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ZINC(II) (*o*-HYDROXYBENZALDOXIMATES) COMPLEXES WITH MONO- AND BIDENTATE LIGANDS

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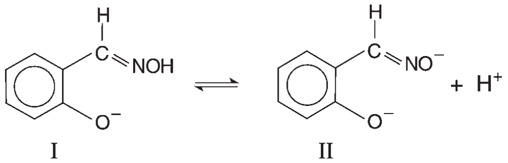
Abstract

New complexes: Zn(Hsalox)(ox), Zn(Hsalox)(NHPh), Zn(Hsalox)(Hsal) and $Zn(Hsalox)_2$(1,2-diMeim) have been synthesised as a result of a reaction of Zn(salox) and $Zn(Hsalox)_2$ (where: $salox^{2-}=OC_6H_4CHNO^{2-}$, $Hsalox^{-}=OC_6H_4CHNOH^{-}$) with 8-hydroxyquinoline (Hox), *o*-aminophenol (NH_2Ph), *o*-hydroxybenzoic acid (H_2Sal) and 1,2-dimethylimidazole (1,2-diMeim). Chemical, X-ray and thermal analyses of the complexes and their sinters have been carried out. Thermal decomposition pathways have been postulated for the complexes. The mixtures about not definite composition have been obtained as a result of a reaction of zinc(*o*-hydroxybenzaldoximates) with imidazole (Him) and 4-methylimidazole (4-MeHim).

Keywords: heteroligand complexes, *o*-hydroxybenzaldoxime, thermal analysis, zinc(II)

Introduction

The formulae of the compounds formed by *o*-hydroxybenzaldoxime and zinc ions are $Zn(Hsalox)_2$ and Zn(salox). The conditions of pH, temperature and molar proportions of the substrates have to be strictly observed to obtain these compounds, otherwise, a mixture of both compounds is crystallised. This is probably due to an equilibrium between two ionic species of the oxime [1]:



I II

In a solution of pH 6.8 oxime occurs in the form I and zinc di(*o*-hydroxybenzaldoximate) is precipitated. When the solution has pH 8.5 oxime occurs in the form II and zinc mono(*o*-hydroxybenzaldoximate) is obtained [2]. Under specific conditions there is an equilibrium between the two forms and their mixtures are precipitated [3].

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The pure mono-compound can also be obtained by thermal decomposition of the dicompound [4].

$$\mathrm{Zn(Hsalox)_2} \rightarrow \uparrow\mathrm{Zn(salox)}+\mathrm{H_2salox} \quad (2)$$

In oximates zinc is coordinatively unsaturated so both zinc di(*o*-hydroxybenzaldoximate) and zinc mono(*o*-hydroxybenzaldoximate) are able to bind further ligands.

The results of the study on the synthesis and properties of heteroligand complexes of metals(II) obtained as a result of reactions between compounds of the ML type and mono- and bidentate ligands (where *ML* – $Zn(NHC_6H_4COO)$, $Cd(NHC_6H_4COO)$ [5], $Cu(OC_6H_4COO)$ [6, 7], $Cd(OC_6H_4COO)$ and $Cd(OC_6H_4CHNO)$ [8]) were published previously.

The present work analyses the products of synthesis of zinc (*o*-hydroxybenzaldoximates) with bidentate ligands: 8-hydroquinoline, *o*-aminophenol, 2,2'-dipyridil, *o*-hydroxybenzoic acid and *o*-aminobenzoic acid; and with monodentate ligands: imidazole, 4-methylimidazole and 1,2-dimethylimidazole. New complexes of the following formulae have been synthesised: Zn(Hsalox)(ox), Zn(Hsalox)(NHPh), Zn(Hsalox)(Hsal) and $Zn(Hsalox)_2(1,2\text{-diMeim})$. The reactions of $Zn(Hsalox)_2$ and Zn(salox) with imidazole resulted in the formation of the same products, but it was impossible to establish their molecular formulae, similar with 4-methylimidazole.

Experimental

Analytically pure $Zn(NO_3)_2{\cdot}6H_2O$, *o*-hydroxybenzaldoxime, *o*-hydroxybenzoic acid, 8-hydroxyquinoline, toluene, (POCh-Gliwice), imidazole, *o*-aminophenol (Fluka Chemia AG), 4-methylimidazole, 1,2-dimethylimidazole (Sigma) were used without additional purification.

Synthesis

Zinc di- and mono(*o*-hydroxybenzaldoximates) were obtained according to methods described in literature [2, 3].

Heteroligand complexes

The synthesis was carried out in a two-phase system between a ligand dissolved in toluene and solid $Zn(Hsalox)_2$ and Zn(salox). The mixture was heated to 70°C and stirred for over 10 h. The precipitate was filtered, washed with toluene and dried in air. The molar ratio of zinc compounds and bidentate ligands was 1:1, and monodentate ligands 1:5.

$Zn(Hsalox)_2(1,2\text{-diMeim})$

$Zn(Hsalox)_2$ was dissolved in a toluene solution of 1,2-dimethylimidazole. After evaporation of the solvent, a yellow precipitate appeared. It was washed with toluene and dried in air.

Chemical analysis

Elemental analysis of the synthesised compounds was carried out; zinc was determined by complexometric titration with EDTA [9]. Formulas presented in Table 1 have been attributed to the complexes on the basis of the results of the analysis and previous studies [5, 6, 10]. The products of reaction of Zn(Hsalox)$_2$ with imidazole differ from the substrates but chemical analysis does not allow to propose definite formulae for them. Zn(salox) does not react with 1,2-dimethylimidazole, 2,2-dipyridil or *o*-aminobenzoic acid while Zn(Hsalox)$_2$ does not react with bidentate ligands.

Table 1 Results of chemical analysis of the compounds (%)

Compound	Zn		C		H		N	
	found	calc.	found	calc.	found	calc.	found	calc.
Zn(Hsalox)(ox)	19.0	18.92	55.1	55.55	3.0	3.18	8.1	8.10
Zn(Hsalox)(NHPh)	21.4	21.12	50.0	50.31	3.2	3.87	9.6	9.05
Zn(Hsalox)(Hsal)	19.5	19.31	50.2	49.62	3.0	3.25	3.4	4.13
Zn(Hsalox)$_2$(1,2-diMeim)	15.1	15.07	46.5	47.04	4.1	4.61	13.2	12.91

Thermogravimetric analysis

The thermal analysis was carried out using a C. J. Electronics thermobalance over temperature range 20–1000°C, at a heating rate of 10°C min^{-1} in air atmosphere, the sample mass was 100 mg.

The sinters were prepared under conditions similar to those of the thermal analysis. One hundred milligram samples were heated in an electric furnace at temperatures determined on the basis of the TG curves. XRD analysis of the sinters was carried out and zinc content was established. Table 2 presents the temperature intervals

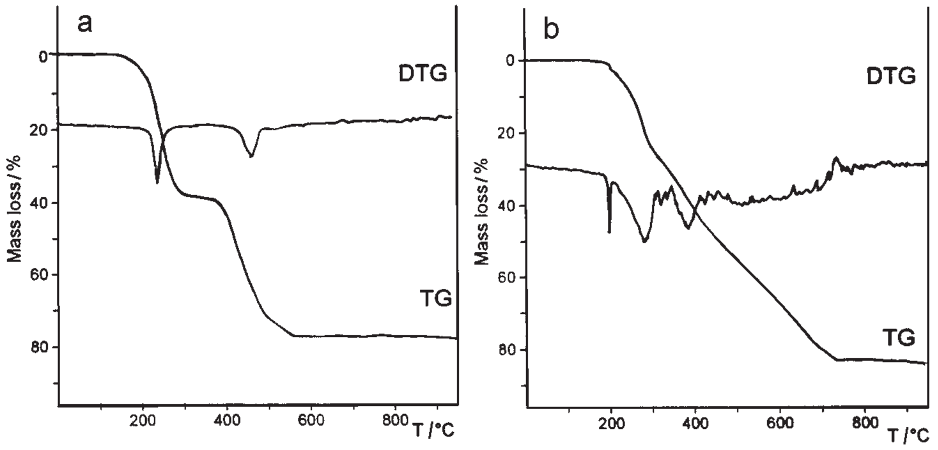

Fig. 1 Thermogravimetric curves: a – Zn(Hsalox)(Hsal); b – Zn(Hsalox)$_2$(1,2-diMeim)

and mass losses in each stage of decomposition of the complexes and mixtures, thermogravimetric curves for the two compounds are shown in Fig. 1.

Table 2 Results of thermal analysis

Compound or mixture	Stage	Temperatures/°C	Total mass loss/%
Zn(Hsalox)(ox)	I	120–285	20.5
	II	285–400	35.0
	III	400–820	79.0*
Zn(Hsalox)(NHPh)	I	130–260	11.0
	II	320–645	71.0*
Zn(Hsalox)(Hsal)	I	155–310	40.0
	II	380–540	77.0*
$Zn(Hsalox)_2(1,2\text{-}diMeim)$	I	180–200	3.5
	II	205–300	24.0
	III	300–725	84.0*
Zn(salox)+5(Him)	I	80–130	18.0
$Zn(Hsalox)_2+5(Him)$	II	130–200	24.0
	III	260–270	29.0
	IV	415–790	71.0
Zn(salox)+5(4-MeHim)	I	60–260	12.0
$Zn(Hsalox)_2+5(4\text{-}MeHim)$	II	270–810	70.0

*Successive theoretical mass losses in the case of ZnO formation are: 76.5, 73.7, 76.0 and 81.2 respectively

X-ray analysis

X-ray analysis was carried out by means of a Siemens D5000 diffractometer, using CuK_α radiation, 2θ range 2–80°. Table 3 presents seven most intense peaks of the obtained complexes and initial compounds. Figure 2 shows diffraction patterns of zinc di(*o*-hydroxybenzaldoximate) and the products of its reaction with imidazole and 4-methylimidazole. (In order to identify inorganic zinc compounds, diffraction patterns of the sinters were compared with the PDF ICDD 36-1451.)

Results and discussion

Chemical, XRD and thermal analyses confirmed that new heteroligand complexes are formed: Zn(Hsalox)(ox), Zn(Hsalox)(NHPh), Zn(Hsalox)(Hsal) and Zn(Hsalox)(1,2-diMeim). Chelating ligands: 8-hydroxyquinoline, *o*-aminophenol and *o*-hydroxybenzoic acid react with zinc mono(*o*-hydroxybenzaldoximate) but do not react with di(*o*-hydroxybenzaldoximate). Monodentate ligands: imidazole and 4-methylimidazole yield new products of undefined molecular formulae in reactions with both zinc mono- and di(*o*-hydroxybenzaldoximate). The synthesis between the above mentioned substrates in a two-phase system was carried out for 15 h. When the time of synthesis was shorter, peaks corresponding to initial substances were observed in

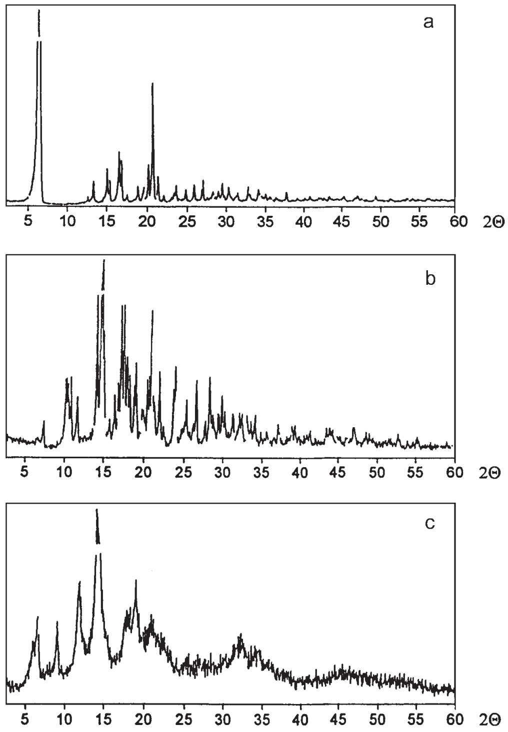

Fig. 2 X-ray diffraction patterns of $Zn(Hsalox)_2$ (a) and products of reaction: $Zn(Hsalox)_2$+Him (b), $Zn(Hsalox)_2$+4-MeHim (c)

the diffraction patterns of the products. The heteroligand 1,2-dimethylimidazole complex was formed only in the reaction with $Zn(Hsalox)_2$. The reaction proceeded in a one-phase system.

Thermal decomposition of the mixed chelate complexes had a multi-stage course (Table 2). The decomposition of Zn(Hsalox)(ox) proceeds in three stages, while Zn(Hsalox)(NHPh) decomposes in two stages. The mass loss, the content of zinc determined in the sinters and temperatures of the successive changes did not allow to attribute defined formulae to the products of the first stage of pyrolysis. In the second stage of decomposition of Zn(Hsalox)(ox), the diffractometric analysis showed the presence of zinc oxide alongside the ligands, decomposition of which had not been completed. Zinc oxide is also the final product of pyrolysis of these two complexes (calculated content of zinc in ZnO – 80.34 found 80.7 and 80.6%, respectively).

Zn(Hsalox)(Hsal) decomposes in two stages (Table 2). The first stage starts at 155 and ends at 310°C. The product of the decomposition is stable within a wide temperature range (310–380°C). The mass loss observed (40.0%) indicates that either a molecule of *o*-hydroxybenzoic acid (theoretical mass loss 40.78%) or of *o*-hydroxybenzaldoxime (theoretical mass loss 40.49%) may be lost by the initial compound.

Table 3 X-ray diffraction data of zinc complexes

[Znsalox]		[Zn(Hsalox)$_2$]		[Zn(Hsalox)(Hsal)]		[Zn(Hsalox)(ox)]		[Zn(Hsalox)(NHPh)]		[Zn(Hsalox)$_2$(1,2-diMeim)]	
d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
12.963	100.00	13.090	100.00	12.644	23.08	12.732	90.44	12.885	100.00	15.589	51.03
6.458	6.45	5.801	4.01	10.652	100.00	12.119	87.03	9.855	15.12	14.153	33.07
4.798	3.00	5.287	5.80	8.379	21.16	11.505	100.00	6.443	7.09	13.487	100.00
4.303	5.49	5.195	4.86	5.370	29.44	11.278	86.28	4.687	9.25	6.379	45.00
4.122	7.64	4.344	4.37	5.235	13.29	10.875	77.28	4.299	5.37	4.747	34.14
4.023	6.44	4.225	13.39	3.894	19.27	9.791	63.75	4.130	5.91	4.388	42.00
2.869	2.54	4.099	3.04	3.487	33.01	4.054	26.94	4.009	4.79	3.513	47.24

On the basis of the analysis of the temperatures at which zinc mono(*o*-hydroxybenzaldoximate) and zinc mono(*o*-hydroxybenzoate) start to decompose (300 and 380°C, respectively), it was established that Zn(sal)[*] is the product of the first stage of the decomposition. The diffraction pattern of this sinter does not exhibit inorganic zinc compounds, and the content of zinc determined in it – 32.6 is in agreement with the calculated 32.47%. Zinc oxide is the product of the second stage of decomposition. The proposed course of the decomposition is the following:

$$\mathrm{Zn(Hsalox)(Hsal)} \rightarrow \mathrm{Zn(sal)} + \uparrow\mathrm{H_2salox} \rightarrow \mathrm{ZnO} \qquad (3)$$

Thus the course of the decomposition of heteroligand chelate complexes depends on the type of the successive ligands bound to zinc. In the case of 8-hydroxyquinoline and *o*-aminophenol, it starts by the destruction of the ligands, which indicates that in the mixed complexes certain bonds in the ligands are weakened and they decompose first. This is not the case with Zn(Hsalox)(Hsal): the weakest bond is the one between the metal ion and the *o*-hydroxybenzaldoximate ion and it is the first to cleave. As a result, mono(*o*-hydroxybenzoate) is formed.

Thermal stability of the chelate complexes, established on the basis of the temperatures of the onset of thermal decomposition t_i[**] increases in the following order:

$$\underset{120^\circ\mathrm{C}}{\mathrm{Zn(Hsalox)(ox)}} < \underset{130^\circ\mathrm{C}}{\mathrm{Zn(Hsalox)(NHPh)}} < \underset{155^\circ\mathrm{C}}{\mathrm{Zn(Hsalox)(Hsal)}}$$

and is lower than the thermal stability of the initial compound Zn(salox) (t_i=300°C).

The course of the TG and DTG curves of $\mathrm{Zn(Hsalox)_2}$(1,2-diMeim) indicates four rapid stages of decomposition in which temperatures of successive changes are difficult to determine (Table 2). The decomposition starts at 180 and ends at 725°C. The final product is zinc oxide.

As mentioned above, the chemical analysis of the products of reaction of Zn(salox)+Him and $\mathrm{Zn(Hsalox)_2}$+Him as well as Zn(Hsalox)+4-MeHim and $\mathrm{Zn(Hsalox)_2}$+4-MeHim, did not lead to the attribution of defined molecular formulae to these products. However, their diffraction patterns clearly differ from those of the substrates (Fig. 2). The diffraction patterns and thermal curves (TG, DTG) are very similar for the products of the reactions two compounds of zinc with imidazole as well as two compounds of zinc with 4-methylimidazole. It was assumed that in these cases mixtures of heteroligand complexes are formed, which was attributed to special properties of zinc (*o*-hydroxybenzaldoximates). The study by Simonsen and Christopher [3] demonstrates that the reaction between zinc and *o*-hydroxybenzaldoxime depends on the experimental conditions and intermediate cationic form of $\mathrm{Zn(Hsalox)^+}$ appears while zinc di(*o*-hydroxybenzaldoximate) is precipitated:

$$\mathrm{Zn^{2+}+OC_6H_4CHNOH^-} \leftrightarrow \mathrm{Zn(OC_6H_4CHNOH)^+} \leftrightarrow \mathrm{Zn/2(OC_6H_4CHNOH)} \qquad (4)$$

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[*] $\mathrm{sal^{2-}}$ – $\mathrm{OC_6H_4COO^{2-}}$

[**] t_i – temperature for the transformation degree = 0.01

The stage of transformation of the cationic form into zinc di(*o*-hydroxybenzaldoximate) is the slowest and since reaction (1) proceeds at the same time, it is possible that the mono compound is precipitated alongside the di-compound. Moreover, digestion of the precipitate transforms the di-compound into the mono-. This transformation plays an important role in the reaction of solid $Zn(Hsalox)_2$ with imidazole dissolved in toluene. $Zn(Hsalox)_2(Him)_x$ and $Zn(salox)(Him)_y$ (where: x, y are numbers of imidazole molecules) are formed alongside. Similar processes take place in the reaction with 4-methylimidazole.

In the case of Zn(salox) the acidic imidazole or 4-methylimidazole proton makes it possible for reaction (5) to proceed and mixed complexes with both the substrate and product of the reaction to form:

$$\mathrm{Zn(salox)+H^+ \leftrightarrow Zn(Hsalox)^+ \leftrightarrow Zn/2(Hsalox)} \tag{5}$$

The lack of acidic proton in 1,2-dimethylimidazole may account for the fact that this compound does not react with Zn(salox).

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