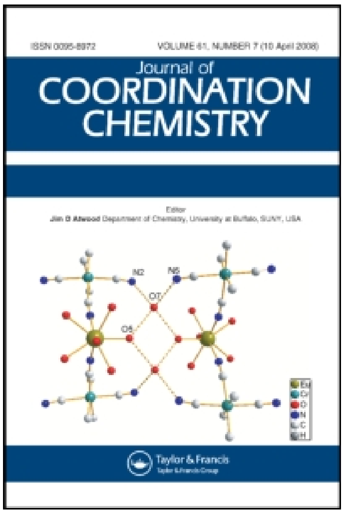

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Spectroscopic properties, structures and thermal decomposition of mixed cadmium(II) complexes of *o*-hydroxybenzoic acid and imidazoles

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Spectroscopic properties, structures and thermal decomposition of mixed cadmium(II) complexes of *o*-hydroxybenzoic acid and imidazoles

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The mixed ligand complexes $Cd(Hsal)_2(Him)_2$, $Cd(Hsal)_2(4\text{-}MeHim)_2$, $Cd(Hsal)_2(4\text{-}MeHim)_4$, $Cd(Hsal)_2(1,2\text{-}diMeim)_2$ (where $Hsal = OHC_6H_4COO^-$, Him = imidazole, 4-MeHim = 4-methylimidazole, 1,2-diMeim = 1,2-dimethylimidazole) have been synthesized and characterized. Single-crystal X-ray structures of $Cd(Hsal)_2(Him)_2$ and $Cd(Hsal)_2(1,2\text{-}diMeim)_2$ have been obtained. Gaseous products of their pyrolysis have been investigated and thermal decomposition pathways are postulated for the complexes.

Keywords: Heteroligand complexes; *o*-Hydroxybenzoic acid; Imidazole; Cadmium(II); X-ray structure; Thermal analysis

1. Introduction

The present work is a continuation of studies on the synthesis and properties of zinc(II) and cadmium(II) heteroligand complexes. Organic ligands of the H_2L type (such as *o*-hydroxybenzoic acid, *o*-aminobenzoic acid, *o*-hydroxybenzaldoxime) and bivalent metals form either di-complexes $M(HL)_2$ or mono-complexes ML (where M = metal ion, $HL = OHC_6H_4COO^-$, $NH_2C_6H_4COO^-$, $OC_6H_4CHNOH^-$, $L = OC_6H_4COO^{2-}$, $NHC_6H_4COO^{2-}$, $OC_6H_4CHNO^{2-}$). The mono-compounds may bind to other monodentate ligands [1, 2] as well as bidentates [3–5], whereas the di-compounds bind only to monodentate ligands [4, 6, 7]. In this investigation, imidazole and its methyl derivatives have been chosen as monodentate ligands.

The metallic centres of metalloproteins and metalloenzymes can be considered as mixed complexes and conclusions from investigations of small molecules and metal ions are the starting points for the interpretation of the structures of the more

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complicated molecules. In many biological important molecules, metal(II) ions are coordinated to imidazoles and carboxylate groups of organic acids [8, 9]. Therefore, complexes containing such ligands are frequently researched by means of spectroscopic, structural and thermal methods. Mixed complexes of imidazoles and aliphatic and amino acids are known [10–13]. However, information concerning mixed complexes with imidazoles and aromatic acids is limited. Cadmium is a toxic element, and may compete with Zn(II), Cu(II), Ca(II) and Fe(II) for the active sites in important biological systems [14, 15]. Research on new medicines to treat heavy metal poisoning (e.g. Cd) is connected with the investigation of heteroligand complexes. Thus, it is important to study Cd(II) complexes and compare them with analogous complexes of other metals.

Results of previous investigations of $Zn(Hsal)_2$ [4], $Zn(Han)_2$ [7], and Cd(sal) [1] with imidazoles have been published. Recently, we prepared new cadmium complexes of *o*-hydroxybenzoic acid and imidazole, 4-methylimidazole or 1,2-dimethylimidazole, $Cd(Hsal)_2(Him)_2$, $Cd(Hsal)_2(4\text{-}MeHim)_2$, $Cd(Hsal)_2(4\text{-}MeHim)_4$ and $Cd(Hsal)_2(1,2\text{-}diMeim)_2$. Structural characteristics and thermal decomposition pathways of these complexes are presented later.

2. Experimental

2.1. *Materials and analyses*

$Cd(NO_3)_2 \cdot 4H_2O$, ethanol (POCH, Gliwice), *o*-hydroxybenzoic acid (Fluka Chemie AG), imidazole, 4(5)-methylimidazole and 1,2-dimethylimidazole (Sigma) were used as received without additional purification. Cadmium was determined by titration with disodium ethylenediaminotetraacetate (EDTA) [16], and carbon, hydrogen, and nitrogen by using a Euro Vector , Euro EA analyzer.

2.2. *Syntheses*

$Cd(Hsal)_2 \cdot 2H_2O$ (**1**) was prepared according to a method described in the literature [17]. $Cd(Hsal)_2(Him)_2$ (**2**) was prepared as follows. A mixture of **1** and imidazole in ethanol was heated to 60°C and stirred. The mixture was allowed to reflux for 6 h, the hot mixture filtered, and solutions left to crystallize. The resulting white precipitates were washed with ethanol. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the remaining solution. Reactions were carried out at different mol ratios, 1 : 3 and 1 : 6, gave the same product. Anal. calcd for $CdC_{20}H_{18}N_4$ (%): Cd, 21.50; C, 45.93; H, 3.44; N, 10.72. Found: Cd, 21.9; C, 45.7; H, 3.4; N, 10.7.

$Cd(Hsal)_2(4\text{-}MeHim)_2$ (**3**) and $Cd(Hsal)_2(4\text{-}MeHim)_4$ (**4**) were obtained as follows. A mixture of **1** and 4(5)-methylimidazole in ethanol was heated to 60°C, and stirred. The mixtures were allowed to reflux for 3 h and then filtered. Filtrates were left to evaporate and oils were obtained. These were treated with ether and yellow precipitates formed. Reactions were carried out at different molar ratios, 1 : 3 and 1 : 6, but the same product was obtained. No single crystals suitable for X-ray diffraction studies were obtained. Anal. calcd for **3** $CdC_{22}H_{22}N_4$(%): Cd, 20.41; C, 47.95; H, 4.00; N, 10.17.

Table 1. Characteristic IR data (cm^{-1}).

Complex	$\nu_{as}COO^-$	ν_sCOO^-	$\Delta\nu$	νCOH	δCOH	νNH	δNH
NaHsal	1581 s	1385 s	196	1248 s	1317 w		
$Cd(Hsal)_2 \cdot 2H_2O$ (**1**)	1533 m	1394 s	139	1248 s	1348 m		
$Cd(Hsal)_2(Him)_2$ (**2**)	1560 m	1394 s	166	1248 s	1331 m	3223 s	1412 sh
$Cd(Hsal)_2$(4-MeHim)$_2$ (**3**)	1556 s	1394 s	162	1254 s	1310 m	3267 m	1420 sh
$Cd(Hsal)_2$(4-MeHim)$_4$ (**4**)	1560 s	1385 s	175	1255 s	1310 m	3280 sh 3412 w 3485 sh	1452 w
$Cd(Hsal)_2$(1,2 diMeim)$_2$ (**5**)	1560 s	1387 s	173	1252 s	1312 w		

Found: Cd, 21.0; C, 47.7; H, 4.1; N, 10.1. Calcd for **4** $CdC_{30}H_{34}N_8$ (%): Cd, 50.35; H, 4.76; N, 15.67. Found: Cd, 49.8; H, 4.8; N, 16.0.

$Cd(Hsal)_2$(1,2-diMeim)$_2$ (**5**) was synthesized as described for **2**, with 1,2-dimethylimidazole instead of imidazole. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the resulting solution. Anal. calcd for $CdC_{24}H_{26}N_4$ (%): Cd, 19.42; C, 49.79; H, 4.15; N, 9.67. Found: Cd, 19.7; C, 49.4; H, 4.2; N, 9.7.

2.3. *Analyses of sinters*

Anal. calcd (found) for sinters (see later) of **2** at 310°C (reaction a) $CdC_6H_6N_4$(%): Cd, 45.62 (45.9); C, 29.22 (29.5); H, 2.46 (2.1); N, 22.72 (13.0); of **3** and **4** at 340°C (reactions b and c) $CdC_8H_{10}N_4$ (%): Cd, 40.96 (41.3); C, 34.99 (33.5); H, 3.64 (3.4); N, 20.41 (17.9); of **5** at 265°C (reaction d) $CdC_7H_4O_3$ (%): Cd, 45.25 (44.9); C, 33.82 (33.1); H, 1.61 (1.4).

2.4. *Physical measurements*

IR spectra (KBr pellets) were recorded using a Zeiss Specord M80 spectrophotometer over the range 400–4000cm^{-1}. Characteristic data are given in table 1. X-ray powder diffraction analyses (XRD) of the complexes and sinters were carried out using a Siemens D 5000 powder diffractometer with Cu-K_α radiation, over the 2θ range 2°–80°. Diffraction patterns of the sinters were compared with PDF ICSD36-1451 in order to identify compounds.

2.5. *Single-crystal X-ray studies*

Colourless crystals, suitable for X-ray experiments, were obtained only for **2** and **5**. All measurements were performed on a Kuma4-CCD *k*-axis diffractometer with graphite-monochromated Mo-K_α radiation at room temperature. The crystals were positioned at 62 mm from the KM4-CCD camera and 496 frames were measured at 1.5 s intervals with a counting time of 25 s. Data were corrected for Lorentz and polarization effects. Multi-scan absorption corrections were applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław) programs [18].

The structures were solved by direct methods [19] and refined using SHELXL 93 [20]. The full-matrix least-squares refinement was based on F^2 with anisotropic temperature factors for all non-H-atoms; positions of all H-atoms were found from electron density maps and were refined in riding mode with isotropic displacement parameters

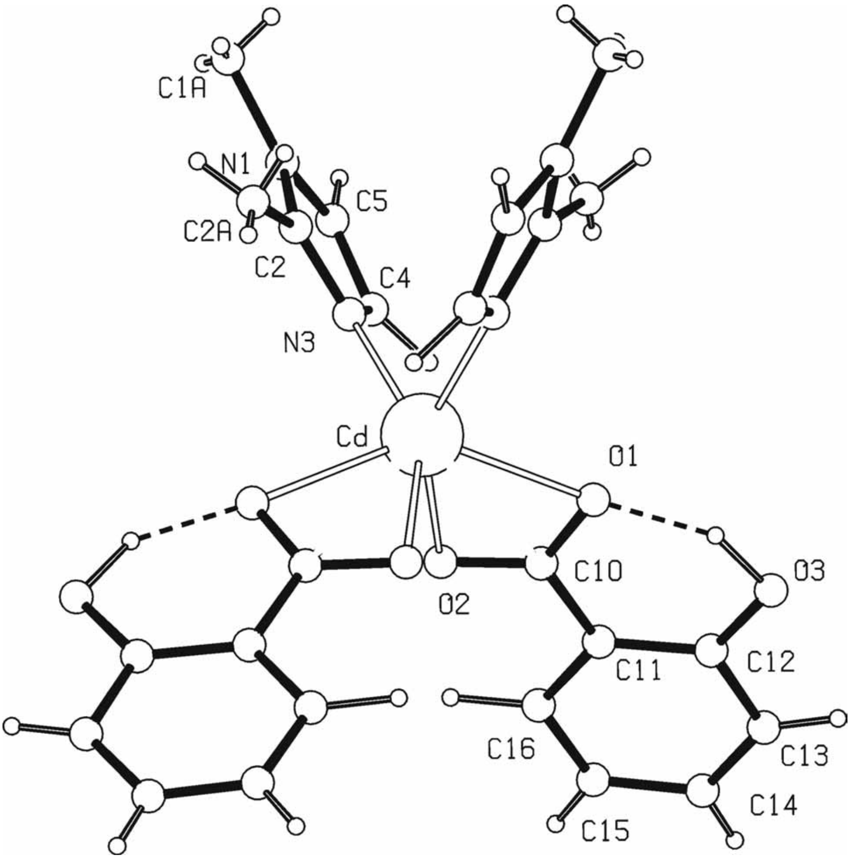


Figure 1. Molecular unit of $Cd(Hsal)_2(1,2\text{-}diMeim)_2$; H-bonds are marked by dashed lines.

1.5 times those of the respective U_{eq} values of the parent atoms. Atomic scattering factors were obtained from SHELXL [20]. Molecular structures of the two compounds are presented in figures 1–3. Crystal data and structure refinement details are gathered in table 2, and final atomic coordinates and equivalent isotropic displacement parameters in table 3. Selected geometrical details and H-bond geometries are given in table 4. Lists of observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors. Crystallographic data (excluding structural factors) for the structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated CCDC 270783 and 270784 deposition numbers. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: Int code + (1223) 336-033; Email:deposit@ccdc.cam.ac.uk).

2.6. *Thermal studies*

Thermoanalytical measurements were carried out using a Balzers TG/DTA-SETSYS-16/18 instrument with a Balzers mass spectrometer. The temperature range was 20–1000°C, the heating rate 10°C min^{-1}, air atmosphere, sample mass *ca.* 10 mg,

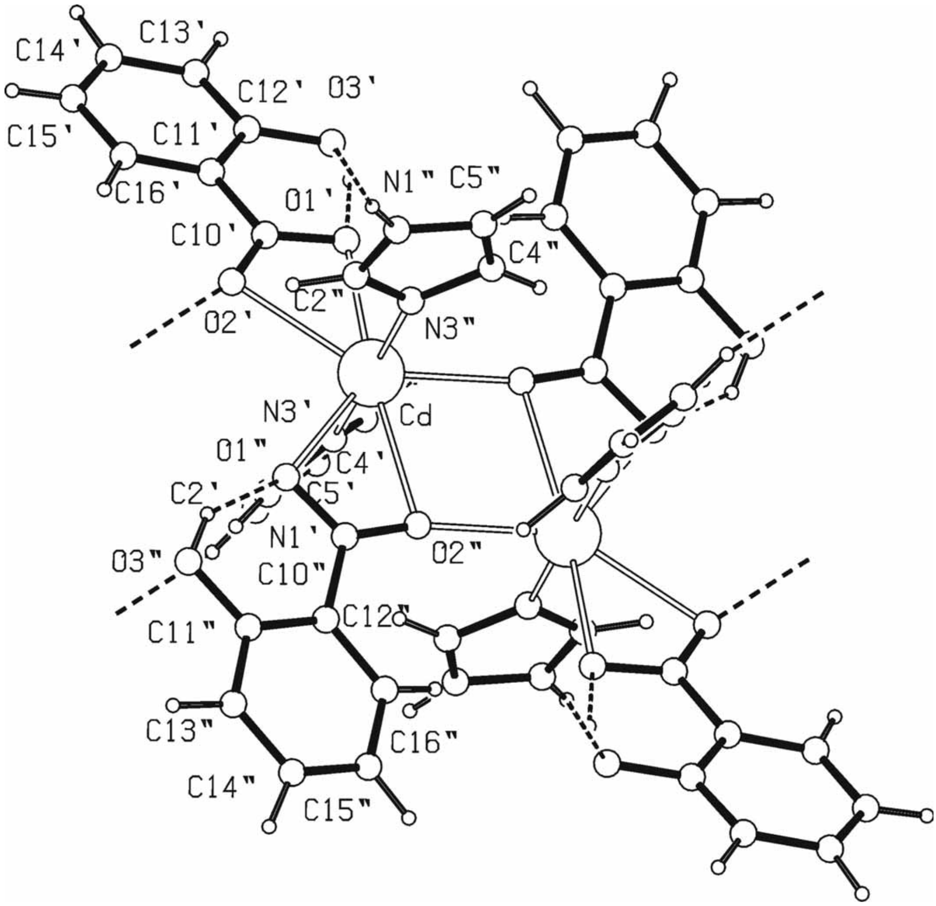
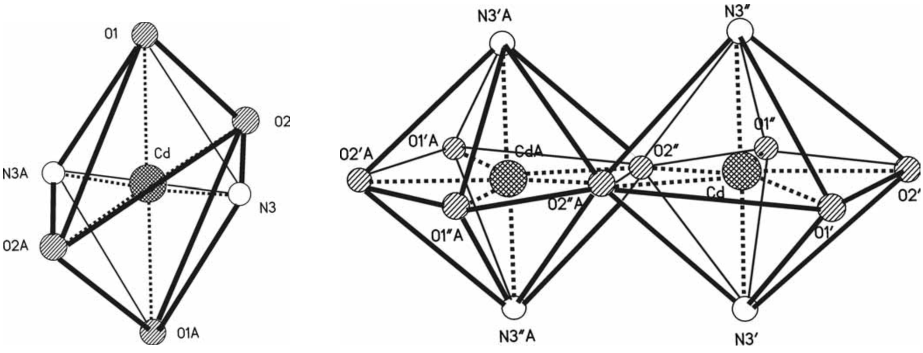


Figure 2. Molecular unit of $Cd(Hsal)_2(Him)_2$; H-bonds are marked by dashed lines.



$Cd(Hsal)_2(1,2\text{-diMeim})_2$

$Cd(Hsal)_2(Him)_2$

Figure 3. Cadmium(II) coordination spheres in the complexes.

Table 2. Crystal data and structure refinement details for **2** and **5**.

	$Cd(Hsal)_2(Him)_2$ (**2**)	$Cd(Hsal)_2(1,2\text{-diMeim})_2$ (**5**)
Chemical formula	$C_{40}H_{36}N_8O_{12}Cd_2$	$C_{24}H_{26}N_4O_6Cd$
Formula weight	1045.59	578.90
Temperature		293 K
Wavelength		0.71073 Å
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pccn*
Unit cell dimensions	$a = 9.309(2)$ Å $b = 9.763(2)$ Å $c = 12.206(2)$ Å $\alpha = 79.22\ (2)^\circ$ $\beta = 86.32(2)^\circ$ $\gamma = 69.85(2)^\circ$	$a = 9.647(2)$ Å $b = 10.830(2)$ Å $c = 24.140(5)$ Å
Volume	1023.1(4) Å^3	2522.1(9) Å^3
Z	1	4
Density (calculated)	1.697 g/cm^3	1.525 g/cm^3
μ (Mo Kα)	1.113 mm^{-1}	0.911 mm^{-1}
$F(000)$	524	1176
Crystal size	$0.2 \times 0.2 \times 0.4$ mm^3	$0.06 \times 0.1 \times 0.3$ mm^3
θ range for data collection	3.1 to 30.1°	3.0 to 20.5°
Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-15 \leq l \leq 16$	$-9 \leq h \leq 9$; $-10 \leq k \leq 10$; $-23 \leq l \leq 23$
Reflections collected	10549	16210
Independent reflections	5062 [$R(\text{int}) = 0.061$]	1266 [$R(\text{int}) = 0.087$]
Method of structure solution	Direct method	
Method of structure refinement	Full-matrix least squares on F^2	
No. of parameters refined	281	155
Goodness-of-fit on F^2	1.05	1.35
Final R_1 [$I > 2\sigma(I)$]	0.0339	0.0637
Final wR_2	0.0915	0.0862
Largest diff. peak and hole	0.78 and -1.13 e Å^{-3}	0.28 and -0.28 e Å^{-3}
Extinction coefficient	0.0026(5)	0.0006(6)

corundum crucible. Sinters were obtained at temperatures determined on the basis of the thermogravimetric (TG) curves. Gaseous decomposition products were analysed. Figure 4 presents TG, differential thermogravimetric (DTG), and differential thermal analysis (DTA) curves for selected complexes (curves of **3** and **4** were analogous).

3. Results and discussion

3.1. *Synthesis and spectroscopic properties*

The heteroligand complexes **2**, **3**, **4** and **5** were obtained by reaction of **1** with imidazole or its methyl derivatives. Depending on the mol ratio of reagents, one mixed complex was obtained for imidazole and 1,2-dimethylimidazole but two for 4-methylimidazole. XRD analysis showed that all the complexes are crystalline.

Positions of the stretching vibrations of COO^-, and NH groups and bending vibrations of NH in the IR were analysed. Characteristic data are given in table 1. Splitting ($\Delta\nu$) of the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands of *o*-hydroxybenzoate is smaller than in the sodium salt, in which COO^- group is monodentate. Based on usual spectroscopic criteria [21,22], chelating bidentate carboxylate groups exist in **1**, **3**, **4** and **5**. The phenyl group of *o*-hydroxybenzoate ion is free because intense ν(COH) bands

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the non-H atoms.

Atom	x/a	y/b	z/c	U_{eq}
$\mathrm{Cd(Hsal)_2(Him)_2}$ (**2**)				
Cd	0.55065(1)	0.31228(1)	0.09955(1)	0.0309(1)
O1′	0.4326(2)	0.2304(2)	0.2654(2)	0.0393(5)
O1″	0.7379(2)	0.2027(2)	−0.0316(2)	0.0430(5)
O2′	0.6281(2)	0.0532(2)	0.2128(2)	0.0444(5)
O2″	0.6053(2)	0.4356(2)	−0.0906(2)	0.0395(5)
O3′	0.2281(2)	0.1768(2)	0.3874(2)	0.0496(6)
O3″	0.9705(2)	0.0659(2)	−0.1380(2)	0.0531(6)
N1′	0.2530(4)	0.1616(3)	−0.0724(3)	0.0591(9)
N1″	0.9358(3)	0.3117(3)	0.2791(2)	0.0521(8)
N3′	0.3663(3)	0.2690(3)	0.0175(2)	0.0400(6)
N3″	0.7248(2)	0.3564(2)	0.1904(2)	0.0356(5)
C2′	0.3851(4)	0.1764(3)	−0.0522(2)	0.0471(8)
C2″	0.8587(3)	0.2575(3)	0.2216(3)	0.0467(8)
C4′	0.2119(3)	0.3148(4)	0.0426(3)	0.0576(9)
C4″	0.8467(4)	0.4534(4)	0.2864(3)	0.0548(9)
C5′	0.1424(4)	0.2483(5)	−0.0131(3)	0.0679(9)
C5″	0.7163(4)	0.4803(3)	0.2324(2)	0.0469(8)
C10′	0.5126(2)	0.0939(2)	0.2716(2)	0.0318(6)
C10″	0.7085(2)	0.3185(2)	−0.1053(2)	0.0309(5)
C11′	0.4590(2)	−0.0149(2)	0.3499(2)	0.0321(5)
C11″	0.8005(2)	0.3117(2)	−0.2093(2)	0.0299(5)
C12′	0.3177(3)	0.0322(3)	0.4037(2)	0.0369(6)
C12″	0.9274(3)	0.1859(2)	−0.2199(2)	0.0365(6)
C13′	0.2664(3)	−0.0709(4)	0.4737(3)	0.0531(9)
C13″	1.0170(3)	0.1837(3)	−0.3161(2)	0.0471(8)
C14′	0.3560(4)	−0.2191(4)	0.4923(3)	0.0593(9)
C14″	0.9782(3)	0.3024(3)	−0.4016(2)	0.0474(8)
C15′	0.4964(4)	−0.2666(3)	0.4410(3)	0.0572(9)
C15″	0.8524(3)	0.4270(3)	−0.3933(2)	0.0469(8)
C16′	0.5466(3)	−0.1653(3)	0.3695(2)	0.0467(7)
C16″	0.7644(3)	0.4312(3)	−0.2971(2)	0.0381(6)
$\mathrm{Cd(Hsal)_2(1,2\text{-}diMeim)_2}$ (**5**)				
Cd*	0.2500	0.2500	0.43477(2)	0.0606(3)
O1	0.1521(4)	0.4436(4)	0.4012(2)	0.074(2)
O2	0.0745(5)	0.2697(4)	0.3705(2)	0.077(2)
O3	0.0724(5)	0.6443(4)	0.3544(2)	0.100(2)
N1	0.0208(7)	0.0941(5)	0.5735(2)	0.078(3)
N3	0.1046(5)	0.1686(5)	0.4964(2)	0.068(2)
C1A	0.0089(9)	0.0333(7)	0.6268(3)	0.129(5)
C2	0.1314(8)	0.1087(6)	0.5410(3)	0.071(3)
C2A	0.2723(7)	0.0607(8)	0.5538(3)	0.120(4)
C4	−0.0385(7)	0.1940(6)	0.4988(3)	0.073(3)
C5	−0.0870(9)	0.1502(7)	0.5442(3)	0.096(3)
C10	0.0737(7)	0.3838(7)	0.3692(2)	0.057(3)
C11	−0.0168(6)	0.4486(6)	0.3291(2)	0.048(3)
C12	−0.0121(6)	0.5757(6)	0.3241(3)	0.060(3)
C13	−0.0949(7)	0.6347(7)	0.2848(3)	0.079(3)
C14	−0.1807(8)	0.5644(9)	0.2530(3)	0.093(4)
C15	−0.1880(8)	0.4406(8)	0.2591(3)	0.094(4)
C16	−0.1070(6)	0.3792(7)	0.2971(2)	0.069(3)

*s.o.f. = 0.5.

Table 4. Selected geometrical data for $Cd(Hsal)_2(Him)_2$ (**2**) and $Cd(Hsal)_2(1,2\text{-}diMeim)_2$ (**5**).

$Cd(Hsal)_2(Him)_2$ **(2)**			$Cd(Hsal)_2(1,2\text{-}diMeim)_2$ **(5)**		
Cd–N3′	2.237(3)		Cd–O1	2.438(4)	
Cd–N3″	2.221(2)		Cd–O2	2.306(5)	
Cd–O1′	2.379(2)		Cd–N3	2.227(5)	
Cd–O2′	2.529(2)		O1–O1A $(1/2-x,1/2-y,z)$	4.599(5)	
Cd–O1″	2.396(2)				
Cd–O2″	2.514(1)				
Cd–O2″ $(1-x,1-y,-z)$	2.374(2)				
Cd–Cd$(1-x,1-y,-z)$	3.849(1)				
X–H···Y	X···Y(Å)	X–H···Y(°)	X–H···Y	X···Y(Å)	X–H···Y(°)
O3′–H12′···O1′	2.479(3)	161	O3–H3···O1	2.568(6)	146
O3–H12″···O1″	2.540(3)	145			
N1′–H1′···O2′$(1-x,1-y,-z)$	2.839(4)	151			
N1″–H1″···O3′$(1+x,y,z)$	2.869(4)	172			

appear near 1248 cm^{-1} and δ(COH) bending vibrations are detectable for all compounds [23–25]. In compounds with a bonding phenol group, δ(COH) is absent [23] and ν(COH) is shifted to lower frequencies [24]. The unassociated imine group gives ν(NH) at 3480 cm^{-1} and δ(NH) at 1449 cm^{-1} [25]. In compounds with metals, ν(NH) bands (one or two) are shifted towards lower frequencies [26] and δ(NH) is often invisible or appears within the range 1400–1450 cm^{-1} [27]. Just the same modifications are observed in the spectra of the present complexes. In the spectrum of the $Cd(Hsal)_2(4\text{-}MeHsal)_4$, three bands at 3280, 3412 and 3485 cm^{-1} are attributed to ν(NH). This suggests that molecules of 4-methylimidazole are bound in different ways.

3.2. *Structures of $Cd(Hsal)_2(Him)_2$ (2) and $Cd(Hsal)_2(1,2\text{-}diMeim)_2$ (5)*

Structure analyses of **2** and **5** confirm the proposed compositions of the respective complexes. In **2**, a binuclear Cd(II) complex (figure 3) with half of the molecule in the asymmetric unit was identified. Each Cd(II) ion adopts pentagonal bipyramidal coordination with two nitrogen atoms (N3′ and N3″ from two imidazole molecules) in axial positions. Oxygen atoms from carboxylate groups are involved in the remaining five bonds. The four carboxylate groups are not identical. Three COO^- groups participate in each cadmium coordination sphere, one as chelating bidentate and two as tridentates, being at once chelated and bridging two Cd(II) ions. In **5**, the Cd(II) occupies a special position (table 4) and adopts a six-coordinate, disordered octahedral shape (figures 2 and 3). The coordination sphere is formed by four oxygen atoms from two bidentate COO^- groups and two nitrogen atoms from 1,2-dimethylimidazoles (table 4). Two oxygens, O1 and O1a $(1/2-x,\ 1/2-y,\ z)$, lie in the axial positions.

In **2**, two intramolecular and two intermolecular H-bonds were identified (table 4). The intermolecular interactions are of particular importance. One could suppose that the two strong N–H···O H-bonds might be responsible for the atypical thermal decomposition of the complex (see later). In both crystals, intramolecular O–H···O1 H-bond (table 4) were identified. Complex **5** has only one intermolecular H-bond.

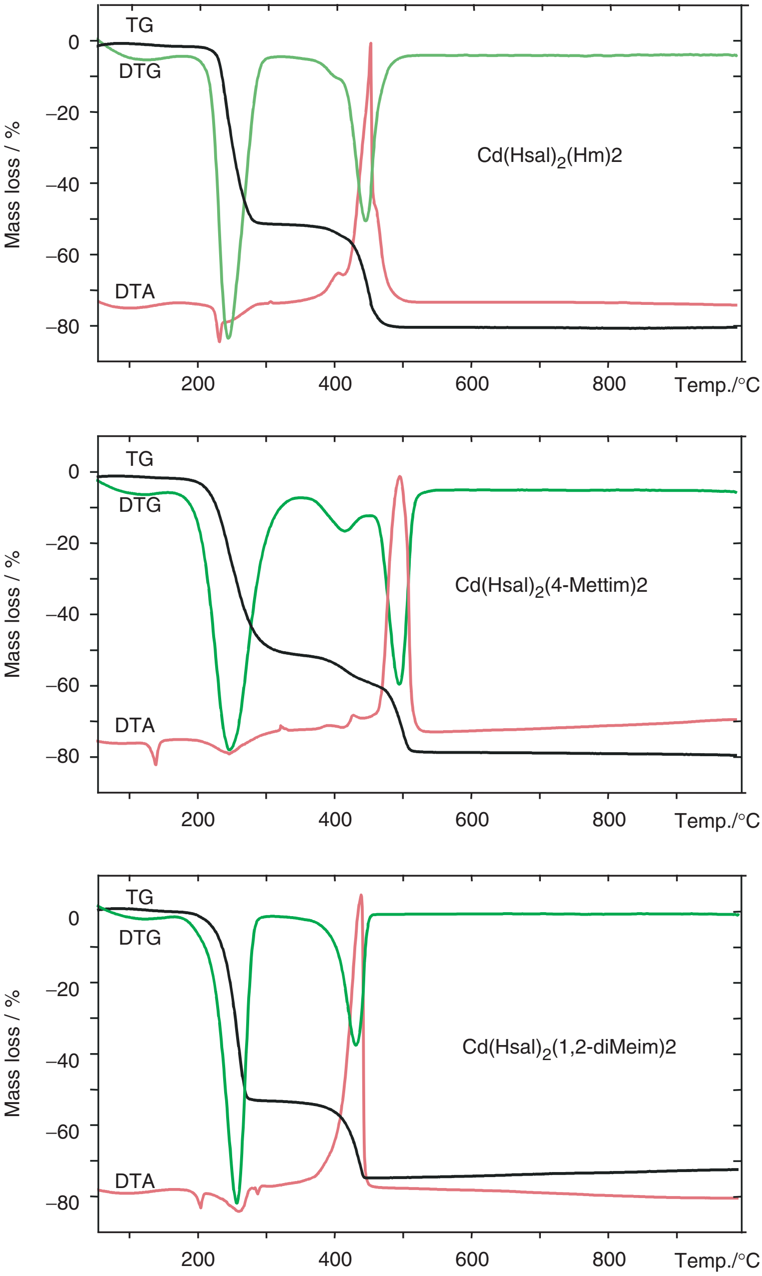


Figure 4. Thermal analysis curves for selected complexes.

3.3. *Thermal analyses*

Thermal analyses indicate that the decomposition of the complexes proceeds in several stages. Complex **2** decomposes in two stages, the first beginning at 110°C. Significant mass loss (50.8%) and a broad peak are observed in the TG and DTG

(260°C) curves. An endothermic peak in the DTA curve was found at 230°C. Mass loss at the beginning of the second stage is slow, but becomes rapid as decomposition proceeds. In DTG, an intense peak is observed at 450°C, and in DTA the endothermic peak is at the same temperature. Mass loss, chemical and XRD analyses of sinters obtained at 310 and 500°C indicate the process in reaction a,

$$\mathrm{Cd(Hsal)_2(Him)_2} \longrightarrow \mathrm{Cd(C_6H_5N_2O_{1.5})} \longrightarrow \mathrm{CdO} \qquad \text{(a)}$$

but analyses do not define a unique stoichiometric formula for the intermediate. The final product is CdO (calcd loss 75.43%, experimental loss 79.6%).

Pyrolysis of **3** and **4** proceeds in four stages and begins with a phase transition (endothermic peaks in DTA at 140 and 145°C, respectively). Fused samples then decompose similarly. In the second stage, significant mass losses and broad peaks are observed in the TG and DTG (calcd loss 50.13%, experimental loss 49.7% in **3**; calcd loss 61.34%, experimental loss 63.5% in **4**). The DTA curves showed an endothermic peak at 250°C for **3** and at 260°C for **4**. For **3** and **4**, the third endothermic stage occurs at 425 and 480°C, respectively. This is accompanied by slow mass loss (experimental 55.58%, calcd 58.4% for **3** and experimental 69.0%, calcd 66.82% for **4**). The final stage is exothermic (500, 560°C) with total mass loss of 78.1% (calcd 76.68%) and 84% (calcd 82.08%), respectively. The following reactions are involved.

$$\mathrm{Cd(Hsal)_2(4\text{-}MeHim)_2} \longrightarrow \mathrm{Cd(4\text{-}Meim)_2} \longrightarrow \mathrm{Cd(im)_2} \longrightarrow \mathrm{CdO} \qquad \text{(b)}$$

$$\mathrm{Cd(Hsal)_2(4\text{-}MeHim)_4} \longrightarrow \mathrm{Cd(4\text{-}Meim)_2} \longrightarrow \mathrm{Cd(im)_2} \longrightarrow \mathrm{CdO} \qquad \text{(c)}$$

Decomposition of **5** proceeds in three stages and begins with a phase transition (endothermic peak at 205°C). The next stages proceed with the gradual mass loss of 53.53 and 72.73% with endothermic peaks at 270, 290°C in the second stage, and an exothermic peak at 450°C in the third. Analyses of sinters showed that cadmium mono(*o*-hydroxybenzoate) formed in the second (calcd loss 57.07%) and cadmium oxide in the third stage (calcd loss 77.80%) (reaction d).

$$\mathrm{Cd(Hsal)_2(1,2\text{-}diMeim)_4} \longrightarrow \mathrm{Cd(sal)} \longrightarrow \mathrm{CdO} \qquad \text{(d)}$$

Analyses of gaseous products of decomposition of all complexes confirms the emission of the following fragments: OH (m/z 17), H_2O (m/z 18), NO (m/z 30), CO_2 (m/z 44, 46), C_6H_6 (m/z 50–52, 76–78), and the molecular ion $C_3N_2H_4$ (m/z 68). In the cases of **3** and **4**, the ionic current from emission of the CH_3 group (m/z 13, 15) does not increase until the second stage. This is confirmed by the formation of $\mathrm{Cd(4\text{-}Meim)_2}$ after the fusion process (reactions b and c).

3.4. *General*

Chemical and spectroscopic (IR) investigations of **2**, **3**, **4** and **5** determined composition and suggested the likely environment of cadmium in the complexes, but gave no answer to two important problems. First, it is still not clear why during reaction with unsubstituted imidazole only one cadmium compound formed. This is contradictory to the cases of Zn(II) [6,7] and Cu(II) [25], where two or three complexes were obtained. The second question is connected with thermal analysis. It is not obvious why the pyrolysis of **2** did not give a mono-ligand salt in the first stages of decomposition. Moreover, it is not clear why the course of decomposition of **2**, under conditions described here, does not lead to the same conclusion about the strength of the metal–ligand bonds as in complexes of zinc [6, 7].

X-ray structure analysis **2** and **5** gave explanations for both of these problems. First, complex **2** is binuclear $[Cd_2(Hsal)_4(Him)_4]$ with seven-coordinate cadmium and inequivalent COO^- groups. Two of them are chelating bidentates, while the other two are tridentate—chelating and bridging. Moreover, two strong intramolecular H-bonds fasten the binuclear species into a two-dimensional network in the crystal. This explains the formation of a single complex.

The strength of metal–ligand bonds is one of several factors that have an influence on the pathway of pyrolysis. Other factors are the molecular structures of the complexes and the functionality of carboxylic groups. In the present compounds, cadmium is always bound with the $Hsal^-$ ion and imidazole, 4-methylimidazole or 1,2-dimethylimidazole (neutral ligands). The strength of the metal–neutral ligand bond decreases in the order imidazole > 4-methylimidazole > 1,2 dimethylimidazole [28].

It should be noticed that in the binuclear complex **2**, breakage of ligand bonds takes place first. As a result, an intermediate, "non-stoichiometric" product is formed (reaction a). However, decomposition of **3** and **4** depends on the strength of Cd–4-MeHim bonds. Two molecules of *o*-hydroxybenzoic acid are lost in the first stage of pyrolysis (reactions b and c). In **5**, the chelating effect of COO^- groups is most important, and the strength of bonds has little significance (table 4). Two molecules of 1,2-dimethyloimidazole and one molecule of *o*-hydroxybenzoic acid are lost at first. Cd(sal) is the intermediate product of decomposition because the temperature range of this stage overlaps with the temperature of pyrolysis of $Cd(Hsal)_2$ to Cd(sal) [1] (reaction d). CdO is the final product of decomposition of all complexes.

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