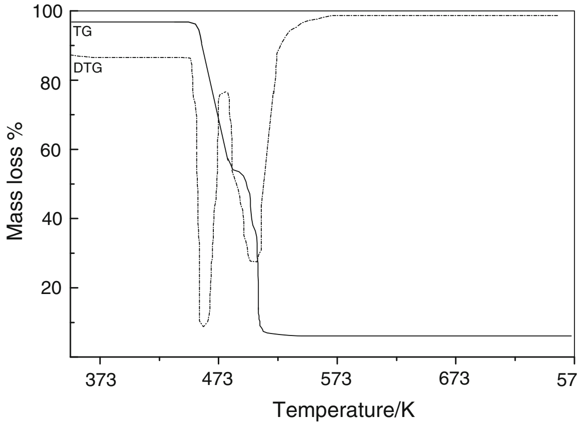


Fig. 1 TG, DTG curves of pyridine-2,3-dicarboxylic acid

Detailed TG, DTG, and DSC curves for analyzed complexes are shown in Figs. 2-4. The thermal decomposition data of compounds I–III are collected in Table 3. The residues were analyzed for percentage of the metal or metal oxide basing on the theoretical mass loss in accordance with the experimental values and additionally, the final product for cadmium complexes was confirmed from XRD patterns.

$[Ca(H_2O)_3(2,3\text{-}pydcH)_2]_n$ (I)

Figure 2a shows that the calcium(II) complex is stable up to 393 K after which it undergoes dehydratation with weight loss 13.3% (calcd. 12.7%). In the DSC (Fig. 2b), two endothermic picks with minimum at 413.6 and 427.9 K are observed. We suppose that can be caused by presence of different bound distances of three water molecules. The product $[Ca(2,3\text{-}pydcH)_2]_n$ obtained after dehydratation of complex I is stable up to 493 K. The degradation continues with a mass loss of 28.3% (calcd. 27.9%), which corresponds to the loss of one mono deprotonated pyridine-2,3-dicarboxylic acid. The decarboxylation of 2,3-pydc ligands occurs in the third stage,

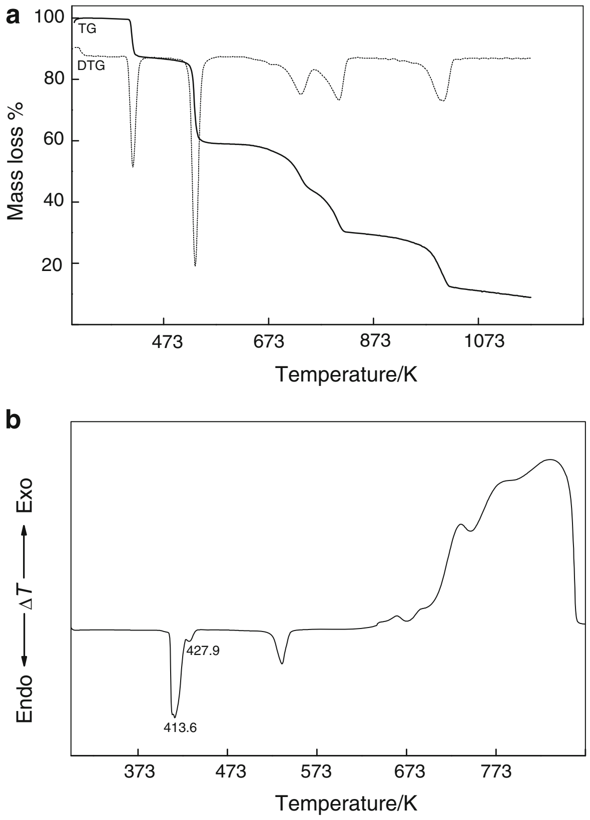


Fig. 2 TG, DTG (**a**), and DSC (**b**) curves of $[Ca(H_2O)_3(2,3\text{-}pydcH)_2]_n$ (I)

with bright exothermic pick in the temperature range of 673–853 K (DSC curve). The conclusion is supported by 30.0% of the losing weight, which is in accordance with the experimental value of 31.0%. Decomposition of the residue of decarboxylated ligand occurred above 923 K, with the accompanied weight loss of 18.1% (calcd. 18.2%). The oxide CaO forms in this stage.

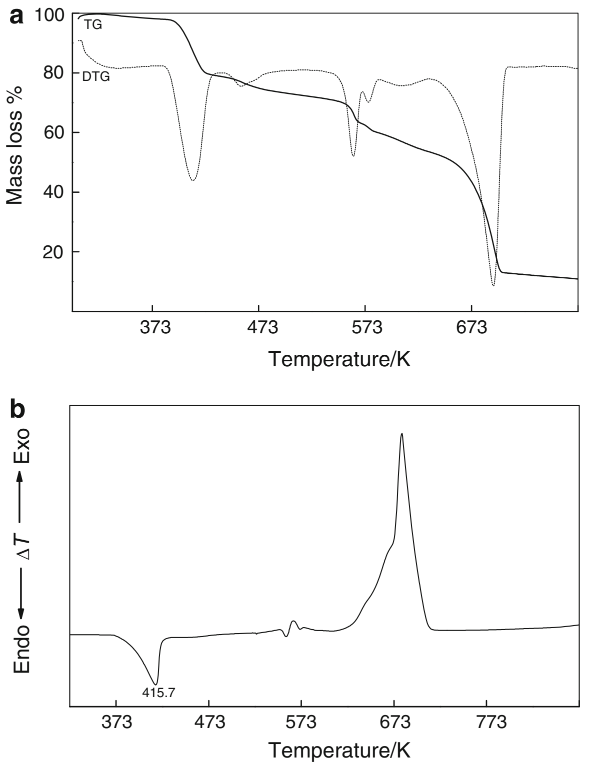


Fig. 3 TG, DTG (**a**), and DSC (**b**) curves of $[Cd(H_2O)_3(2,3\text{-pydc})]_n$ (II)

$[Cd(H_2O)_3(2,3\text{-pydc})]_n$ (II)

The thermal model of complex II is shown in Fig. 3a. The decomposition of complex II starts at 383 K. The first step in the TG curve corresponds to the loss of the three aqua molecules (exp. 14.2%; calcd. 16.3%). The dehydratation is an endothermic process (DSC curves Fig. 3b) at minimum of 415.7 K. The second step of degradation $[Cd(2,3\text{-pydc})]_n$ occurs at 443 K and is accompanied by mass loss of 14.0% suggesting the loss of one molecule carbon dioxide (calcd. 13.2%) [25]. The following step represents the decomposition of the organic moiety (2,3-pydc). The final residue of the decomposition is CdO which was additionally confirmed from XRD patterns and identified on the basis of ICDD using XRAYAN package [26]. Theoretically, the complete mass loss is 60.3% while the actual value is 61.5%.

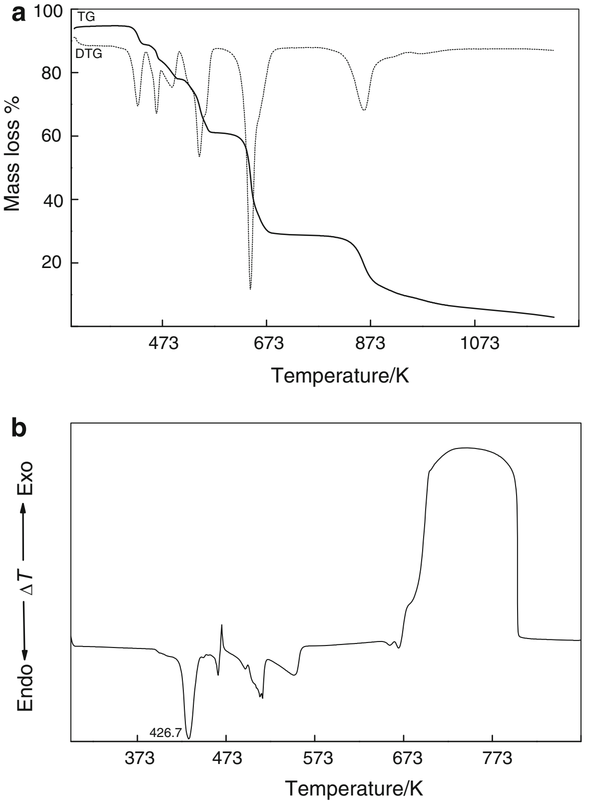


Fig. 4 TG, DTG (**a**), and DSC (**b**) curves of $[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ (III)

$[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ (III)

Cadmium complex III upon heating decomposes in five steps (Fig. 4a). The six molecules of water are released in the temperature range of 403–443 K (exp. 6.4%; calcd. 7.5%). In the DSC curve (Fig. 4b), an endothermic peak at 426.7 K is observed. The fact that all water molecules are eliminated from the complex at such a high temperature it may refer to coordinate water molecules. The dehydrated product $[Cd_{1.5}(2,3\text{-pydcH})_3]_2$ undergoes as slow decomposition to the final product, CdO. This is followed by two mass loss steps in the temperature ranges of 443–473 K and 472–513 K which are associated with the evaporation of six molecules of carbon oxide and carbon dioxide. The experimental values are in agreement with calculated percentages for anhydrous complex III (exp. 11.7%, 18.0%; calcd. 12.0%, 18.4%). A further step of the thermal decomposition is a release of six pyridine molecules and oxygen atoms coordinating directly with central cadmium (II) ion. The degradation of organic moiety may result from oxidation of the ligand and is accompanied by exothermic process (maximum on the DSC curve at 713 K). The actual remaining weight of 29.1% corresponds to the theoretical percentage 26.8%, indicating that the final products is CdO. It was confirmed from their XRD patterns [26].

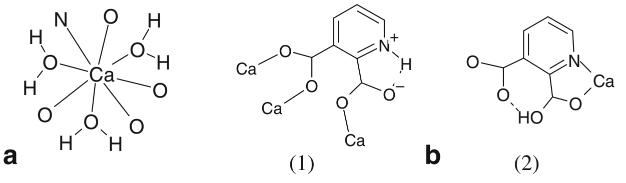
Table 3 Thermoanalitical data (TG, DTG, (DSC)) for complexes I–III

Complex	Stage	TG results, T_{range}/K	DTG (DSC) results, $T_{max.\ peaks}$/K	Peak nature	Mass loss/%		Loss	Final residue
					Calc.	Found		
$[Ca(H_2O)_3(2,3\text{-pydcH})_2]_n$ (I)	I	393–458	413.5 (413.6, 427.9)	Endo	12.7	13.3	3 H_2O	
	II	458–573	533.7 (533.5)	Endo	27.9	28.3	pycH	
	III	573–853	733.3, 806.8 (733.0)	Exo	31.0	30.0	3 CO_2	
	IV	853–1073	1004.7		18.2	18.1	py	
				Σ	89.8	89.7		
					9.4	10.3		CaO
$[Cd(H_2O)_3(2,3\text{-pydc})]_n$ (II)	I	383–443	411.3 (415.7)	Endo	16.3	14.2	3 H_2O	
	II	443–523	455.9		13.2	14.0	CO_2	
	III	523–733	577.0, 693.0 (557.2, 680.0)	Exo	30.8	33.3	py, CO	
				Σ	60.3	61.5		
					38.7	38.5		CdO
$[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ (III)	I	403–443	426.7 (426.7)	Endo	7.5	6.4	6 H_2O	
	II	443–473	462.3 (464.2, 467.1)	Endo, exo	12.0	11.7	6 CO	
	III	473–512	490.2 (499.1)	Endo				
	IV	512–583	546.0 (547.0)	Endo	18.4	18.0	6 CO_2	
	V	583–713	642.5 (696.6)	Exo	34.3	34.8	6 py, 1.5 O_2	
				Σ	72.2	70.9		
					27.8	29.1		CdO

Thermal stability and structure correlation

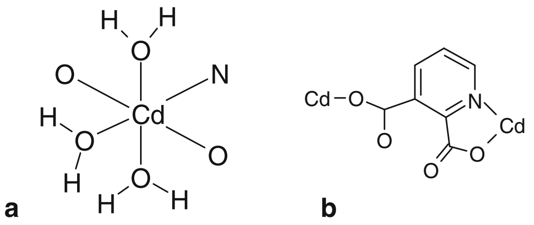
The decomposition procedure of the researched complexes can also be supported by their crystal structure presented by us in [17]. The calcium ion is in distorted dodecahedral coordination involving three water molecules and two mono deprotonated pyridine-2,3-dicarboxylic acid in the CaO_7N_1 polyhedron (Scheme 2a).

In one unit of the complex I, there exist two 2,3-pydcH anions. One of them exists as the deprotonated dicarboxylate anion in which the proton from one of the carboxyl groups is attached to the nitrogen atom, and the other one exists as the mono deprotonated dicarboxylic acid (2,3-pydcH) in which the carboxyl groups are bound to each other by a very short, strong asymmetrical hydrogen bond. Correspondingly, two types of coordination modes of ligands exist in the structure (Scheme 2b): (1) zwitterions form of ligand coordinates with Ca(II) only by oxygen atoms of carboxylate groups. One of the groups in the second position acts as monodendate but in the bridging fashion. The group in the third position donated only one atom to Ca(II) ion; (2) The 2,3-pydcH anion acts as bidendate N,O-donor, forming a five-membered chelate rings with central ion. The DSC data (Fig. 2b) correlate very well with the X-ray data characterizing coordination of three molecules of water in complex I. Two endothermic picks with minimum at 413.6 and 427.9 K are according to two types of water bound with different Ca–O(W) distances. Two of them are shorter with Ca–O(2W) 2,353(3) and Ca–O(3W) 2,389(3) Å, but the third one is much longer with Ca–O(1W) distance of 2,638(3) Å [17]. According to the structure of the calcium complex I (Scheme 2a), after dehydratation at 533 K part of nonchelating anion 2,3-pydcH is released (see Scheme 2b (1)). Additionally, such degradation confirms the existence of the longest Ca(1)–$O(29)_{-x,-y+1,-z+1}$ bond (2,555(3) Å) in form (1). In the next stage, decarboxylation and decomposition of the remaining ligand molecule acting as bidendate N,O-donor with Ca(II) ion is observed.

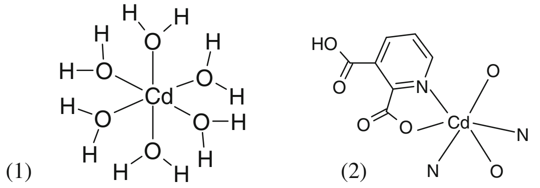


Scheme 2 The environment around an eight coordination calcium of $[Ca(H_2O)_3(2,3\text{-pydcH})_2]_n$ (**a**), and coordination modes (*1*), (*2*) of the 2,3-pydcH ligand (**b**)

The coordination environment of Cd(II) (complex II) formed by 2,3-pydc—doubly deprotonated dicarboxylate anion and three aqua ligands is distorted octahedron (CdO_5N) (Scheme 3a). The longest bond distance Cd–O(7W) of one molecule of coordinated water in complex II (2,396(3) Å) in comparison with the next two (Cd–O(5W) 2,259(3) Å and Cd–O(6W) 2,281(4) Å) [17] elucidate very broad endothermic peak on DSC curve.



Scheme 3 The environment around Cd(II) ion in $[Cd(H_2O)_3(2,3\text{-pydc})]_n$ (**a**) and coordination modes of the 2,3-pydcH (**b**)



Scheme 4 The environment around Cd(II) ion (*1*), (*2*) in $[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ complex

The III compound is composed of two complex ions $[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ linked by hydrogen bonds. The coordination sphere is in both ion distorted octahedral (Scheme 4).

Hexacoordination around Cd(2) is achieved by bonding of three ions of the 2,3-pydcH (CdN_3O_3) and Cd(1) coordinated to six water molecules (CdO_6) with the same bond distances (2.254(2) Å), which corresponds to only one endothermic peak at 426.7 K in the DSC curve (Fig. 4b). The fact that all water molecules are eliminated from the complex at such a high temperature confirms the existence of coordination-bounded water molecules. According to Scheme 3, the pyridine nitrogen atom and oxygen from the carboxylic group formed a very stable, five-membered chelate ring with Cd(2) ion. Consequently, the first step of decomposition begins at 443 K and the second at 473 K refers to the six molecules of the carbon oxide and carbon dioxide, released from the uncoordinated carboxylate groups.

Conclusions

The thermal decomposition of the researched complexes is a multistage process. The hydrated complexes of calcium (II) and cadmium (II) with pyridine-2,3-dicarboxylate lose all coordination water in one step which is connected with strong endothermic effects. The DSC data correlate very well with the X-ray data characterizing coordination of three molecules of water in complexes I and II. Comparing the temperatures of the dehydration process of Ca(II) and Cd(II) complexes, it is possible to suggest that coordination water molecules are more strongly bound in $[Cd(H_2O)_6][Cd(2,3\text{-pydcH})_3]_2$ than in the rest of the complexes, for example, even if in complex I, when the coordinated H_2O molecule have effectively filled the void space generated within the 3D network. In the next stages, the anhydrous complexes decompose exothermally to finally give metal oxides. We suppose that the highest thermal stability observed for complex III can be a result of ionic structure because releasing of even all the coordination water molecules from positive charged ion does not weaken the structure of anion. Lower thermal stability of cadmium and calcium polymer could result from a breakdown of 1D and 3D framework or, partially, from lesions structure after dehydratation. Complexes II and III determine a similar decomposition through three stages: dehydratation, decarboxylation, and finally decomposition pyridine-2,3-dicarboxylic acid fragments. It is important to emphasize that the thermal stability of the anhydrous complexes can be ordered in the following sequence: I > II ~ III, which is opposite to the thermal stability of hydrated complexes.

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