Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 141–146

THERMAL DECOMPOSITION OF Cu(II) COMPLEXES WITH 2-CHLORO- AND 2,6-DICHLOROBENZOIC ACID AND IMIDAZOLE

W. Wołodkiewicz

Department of Inorganic and General Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Pl-20-031 Lublin, Poland

(Received in revised form August 1, 2001)

Abstract

The reaction products of Cu(II) 2-chlorobenzoate and the imidazole **(1)**, and of Cu(II) 2,6-dichlorobenzoate and the imidazole **(2)** formulated as $CuL'_2{\cdot}2imd{\cdot}2H_2O$ and $CuL''_2{\cdot}2imd{\cdot}2H_2O$ (L'=$C_7H_4ClO_2^-$, L''=$C_7H_3Cl_2O_2^-$, *imd*=imidazole), were prepared and characterized by means of spectroscopic measurements and thermochemical properties. The blue **(1)** and green **(2)** complexes were obtained as solids with a 1:2:2 molar ratio of metal to carboxylate ligand to imidazole. When heated at a heating rate of 10 K min^{-1} the hydrated complexes, **(1)** and **(2)**, lose some of the crystallization water molecules and then decompose to gaseous products.

Keywords: 2-chlorobenzoic acid, complexes, copper, 2,6-dichlorobenzoic acid, thermal analysis, X-ray analysis

Introduction

A general survey of literature on complexes of Cu(II) with nitrogen donors reveals that a considerable amount of work has been carried out on the preparation and characterisation of addition complexes of Cu(II) carboxylates with nitrogen donors.

During the course of this investigation some adducts of Cu(II) chlorobenzoate appeared with 1,3-propanodiamine [1–3] and with pyridine [4]. Carboxylates of divalent metals are noted to give with various donor ligand complexes of three different stoichiometries, viz. 1:1, 1:2 and 1:4.

In some cases a metal carboxylate may give adducts of two different stoichiometries with the same ligand under different experimental conditions [5, 6].

The complexes of bridged bis(imidazole) and bis(benzimidazole) ligands of various bridge types with transition metals have been examined as potential models of structure and mobility of biological metal binding sites in metalloproteins like haemerythrin, hemocyanin, tyrosinase or azurin [7–13].

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

One of these N-donor ligands is imidazole. This work is a continuation of our study on the structure and physico-chemical properties of metal complexes with dichlorobenzoic acids and N-donor ligands.

Experimental

2-Chloro- and 2,6-dichlorobenzoates of Cu(II) were obtained by the modified method given in [14, 15]. The basic Cu(II) carbonate [$CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$] 0.01 mole was added to a hot solution of 2-chlorobenzoic acid (0.02 mole in 0.2 dm^{-3} of water) and the suspension was heated while stirring for about 4 h. The same procedure was applied preparing 2,6-dichlorobenzoate of Cu(II). After filtering the saturated solutions, the Cu(II) complexes were subjected to slow crystallization. The precipitates formed were filtered, washed with water and dried at 303 K to a constant mass.

The title complexes were obtained by dissolving the Cu(II) complex with 2-chlorobenzoic acid **(1)** and of Cu(II) with 2,6-dichlorobenzoic acid **(2)** (0.01 mole) in 0.2 dm^{-3} 0.1 M solution of imidazole in water, with a 1:2 molar copper–imidazole ratio. The solutions of Cu(II) complexes with 2-chloro- and 2,6-dichlorobenzoic acids and imidazole were subjected to slow crystallization.

Blue **(1)** and green **(2)** crystals suitable for X-ray data collection were deposited after three weeks. The products were filtered off, washed with water and dried at 303 K to constant mass.

The carbon, hydrogen and nitrogen content in the complexes were determined by elemental analysis using a Perkin Elmer CAN 2000 analyzer. The chlorine content was measured by the Schöniger method. The Cu(II) content was determined by AAS method using an Atomic Absorption Spectrophotometer AAS-3 (Carl Zeiss, Jena). The experimental results are concordant with the calculated data (Table 1).

IR spectra were recorded over the range of 4000–400 cm^{-1} using a FT-IR 1725X Perkin Elmer spectrophotometer. The thermal stability of the Cu(II) complexes was determined using a Q1500 D derivatograph with a Derill converter: TG, DTG and DTA curves were recorded. Measurements were made at sensitivity of 100 mg (TG). Samples (100 mg) were heated in platinum crucibles to 1273 K in static air at a heating rate of 10 K min^{-1}.

The solubility of the complexes in water was determined at 295 K. The saturated solution was prepared under isothermal conditions. The content of Cu(II) ions was determined by the AAS method.

Results and discussion

The addition complexes of Cu(II) 2-chlorobenzoate with imidazole and of Cu(II) 2,6-dichlorobenzoate with imidazole with the formula $CuL'_2 \cdot 2imd \cdot 2H_2O$ **(1)** and $CuL''_2 \cdot 2imd \cdot 2H_2O$ **(2)** ($L'=C_7H_4ClO_2^-$, $L''=C_7H_3Cl_2O_2^-$, *imd*=imidazole) were prepared as blue and green, respectively, crystalline solid.

Table 1 Analytical data and solubility of Cu(II)2-chloro- and 2,6-dichlorobenzoates with imidazole

Empirical formula	Formula mass	Cu/%		H/%		Cl/%		N/%		C/%		Solubility/ mol dm^{-3}
		calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	
(1)	545.5	11.65	11.6	3.67	3.8	13.02	12.9	10.27	10.2	44.00	44.0	$4.5 \cdot 10^{-2}$
(2)	615.5	10.32	10.3	2.92	3.0	23.07	22.9	9.10	9.0	39.00	39.3	$4.4 \cdot 10^{-3}$

(1) = $Cu(C_7H_4ClO_2)_2 \cdot 2imd \cdot 2H_2O$
(2) = $Cu(C_7H_3Cl_2O_2)_2 \cdot 2imd \cdot 2H_2O$

Table 2 Frequencies of characteristic absorption bands in IR spectra (in cm^{-1}) of Cu(II) complexes with 2-chloro- and 2,6-dichlorobenzoic acids and imidazole

$CuL'_2{\cdot}H_2O$	$CuL''_2{\cdot}H_2O$	imd	**(1)**	**(2)**	Assignment
3456	3480		3480	3464	ν(OH)
		3024–2824	3144–2880	3160	ν(N–H)
		1668			ν(C=N)
1616	1616		1610	1600	δ(H_2O)
1604	1604		1592	1584	ν(OCO^-)
1476			1456		ν(C–C)
		1448			ν(C–C)
	1432		1432	1432	ν(C–C)
1400	1392		1368	1362	ν_s(OCO^-)
		1328	1328	1328	ν(C–N)
		1264	1264	1264	
	1200			1192	
1160	1168		1148	1164	β(C–H)
		1072	1072	1072	ν(C–N)
		936	960	960	ν(C–N)
752	776		752	776	ν(C–Cl)
			648	656	ν(Cu–N)
		616	616	616	
512	512				ν(C–H)
			488	488	ν(C–H)
				448	ν(C–H)

IR spectroscopic data of the compounds under investigation are summarized in Table 2. IR spectra of **(1)** and **(2)** shows three strong bands at 1328, 1072 and 960 cm^{-1}, due to valence C–N vibrations of imidazole. They are shifted toward higher energy compared with corresponding C–N vibrations of the uncoordinated ligand. The ν(Cu–N) band is observed at 648 cm^{-1} for **(1)** and 656 cm^{-1} for **(2)**. These bands are observed neither in the IR spectra of free imidazole nor in Cu(II)-2-chlorobenzoate [14] and Cu(II)-2,6-dichlorobenzoate [15]. In the IR spectrum of the free acid there is a single strong absorption band at 1688 cm^{-1} for **(1)** and 1716 cm^{-1} for **(2)** (COOH group). In the IR spectrum of the title compounds, this absorption band disappears, and a split band of asymmetrical (COO^-) vibrations (ν_{as}) at 1592 cm^{-1} as well as band of symmetrical vibrations (ν_s) at 1368 cm^{-1} for **(1)** and 1584 cm^{-1} and 1362 cm^{-1} for **(2)** appear, respectively. The split band of ν_{as} (COO^-) and ν_s(COO^-), as well as the separation (Δν) of ν_{as}(COO^-) and ν_s(COO^-) of 224 cm^{-1} for **(1)** and 222 cm^{-1} for **(2)** suggests that the carboxylate groups act as bidentate asymmetric ligand [16–18]. This was confirmed by X-ray analysis. C···C and C–H vibrational bands of the Cu(II) complexes change their frequencies only insignificantly compared to the corresponding bands of the imidazole and the free acids, thus indicating that Cu(II) ion in the complexes does not deform the rings of phenyl and imidazole to a noticeable extent, an assumption which was confirmed by the crystal structure determination.

The complexes of Cu(II) 2-chlorobenzoate with imidazole **(1)** and Cu(II) 2,6-dichlorobenzoate with imidazole **(2)** with general formula $CuL_2 \cdot 2imd \cdot 2H_2O$ (L=L'–$C_7H_4Cl_2O_2^-$ or L=L"–$C_7H_3Cl_2O_2^-$) are stable at room temperature and can be stored for several months in air atmosphere. They are stable up to 353 K and next during heating they are dehydrated in different way.

Complex **(1)** loses two water molecules at 353 K under going in the anhydrous compound (Tables 3 and 4), which is stable in the range 383–483 K. On the DTA curve exhibit endothermic effect at 373 K, what suggest melting process of anhydrous compound, which begins to decompose at 483 K. The processes of dehydration, melting and decomposition of the complex are connected with endothermic effects. The exothermic effects at 543 and 943 K are connected with combusting of organic ligand and products of decomposition. At 1073 K the studied complex decomposes to gaseous product (similarly behave Cu(II) complexes with 2,3- [19], 2,4- [20], 2,5- [21], 2,6- [22], 3,4- [23] and 3,5- [24] dichlorobenzoic acids) with intermediate formation of indefinite product.

Table 3 Data on dehydration of Cu(II) complexes with 2-chloro- and 2,6-dichlorobenzoic acids and with imidazole

Complex	T_1–T'_1/K	T_2/K	Mass loss/%		Loss of H_2O/mol	Compound
			calcd.	found		
(1)	353 – 383	373	6.58	6.3	2	$Cu(C_7H_4ClO_2)_2$
(2)	353 – 413	403	2.92	3	1	$Cu(C_7H_3Cl_2O_2)_2 \cdot 2H_2O$

(1)=$Cu(C_7H_4ClO_2)_2 \cdot 2imd \cdot 2H_2O$
(2)=$Cu(C_7H_2Cl_2O_2)_2 \cdot 2imd \cdot 2H_2O$
T_1–T'_1=temperature range of dehydration
T_2=endotermic peaks on DTA

Table 4 Data on decomposition of Cu(II) complexes with 2-chloro- and 2,6-dichlorobenzoic acids and with imidazole

Compound	T_1–T'_1/K	T_2–T'_2/K	T_3–T'_3/K
(1)	383–483	483–1053	483–663 (max. 543) 863–1053 (max. 783)
(2)	413–493	493–1053	503–733 (max. 543) 953–1053 (max. 1013)

(1)=$Cu(C_7H_4ClO_2)_2 \cdot 2imd \cdot 2H_2O$
(2)=$Cu(C_7H_3Cl_2O_2)_2 \cdot 2imd \cdot 2H_2O$
T_1–T'_1=temperature range of stable
T_2–T'_2=temperature range of decomposition
T_3–T'_3=temperature range of exothermic peaks on DTA

Complex **(2)** heated over 353 K loses one water molecule forming monohydrate, which is stable up to 483 K and next decomposes to gaseous products at 1053 K with intermediate formation of indefinite product (Tables 3 and 4). The dehydration process is connected with a weak endothermic effect at 403 K. The strong exothermic effects at 513 and 1003 K are connected with combustion of the organic ligand and of the product decomposition.

The results obtained can be presented as:

$$\mathrm{CuL'_2{\cdot}2imd{\cdot}2H_2O \rightarrow CuL'_2{\cdot}2imd \rightarrow gaseous\ product}$$

$$\mathrm{CuL''_2{\cdot}2imd{\cdot}2H_2O \rightarrow CuL''_2{\cdot}2imd{\cdot}H_2O \rightarrow gaseous\ product}$$

Thermal analysis of the studied complexes shows on the additional influence of the chlorine atom in 6 position in benzene ring on the mode of coordination of water molecules and different energy of bonding Cu–O(H_2O).

References

1 R. Uggla, O. Orama, N. Sundberg, E. Tirronen and N. Klinga, Finn. Chem. Lett., (1974) 185.
2 N. Sundberg and R. Kivekas, Eur. Cryst. Meeting, 9 (1985) 309.
3 H. L. Alten, G. van Koten, E. Riethorat and C. H. Stam, Inorg. Chem., 26 (1989) 4141.
4 K. Nakatani, J. Slecten, S. Halut-Desporte, S. Jeannin, Y. Jeannin and O. Kahn, Inorg. Chem., 30 (1991) 164.
5 N. Kitajima, K. Fujisawa and Y. Noro-oka, Inorg. Chem., 29 (1990) 357.
6 T. Kawatw, N. Yamanaka, S. Chba, T. Nichida, N. Nagamateu, T. Tokii and N. Kato, Bull. Chem. Soc. Jpn., 65 (1992) 2739.
7 H. Adams, A. B. Neil, J. D. Crane, D. E. Fenton, J. M. Latour and J. M. Wiliams, J. Chem. Soc. Dalton Trans., (1990) 1727.
8 T. N. Sorrell and M. L. Garrity, Inorg. Chem., 30 (1991) 210.
9 S. Chen and J. Richardson, Inorg. Chem., 33 (1994) 2376.
10 S. Tandon, Thomson, J. Bridson and J. Dewan, Can. J. Chem., 70 (1992) 2771.
11 J. Sessler, J. Hugdahl and B. Lynch, Inorg. Chem., 30 (1991) 334.
12 A. van Steenberger, E. Bouwman, A. de Graaf, W. Driessen, J. Reedijk and P. Zanello, J. Chem. Soc. Dalton Trans., (1990) 3175.
13 J. Lockhart, W. Clegg, M. Hill and D. Rushton, J. Chem. Dalton Trans., (1990) 3541.
14 T. Kawata, S. Chba, T. Tokii and N. Kato, Acta Cryst., 48 (1992) 1590.
15 W. Wołodkiewicz and W. Brzyska, Polish J. Chem., 72 (1998) 2366.
16 A. Gross and R. Jonews, An Introduction to Practical Infrared Spectroscopy, Butterworhs, London 1969.
17 B. Manhas and A. K. Trikha, J. Indian Chem., 59 (1982) 315.
18 K. Nakamoto, Infrared and Raman Spectra of Inorganic Compounds, Wiley, New York 1978.
19 W. Wołodkiewicz and W. Brzyska, Polish J. Chem., 71 (1997) 16.
20 W. Wołodkiewicz and W. Brzyska, J. Therm. Anal. Cal., 55 (1999) 639.
21 W. Brzyska and W. Wołodkiewicz, Thermochim. Acta, 242 (1994) 131.
22 W. Brzyska and W. Wołodkiewicz, Polish J. Chem., 69 (1995) 1109.
23 W. Wołodkiewicz and W. Brzyska, Monatshefte für Chemie, 129 (1998) 111.