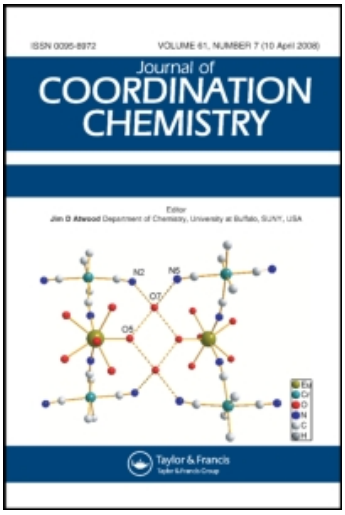

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Synthesis, characterization and thermal degradation kinetics of cadmium halide adducts with imidazole

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SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION KINETICS OF CADMIUM HALIDE ADDUCTS WITH IMIDAZOLE

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The synthesis, characterization and a nonisothermal thermal degradation kinetic study performed for the adducts $CdCl_2 \cdot Imi$, $CdCl_2 \cdot 2Imi$, $CdBr_2 \cdot 2Imi$ and $CdBr_2 \cdot 3Imi$ (Imi = imidazole) are reported. For cadmium bromide the maximum number of imidazole molecules per cadmium cation to produce a stable (from a thermodynamic point of view) compound is three, at least for compounds prepared at room temperature and pressure. The kinetic study performed by the Coats–Redfern and Szákо methods using thermogravimetric data shows that for all compounds the activation energy values associated with the release of imidazole molecules decreases as the thermal degradation process proceeds.

Keywords: Imidazole; Cadmium adducts; Kinetics; Thermogravimetry

INTRODUCTION

Thermochemical techniques such as thermogravimetry, scanning differential calorimetry and solution calorimetry can be successfully employed to study the interaction between transition metal cations and molecules of biological interest. A variety of coordination compounds of Zn(II), Cd(II), Co(II), Cu(II), Mn(II), Ni(II), Sn(II) and Ce(IV) with amino acids, or model molecules of biological interest, such as ethyleneurea, ethylenethiourea and propyleneurea [1–13] have been investigated. Imidazole is a very important model molecule since the imidazole ring occurs in a number of biological molecules, such as histidine, vitamin B_{12} and biotin, as well as in many chemotherapeutic agents [14].

The major studies involving coordination of imidazole with Group 12 cations are dedicated to zinc compounds. However, some studies can be found involving cadmium–imidazole compounds with octahedral or tetrahedral geometries [15–17]. In a study performed by Jensen [18] with several cadmium salts, a reduction of cadmium has been proposed leading to the formula $Cd^{II}_4(Cd^{I}_2)Imi_2Cl_{10}$ for one of the synthesized compounds.

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The present work is connected with the above mentioned investigation, and its aim is to report the synthesis, characterization and kinetic study of the nonisothermal degradation of the adducts $CdCl_2 \cdot Imi$, $CdCl_2 \cdot 2Imi$, $CdBr_2 \cdot 2Imi$ and $CdBr_2 \cdot 3Imi$ (Imi = imidazole).

EXPERIMENTAL

All reagents were of analytical grade and were employed without further purification.

The compounds $CdCl_2 \cdot Imi$, $CdCl_2 \cdot 2Imi$, $CdBr_2 \cdot 2Imi$ and $CdBr_2 \cdot 3Imi$ were prepared by dissolution of cadmium halides and imidazole in ethanol; the white precipitates formed were filtered off, washed with ethanol and dried under vacuum for 72 h. The metal halide–imidazole ratios employed in each case were 1 : 1, 1 : 2, 1 : 2 and 1 : 4, respectively. For cadmium bromide the maximum number of imidazole molecules per each cadmium cation to produce a stable (from a thermodynamic point of view) compound is three, at least for compounds prepared at room temperature and pressure.

Carbon, hydrogen and nitrogen elemental analyses were performed on a Perkin-Elmer microanalyzer. The metal and halide quantitative determinations were performed through volumetric titration with EDTA and potentiometric titration with aqueous silver nitrate solutions, respectively.

The infrared spectra were obtained on a Perkin-Elmer apparatus by using KBr discs or CsI windows. The thermogravimetric curves were obtained in a TGA-7 Perkin-Elmer apparatus under nitrogen atmosphere with a heating rate of $10\,K\,min^{-1}$.

Nonisothermal thermal degradation kinetic calculations were performed using the Coats–Redfern [19] and Szákо [20] methods.

RESULTS AND DISCUSSION

Results of elemental analyses are summarized in Table I, and are in good agreement with the proposed formulas for the synthesized adducts.

The main infrared bands are summarized in Table II. From these data, coordination through nitrogen can be inferred.

Comparison of the thermogravimetric curves gives the following sequences of thermal stabilities taking into account the release of imidazole molecules: $CdCl_2 \cdot Imi$ > $CdCl_2 \cdot 2Imi$ > $CdBr_2 \cdot 2Imi$ > and $CdBr_2 \cdot 3Imi$. The thermogravimetric and derivative curves for the synthesized compounds are shown in Fig. 1. For $CdBr_2 \cdot 3Imi$

TABLE I Elemental analysis results for imidazole adducts with cadmium halides

Adduct	*Element content (%)*				
	C	*H*	*N*	*M*	*X*
$CdCl_2 \cdot Imi$	14.7 (14.3)	1.6 (1.6)	11.0 (11.2)	44.7 (44.8)	28.1 (28.2)
$CdCl_2 \cdot 2Imi$	22.4 (22.5)	2.5 (2.5)	17.4 (17.5)	23.0 (22.2)	34.9 (35.2)
$CdBr_2 \cdot 2Imi$	16.9 (16.9)	1.8 (1.9)	12.5 (12.5)	27.6 (27.6)	39.7 (39.2)
$CdBr_2 \cdot 3Imi$	22.4 (22.7)	2.6 (2.5)	17.7 (17.6)	24.4 (23.6)	33.6 (33.6)

Results are given as found (calcd.).

TABLE II Main infrared bands (cm^{-1}) for imidazole adducts with cadmium halides

Compound	$\nu_a(NH)$	$\nu_s(NH)$	$\delta_a(HN–)$	$\delta_s(HN–)$	$\rho_r(HN–)$
Imidazole	3330	3124	1542	1098	620
$CdCl_2 \cdot$ Imi	3342/3236	3138	1536	1092	610
$CdCl_2 \cdot$ 2Imi	3340/3236	3138	1538	1092	610
$CdBr_2 \cdot$ 2Imi	3264	3130	1532	1096	606
$CdBr_2 \cdot$ 3Imi	3260	–	–	–	–

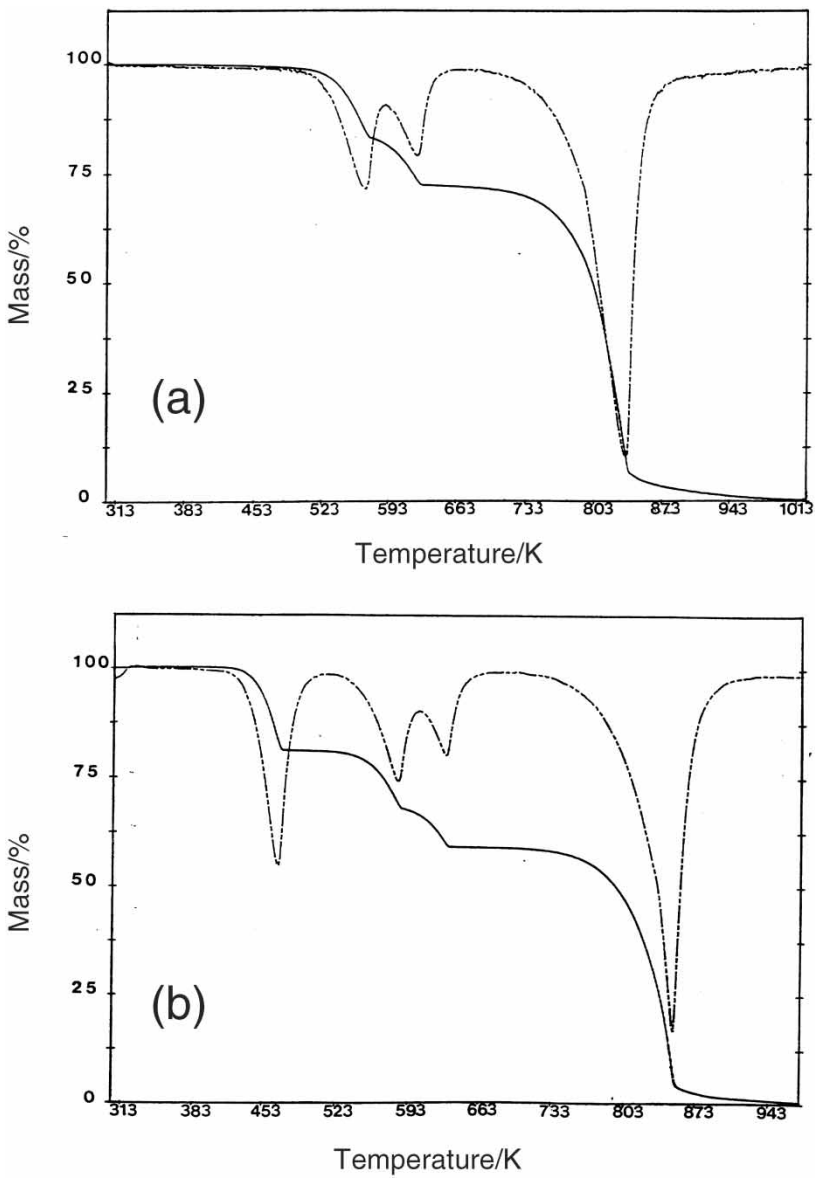

FIGURE 1 Thermogravimetric and derivative curves for (a) $CdCl_2 \cdot$ Imi, (b) $CdCl_2 \cdot$ 2Imi, (c) $CdBr_2 \cdot$ 2Imi and (d) $CdBr_2 \cdot$ 3Imi.

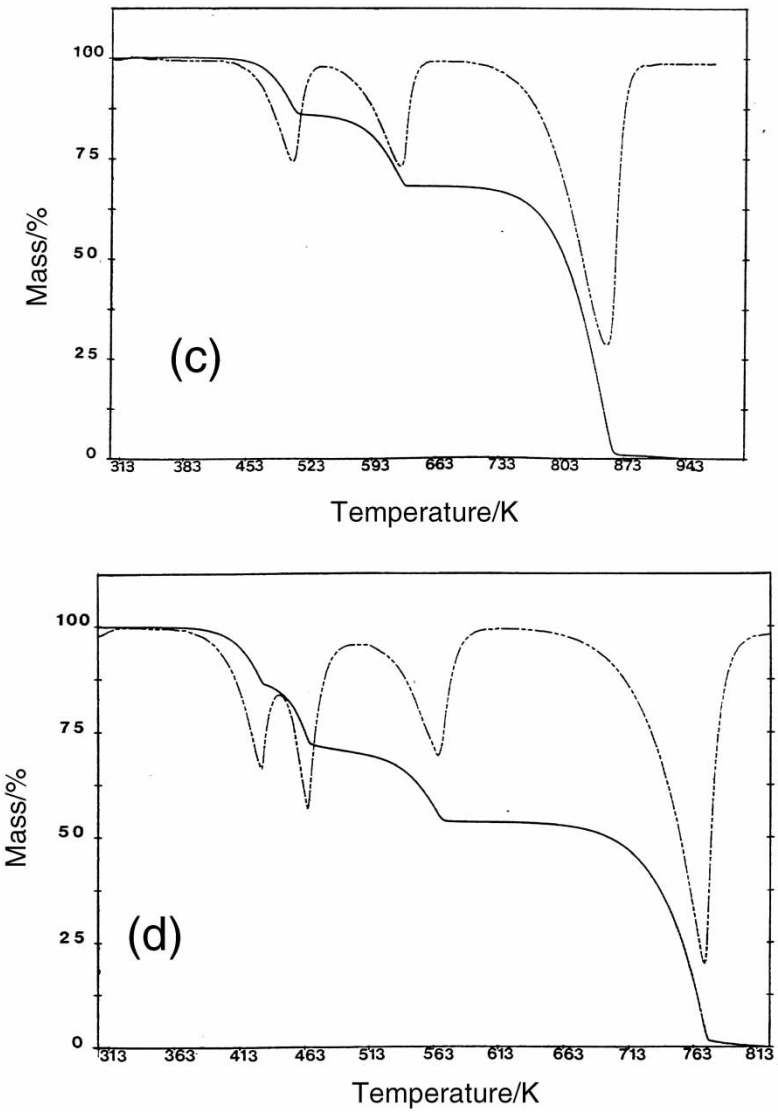

FIGURE 1 Continued.

the thermal degradation process sequence is:

$$CdBr_2 \cdot 3Imi(s) \rightarrow CdBr_2 \cdot 2Imi(s) + Imi(g) \quad (1)$$

$$CdBr_2 \cdot 2Imi(s) \rightarrow CdBr_2 \cdot Imi(s) + Imi(g) \quad (2)$$

$$CdBr_2 \cdot Imi(s) \rightarrow CdBr_2(s) + Imi(g) \quad (3)$$

$$CdBr_2(s) \rightarrow CdBr_2(g) \quad (4)$$

Similar thermal decomposition sequences are proposed for all the compounds studied. For all compounds the experimental values of the ligand mass loss steps are in good

agreement (± 5) with the calculated values, taking into account the elemental analysis formulas.

As verified in Table III, for cadmium chloride the monoadduct is more stable than the bisadduct. This can be understood from either an ionic or a covalent view of the metal–imidazole bond formation. From an ionic point of view, in the monoadduct the positive charge of the cation is attracting only one electron pair of the ligand molecule, whereas in the bisadducts two electron pairs are attracted, resulting in weaker bonds. From a covalent point of view the overlapping of metal and ligand frontier orbitals is more effective in the monoadduct, resulting in stronger bonds. Since for all compounds the release of imidazole molecules occurs in two or three steps, the imidazole molecules are not located at equivalent (from an energetic point of view) coordination sites.

The kinetic calculation results are summarized in Tables IV and V. Only the thermal degradation steps involving release of imidazole molecules were considered for the calculations. Since it is not possible to provide a straightforward interpretation

TABLE III Mass-loss steps observed in TG curves for imidazole adducts with cadmium halides

Adduct	*Mass-loss step*	*Mass loss* (%)	Δt (K)
$CdCl_2 \cdot Imi$	1	16.6	493–573
	2	10.7	573–633
	3	71.7	633–973
$CdCl_2 \cdot 2Imi$	1	19.1	403–473
	2	13.1	473–593
	3	8.8	593–633
	4	58.7	633–953
$CdBr_2 \cdot 2Imi$	1	13.9	383–478
	2	16.4	478–583
	3	66.5	583–813
$CdBr_2 \cdot 3Imi$	1	13.6	373–433
	2	14.5	433–473
	3	18.0	473–573

TABLE IV Non-isothermal kinetic calculation results for the thermal degradation of cadmium halides adducts with imidazole by the Coats–Redfern method

Compound	*Step*	*r*	E_a	*A*	*n*	*P*
$CdCl_2 \cdot Imi$	1	0.98	85.5	2.6×10^2	0	20
	2	0.99	24.6	1.3×10^{-4}	0	15
$CdCl_2 \cdot 2Imi$	1	0.99	90.7	3.9×10^5	0	18
	2	0.92	30.9	1.2×10^{-3}	0	24
	3	0.98	17.9	3.2×10^{-5}	0	19
$CdBr_2 \cdot 2Imi$	1	0.99	94.5	2.2×10^5	0	20
	2	0.98	25.7	3.0×10^{-4}	0	11
$CdBr_2 \cdot 3Imi$	1	0.99	72.4	4.3×10^3	0	25
	2	0.95	25.8	1.6×10^{-3}	0	20
	3	0.84	9.2	3.7×10^{-6}	0	15

E_a is the activation energy ($kJ\,mol^{-1}$) for the thermal degradation process, r is the correlation coefficient, A is the pre-exponential factor, n is the order of the reaction and P is the number of data used for the calculations.

TABLE V Non-isothermal kinetic calculation results for the thermal degradation of cadmium halides adducts with imidazole by the Szàko method

Compound	*Step*	*r*	E_a	*A*	*n*	*P*
$CdCl_2 \cdot Imi$	1	0.99	85.5	3.0×10^2	0	20
	2	0.99	25.0	1.9×10^{-4}	0	15
$CdCl_2 \cdot 2Imi$	1	0.99	90.5	4.4×10^5	0	18
	2	0.95	31.6	1.8×10^{-3}	0	24
	3	0.99	19.2	6.4×10^{-5}	0	19
$CdBr_2 \cdot 2Imi$	1	0.99	94.2	2.4×10^5	0	20
	2	0.99	26.8	5.0×10^{-4}	0	11
$CdBr_2 \cdot 3Imi$	1	0.99	72.3	4.9×10^{-3}	0	25
	2	0.97	26.4	2.5×10^{-3}	0	20
	3	0.85	10.8	1.0×10^{-5}	0	15

E_a is the activation energy ($kJ\,mol^{-1}$) for the thermal degradation process, *r* is the correlation coefficient, *A* is the pre-exponential factor, *n* is the order of the reaction and *P* is the number of data used for the calculations.

for the *A* values [21,22], only activation energy will be considered for discussion. The activation energy values calculated by the two methods are in good agreement.

For all compounds the activation energy values associated with the release of imidazole molecules decrease as thermal degradation proceeds. Furthermore, comparing the activation energy values for $CdCl_2 \cdot 2Imi$ and $CdBr_2 \cdot 2Imi$ verifies that steps 1 and 2 exhibit similar values, consistent with a possible structural similarity between the two compounds.

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