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Synthesis and thermal analysis of cadmium complexes of imidazole and its derivatives

M. Olczak-Kobza

Institute of General and Ecological Chemistry, Technical University, 90-924 Lodz, Poland

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Abstract

Mixed complexes of the type: $Cd(Sal)(HIm)_2$, $Cd(Sal)(HIm)_4 \cdot H_2O$, $Cd(Sal)(4\text{-}MHIm)_4$, $Cd(Im)_2(HIm)$ and $Cd(Salox)(4\text{-}MHIm)_2$ (where Sal = $OC_6H_4COO^{2-}$, Salox = $OC_6H_4CHNO^{2-}$, HIm = imidazole and 4-MHIm = 4-methylimidazole) have been synthesised. The complexes and the corresponding sinters, obtained at temperatures determined on the basis of the TG curves have been analysed by chemical, thermal, X-ray and IR methods. Thermal decomposition pathways have been postulated for these complexes. © 2001 Published by Elsevier Science B.V.

Keywords: Imidazole; 4-methylimidazole; Cadmium; Heteroligand complexes; Thermal analysis

1. Introduction

Organic ligands of the H_2L type (such as *o*-hydroxybenzoic acid, *o*-aminobenzoic acid or *o*-hydroxybenzaldoxime) and bivalent metals form either di-complexes $M(HL)_2$ or mono-complexes ML (where M^{2+} = metal ion, HL^- = $OHC_6H_4COO^-$, $NH_2C_6H_4COO^-$, $OC_6H_4CHNOH^-$, L^{2-} = $OC_6H_4COO^{2-}$, $NHC_6H_4COO^{2-}$, $OC_6H_4CHNO^{2-}$). The di-complexes are relatively easy to obtain by precipitation from solutions at a specific pH [1]. The mono-compounds are difficult to obtain in this way. Dissociation of a further hydrogen ion from the ligand requires a high pH which leads to precipitation of metal hydroxides. The literature reports only a few mono-complexes obtained by precipitation from solutions: Cu(II) mono(*o*-hydroxybenzoate) [2], Zn(II) mono(*o*-hydroxybenzaldoximate) [3], Cd(II) mono(*o*-hydroxybenzaldoximate), and Pb(II) mono(*o*-hydroxybenzaldoximate) [4]. Other mono-compounds can be obtained by thermal decomposition of di-compounds [5,6]. The first stage of the decomposition proceeds according to the following reaction:

$$M(HL)_2 \rightarrow ML + \uparrow H_2L$$

In the mono-complexes, the metal is coordinatively unsaturated and, under certain conditions may bind to other mono- or bidentate ligands. Previously, we have reported the synthesis and properties of heteroligand complexes obtained by reaction of Zn(II) and Cd(II) mono(*o*-aminobenzoate) [7], and Cu(II) mono(*o*-hydroxybenzoate) [8] with bidentate ligands. The thermal stability of these compounds is lower than that of the corresponding homoligand complexes and their thermal decomposition differs from the decomposition of $M(HL)_2$, as mono-ML compounds are not formed as intermediates.

E-mail address: mkobza@hotmail.com (M. Olczak-Kobza).

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The present work is a continuation of our studies on the synthesis and properties of heteroligand metal(II) complexes obtained in this case through a reaction of mono-complexes with monodentate ligands [9]. Imidazole and its methyl derivatives have been chosen as monodentate ligands. These compounds are interesting as the imidazole ring is common in biologically important molecules (biocatalysts, Vitamin B_{12} and its derivatives or metaloenzymes) in which it is a metal binding ligand. Therefore, coordination complexes containing imidazole are suitable modele to study different aspects of biological molecules [10,11].

Cadmium is a toxic element, and may compete with zinc for the active site in enzymes in the living organisms [12]. Thus, it seems important to study its complexes and compare them with analogous complexes of zinc.

We have prepared new cadmium complexes of general formulae $Cd(Sal)(HIm)_2$ (I), $Cd(Sal)(HIm)_4 \cdot H_2O$ (II), $Cd(Sal)(4\text{-}MHIm)_4$ (III), $Cd(Im)_2(HIm)$ (IV) and $Cd(Salox)(4\text{-}HIm)_2$ (V). Structural and thermal characteristics of these complexes are presented.

2. Experimental

The analytically pure salt $CdCl_2 \cdot 2H_2O$, *o*-hydroxybenzoic acid, *o*-hydroxybenzaldoxime, toluene (POCh — Gliwice), imidazole (Fluka Chemii AG), 4-methylimidazole, 1,2-dimethylimidazole (Sigma) were used without further purification.

2.1. Preparation

2.1.1. Cd(Sal), Cd(Salox)

Cadmium mono(*o*-hydroxybenzoate) (cadmium mono(*o*-hydroxybenzoate) cannot be obtained by precipitation from a solution) was obtained by decomposing di(*o*-hydroxybenzoate) at 230°C as determined from the TG curve. The decomposition proceeds according to

$$Cd(HSal)_2 \xrightarrow{230^\circ C} Cd(Sal) + \uparrow H_2Sal$$

where H_2Sal — HOC_6H_4COOH, $HSal^-$ — $OHC_6H_4\text{-}COO^-$.

Cadmium mono(*o*-hydroxybenzaldoximate) was obtained by precipitation from aqueous solution according to the method described by Lumme and Knuuttila [4].

2.2. Heteroligand complexes

The synthesis was carried out in a two-phase system consisting of Cd(Sal) and Cd(Salox) and a toluene solution of imidazole, 4-methylimidazole or 1,2-dimethylimidazole. The mixture was heated to 70°C and stirred for over 10 h. The reaction was performed at different molar ratios of substrates: 1:2 (I); 1:4 (II, IV) and 1:5 (III, V). The synthesis with 1,2-dimethylimidazole was unsuccessful when two-, four- and six-fold excess of the ligand was used.

2.3. Chemical analysis

The Cd(II) was determined by complexometric titration with EDTA [13], and carbon, hydrogen and nitrogen by elemental analysis. The results are presented in Table 1.

2.4. Thermal analysis

Thermal analysis was carried out using a C.J. Electronics thermobalance with computer control; temperature range 20–800°C; heating rate 10°C/min, in air atmosphere. The sample mass was 100 mg.

The sinters were obtained at temperatures determined on the basis of the TG curves and under conditions similar to those used for thermal analysis.

2.5. X-ray analysis

The X-ray analysis was carried out by means of a Siemens D5000 powder diffractometer, using Cu Kα radiation. The analysis included the products of synthesis and the sinters formed as a result of thermal decomposition. Fig. 1 presents powder diffraction patterns of $Cd(Sal)(HIm)_4 \cdot H_2O$ and corresponding sinters. (In order to identify inorganic cadmium compounds, diffraction patterns of the sinters were compared with the Inorganic Crystal Structure Database).

2.6. IR analysis

IR spectra were recorded using a Zeiss Specord M80 spectrophotometer over the range 400–

Table 1
Results of chemical analysis

Complex	C (%)		H (%)		N (%)		Cd (%)	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
$Cd(Sal)(HIm)_2$	40.9	40.58	4.1	3.38	14.8	14.56	30.0	29.23
$Cd(Sal)(HIm)_4{\cdot}H_2O$[a]	43.0	42.34	4.5	4.64	20.9	20.80	21.2	20.87
$Cd(Sal)(4\text{-}MHIm)_4$	48.2	47.88	5.2	4.86	20.3	19.43	19.4	19.50
$Cd(Im)_2(Him)$	34.3	34.33	2.8	3.18	25.5	26.70	35.0	35.73
$Cd(Salox)(4\text{-}MHIm)_2$	44.1	43.74	4.5	4.13	19.0	17.00	27.9	27.31
$Cd(Im)_2$[b]	29.0	29.21	2.1	2.43	22.1	22.72	45.1	45.60
$Cd(Sal)(4\text{-}MHIm)_3$[b]	46.5	46.11	4.6	4.45	17.6	17.0	22.4	22.73

[a] H_2O found from the TG curve 4.0%; calculated 3.34%.
[b] Sinters.

4000 cm^{-1}. The samples were prepared in the form of KBr pellets. The spectra of the complexes were compared with the spectra of free ligands and monocompounds Cd(Sal) and Cd(Salox).

3. Results and discussion

Depending on the molar ratio of the reagents, two different heteroligand complexes: $Cd(Sal)(HIm)_2$ and $Cd(Sal)(HIm)_4{\cdot}H_2O$ were obtained in the reaction of cadmium mono(*o*-hydroxybenzoate) with imidazole. Under the same conditions, cadmium mono(*o*-hydroxybenzaldoximate) does not bind with another ligand. The diffractometric analysis of the products of the reaction of Cd(Salox) with nHIm ($n = 2, 3, 4$) demonstrated that when the excess of imidazole is two- or three-fold, a mixture of Cd(Salox) and $Cd(Im)_2$ is formed. Conversely, the 4-fold excess, leads to the formation of a homogenous product $Cd(Im)_2(HIm)$. In the case of 4-methylimidazole complexes, the composition is always $Cd(Sal)(4\text{-}MHIm)_4$ and $Cd(Salox)(4\text{-}MHIm)_2$.

The analysis of powder diffraction patterns showed that the imidazole complexes have a crystalline structure (Fig. 1a) whereas 4-methylimidazole complexes are amorphous. No heteroligand complexes are obtained with 1,2-dimethylimidazole. (Coordination of metal may be inhibited in imidazole derivatives in which both nitrogen atoms are adjacent to the carbon atom that caries a substituent [14]).

The results of the thermal analysis indicate that the decomposition of the complexes proceeds in several stages. Only $Cd(Sal)(HIm)_4{\cdot}H_2O$ crystallizes with water. The thermal stability determined by t_i[1], exhibits the following order:

$$\underset{55^\circ C}{Cd(Salox)(4\text{-}MHIm)_2} < \underset{80^\circ C}{Cd(Sal)(4\text{-}MHIm)_4} < \underset{120^\circ C}{Cd(Im)_2(HIm)_4} < \underset{140^\circ C}{Cd(Sal)(HIm)_4} < \underset{170^\circ C}{Cd(Sal)(HIm)_2}$$

and is lower than the thermal stability of the salts Cd(Salox) — 265°C, Cd(Sal) — 325°C.

The mass loss for established in individual stages of the decomposition, the chemical analysis and diffractometric investigation of the sinters indicate the following decomposition processes (Scheme 1).

As shown in Scheme 1, in the first stage of decomposition, anhydrous cadmium complexes of imidazole decompose to form $Cd(Im)_2$ which indicates that the bond between imidazole and the metal is stronger than that between the Sal^{2-} ion and the metal. The four molecules of imidazole in $Cd(Sal)(HIm)_4$ are bound in different ways. Two of them are lost in the first stage with the $OC_6H_4COO^{2-}$ ion and two protons. The final product of the decomposition of both complexes is cadmium oxide.

The course of the TG and the DTG curves of $Cd(Sal)(4\text{-}MHIm)_4$ indicates that in the first stage

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[1] Temperature for transformation ratio $\alpha = 0.01$.

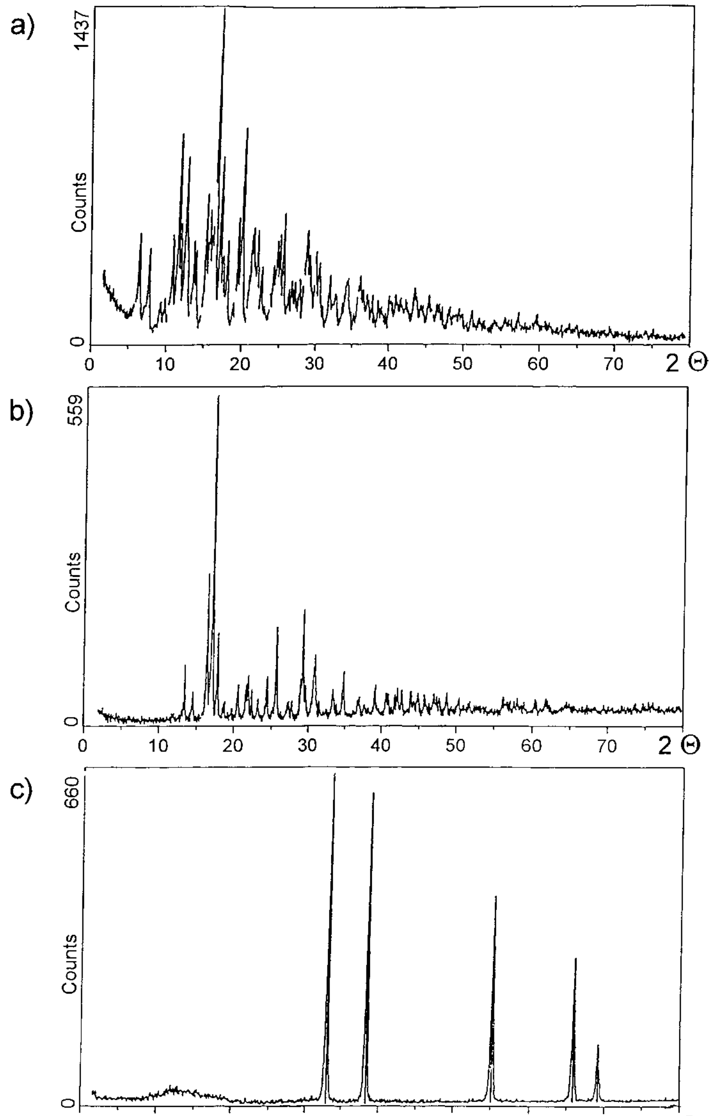
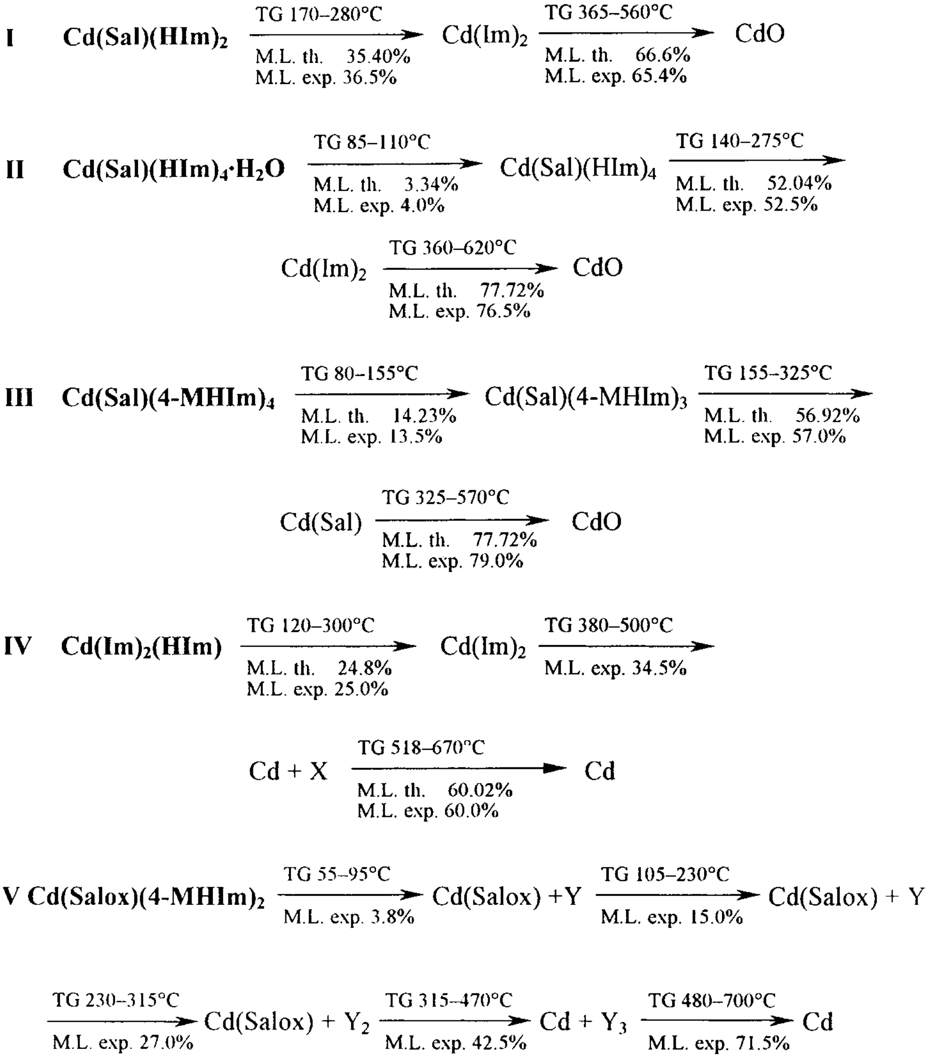


Fig. 1. X-ray analysis of complex Cd(Sal)(Him)$_4$·H_2O, (a) before sintering; (b) after sintering at 300°C (Cd(Im)$_2$); (c) after sintering at 650°C (CdO).

of decomposition, one molecule of 4-methylimidazole is lost and the other three are released in the second stage. The mass loss in the second stage suggests that cadmium mono(*o*-hydroxybenzoate) is formed. The temperature (325°C) at which this sinter forms is the same as the temperature of the onset of decomposition of Cd(Sal). The CdO is the final product of the decomposition. The decomposition of Cd(Salox)(4-MHIm)$_2$ differs from the decomposition of the other complexes but as in the case of Cd(Sal)(4-MHIm)$_4$, the bond between 4-methylimidazole and the metal is weaker than between the chelating ligand and the metal.

The differences in thermal stability and in the processes of decomposition of the complexes with imidazole and 4-methylimidazole may result from the fact that imidazole forms stronger bonds with metals than 4-methylimidazole. The methyl group decreases the π-acceptor property of the imidazole ring and



X, Y, Y_1, Y_2, Y_3 – unidentified solid decomposition products

Scheme 1

although the basicity of 4-methylimidazole is higher, its bond with metals is weaker [14,15].

The homoligand $Cd(Im)_2(HIm)$ complex decomposes in three stages. In the first stage, the neutral imidazole molecule is lost and the cadmium imidazolate formed decomposes to form metallic cadmium.

The characterise metal centre in these complexes, it is necessary to identify if the acidic proton bound to nitrogen N-1 is transferred to the strongly basic compounds Cd(Sal) and Cd(Salox) as is the case in the following reaction [7]:

$$ZnA + H_2Sal \rightarrow Zn(HA)(HSal)$$

where $A^{2-} = NHC_6H_4COO^{2-}$, $HA^- = NH_2C_6H_4COO^-$.

The position of stretching and deformation vibration bands of the N–H group of imidazole and 4-methylimidazole was analysed. In IR, the unassociated N–H group gives a ν_{NH} band at 3480 cm^{-1} and δ_{NH} band at 1449 cm^{-1} [16]. In compounds with metals the ν_{NH} band is shifted towards lower frequencies to about 3300 cm^{-1} and the δ_{NH} band is often invisible or appears within the range 1400–1450 cm^{-1} [17]. For $Cd(Im)_2(HIm)$, a ν_{NH} band is observed at 3381 cm^{-1}(s) and a δ_{NH} band appears at 1418 cm^{-1} (m). These bands are not found in the spectrum of $Cd(Im)_2$. In the spectra of $Cd(Sal)(HIm)_4$ and $Cd(Sal)(HIm)_2$, ν_{NH} bands are present at 3385 cm^{-1} (m) and 3380 cm^{-1} (sh), respectively. Their intensity diminishes as the number of imidazole molecules in the complex decreases. The δ_{NH} band observed at 1410 cm^{-1} (sh) in the spectrum of $Cd(Sal)(HIm)_4$ disappears in the case of the complex with two molecules of imidazole. The presence of ν_{NH} and δ_{NH} bands in the spectrum suggests that neutral molecules of imidazole also join with the mono-complex of cadmium, although it does not show whether they are all unassociated.

The spectra of compounds with 4-methylimidazole are considerably more difficult to interpret. The bands in the spectra of $Cd(Sal)(4\text{-}MHIm)_4$ and $Cd(Salox)(4\text{-}MHIm)_2$ observed at 3393 cm^{-1} (w) and 3360 cm^{-1} (w), respectively, may be attributed to ν_{NH} vibrations which indicates the presence of neutral 4-methylimidazole molecules in the complex. This conclusion may confirm the proposed course of thermal decomposition involving the presence of Cd(Sal) and Cd(Salox) in the solid products.

4. Conclusions

- Simple and mixed Cd(II) complexes of the type $Cd(Im)_2(HIm)$, $Cd(Sal)(HIm)_2$, $Cd(Sal)(HIm)_4 \cdot H_2O$, $Cd(Sal)(4\text{-}MHIm)_4$ and $Cd(Salox)(4\text{-}MHIm)_2$ have been prepared.
- No mixed complexes have been obtained in reactions of Cd mono(*o*-hydroxybenzoate) and cadmium mono(*o*-hydroxybenzaldoximate) with 1,2-dimethylimidazole.
- Complexes with imidazole have a crystalline structure while complexes with 4-methylimi-dazole are amorphous.
- IR spectra analysis demonstrated that in the synthesis reaction, neutral molecules of imidazole or 4-methylimidazole are bound with Cd(Sal) and Cd(Salox); the acidic hydrogen bound to N-1 nitrogen is not transferred to cadmium mono-complexes.
- The thermal decomposition of the complexes is a multi-stage process. The intermediate product is $Cd(Im)_2$ in the case of imidazole complexes, and Cd(Sal) and Cd(Salox) in the case of 4-methylimidazole complexes.
- The thermal stability of the complexes is lower than the stability of cadmium mono(*o*-hydroxybenzoate) or cadmium mono(*o*-hydroxybenzaldoximate). $Cd(Sal)(HIm)_2$ ($t_i = 170°C$) is the most stable, and $Cd(Salox)(4\text{-}MHIm)_2$ ($t_i = 55°C$) the least stable of the complexes.

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