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Short communication

Crystal structure and thermoanalytical study of a cadmium(II) complex with 1-allylimidazole

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ABSTRACT

The crystal structure of a cadmium(II) 1-allylimidazole complex ($[Cd(1\text{-}AIm)_3(NO_3)_2]$, where 1-Aim = 1-allylimidazole), was characterized by single-crystal X-ray diffraction analysis. Thermogravimetry (TG) coupled with an FTIR unit was used to study the thermal behaviour of the complex. A multi-step decomposition occurred in the complex due to the release of the ligand molecules, followed by oxidation. The final residue at 1073 K was found to be cadmium(II) oxide. The oxidative decomposition pattern of the examined complex initially proposed by the percentage mass loss data was proved by the evolved gas analysis. Finally, a kinetic analysis of the oxidative decomposition steps was made using the Kissinger equation, while the complex nature of the decomposition kinetics was revealed by the isoconversional Ozawa–Flynn–Wall method.

1. Introduction

In the last 10 years an increasing interest has been devoted to imidazole derivatives, because of their remarkable application in biology (e.g., biocatalysis) and industry (e.g., as effective corrosion inhibitors or hidden curing agents for epoxy resins [1]). Recently, different authors studied the thermal behaviour of imidazole derivatives complexes with divalent transition metal ions [2–4]. Spectral, magnetic and thermal behaviour of imidazole derivative complexes with divalent cadmium ions were investigated using several techniques in conjunction with thermal analysis techniques [5–7]. Our research group has been involved in a systematic experimental study about the synthesis, X-ray crystal structure characterization, thermal behaviour and kinetic investigation of the thermal decomposition processes occurring in imidazole derivative complexes with divalent transition metal ions [2,8–11]. As a continuation of this research the aim of this paper is to fully characterize the crystal structure of the 1:3 metal:ligand dinitrate Cd(II) complex with 1-allylimidazole and to investigate in detail its thermal behaviour using several different but complementary techniques: X-ray diffraction (XRD) spectroscopy, thermogravimetry (TG) and first-order thermogravimetry (DTG) and TG unit coupled with FTIR spectroscopy by means of a heated transfer line in a proper temperature range (TG-FTIR). A possible degradation pathway is also proposed for all the degradation steps according to the mass losses recorded by the TG unit, and a substantial confirmation is obtained with the TG-FTIR evolved gas analysis.

2. Materials and methods

2.1. Materials

The 1-allylimidazole, propan-2-ol, trimethyl orthoformate and $Cd(NO_3)_2{\cdot}xH_2O$ were purchased from Aldrich Chemical Co. and were used without further purification, while the solvents used were RPE grade.

The complex studied was obtained in the following way: 1 mmol of $Cd(NO_3)_2{\cdot}6H_2O$ was dissolved in 25 cm^3 of the mixture of propan-2-ol (15 cm^3) and trimethyl orthoformate (10 cm^3). The solution was added, stirring constantly, to the solution of 4 mmol of 1-allylimidazole in the same mixture of solvents. Evaporating of the solution for a week gave colourless crystals, which then were washed with ethyl ether and resulted suitable for X-ray diffraction

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study. Elemental analysis data of the complex considered in this study were summarized as follows: Cd 20.0% (20.0%), C 38.4% (38.5), H 4.5% (4.3), N 20.1% (20.0). As a result of the good agreement between experimental and calculated data (in brackets) a general formula $[Cd(1\text{-}Aim)_3(NO_3)_2]$ can be hypothesized.

2.2. Methods

Elemental analysis was performed by a VarioEl III CHN Analyzer.

The crystal of $[Cd(1\text{-}Aim)_3(NO_3)_2]$ complex was mounted on a glass fibber and flash-frozen to 100 K (Oxford Cryosystem-Cryostream Cooler). Preliminary examination and intensity data collection were carried out using a KM4-CCD diffractometer, ω scans, and graphite-monochromated Mo Kα radiation generated from a diffraction X-ray tube operating at 50 kV and 20 mA. The data were corrected for Lorentz and polarization effects. Absorption corrections were performed for the intensity data (T_{min} = 0.797 and T_{max} = 0.810) [12]. The images were indexed, integrated, and scaled using the CrysAlis data reduction package [12]. The structure was solved by direct methods (SHELXS97) [13] and refined by the full-matrix least-squares method on all F^2 data (SHELXL97) [14]. H atoms were included from geometry of molecules and were not refined. Crystal data and details of data collection and refinement procedure are collected in Table 1.

The TG curves were recorded using a PerkinElmer TGA7 equipment in the temperature range between 20 and 800 °C, the atmosphere was pure nitrogen or air under a flow rate of 100 mL min^{-1}. First-order derivative of TG data (DTG curve) was also provided for a better evaluation of initial and final temperature as well as of the corresponding percentages of mass loss. TG experiments were carried out using 7–8 mg of sample at several heating rates between 2.5 and 20 K min^{-1} for the kinetic study, while the thermal behaviour was investigated using TG data at 10 K min^{-1} because of its best resolution. IR spectra of the gases evolved during the experiments were recorded since the TG apparatus was coupled with a PerkinElmer FTIR spectrometer, model 1760X. The TGA7 was linked to the heated gas cell of the FTIR instrument by means of a heated transfer line, the temperatures of the cell and of the transfer line being independently selected.

Table 1
Crystal data and structure refinement for complex $[Cd(1\text{-}AIm)_3(NO_3)_2]$.

	$[Cd(1\text{-}AIm)_3(NO_3)_2]$
Empirical formula	$C_{18}H_{24}N_8CdO_6$
Molar mass (g mol^{-1})	560.85
Temperature (K)	100(2)
Radiation	Mo Kα (λ = 0.71073 Å)
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.596(2)
b (Å)	14.379(3)
c (Å)	15.252(3)
β (°)	99.35(3)
V (Å^3)	2292.9(8)
Z, calculated density (Mg m^{-3})	4, 1.625
μ (mm^{-1})	1.004
$F(000)$	1136
Crystal size (mm)	0.20 × 0.20 × 0.18
Limiting indices	$-12 \le h \le 12$, $-16 \le k \le 17$, $-18 \le l \le 17$
Reflections collected	12914
Independent reflections	4001, [R(int) = 0.0280]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4001/0/298
Goodness-of-fit on F^2	1.082
Final R indices, [$I > 2\sigma(I)$]	R_1 = 0.0265, wR_2 = 0.0643
R indices (all data)	R_1 = 0.0371, wR_2 = 0.0674
Largest differential peak and hole e (Å^{-3})	1.376 and −0.490

3. Theory

The kinetic methods proposed in this study are based on the assumption that kinetic parameters do not depend on the selected heating rate. The basic kinetic equation is:

$$\frac{d\alpha}{dt} = k(T)\, f(\alpha) \tag{1}$$

where t is the time, α is the fraction decomposed defined as $\alpha = (w_i - w_T)/(w_i - w_f)$, $f(\alpha)$ is the model function, which assumes different mathematical forms depending on the reaction mechanism [15] and $k(T)$ is the specific rate constant, whose temperature dependence is commonly described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where E is the activation energy, A is the pre-exponential factor, R is the gas constant and T is the absolute temperature. Moreover, taking into account that under non-isothermal condition the heating rate $\beta = dT/dt$, $d\alpha/dt = d\alpha/(dT/\beta)$, combining Eqs. (1) and (2), gives:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{3}$$

However, due to the complexity of the kinetic description concerning the solid state decomposition processes it is usually assumed that the activation energy is not a constant value but depends on α [16–18]. Therefore, in order to establish if such dependence exists or not, the kinetic procedure adopted in this work was firstly based on two multi-heating rates methods. Both approaches determine the activation energy using thermal analysis data carried out at different fixed heating rates without choosing a priori a defined model function. In particular, the first kinetic method used was Kissinger method [19] that uses the following equation:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \left(\frac{E}{R}\right)\left(\frac{1}{T_m}\right) \tag{4}$$

where T_m is the DSC peak temperature at a given heating rate β. From the slope of Eq. (4) a single activation energy value for each step of mass loss is given. In order to test the dependence of activation energy on the fraction decomposed α the isoconversional method of Ozawa–Flynn–Wall (OFW) [20,21] was also considered. This method is based on the integral form of Eq. (1) according to the following isoconversional equations

$$\ln \beta_\alpha = \ln\left(\frac{A_\alpha R}{E_\alpha}\right) - \ln g(\alpha) - 5.3305 - 1.052\left(\frac{E_\alpha}{R}\right)\left(\frac{1}{T_\alpha}\right) \tag{5}$$

Once the Doyle's approximation [22]: $\ln p(x) \approx -5.3305 - 1.052x$, where $x = E_\alpha/(RT_\alpha)$ and $20 \le x \le 60$ is verified to be valid over the entire range of α, then at any selected value of α, from the slope of the related regression straight line derived by the $\ln(\beta)_\alpha$ *vs.* $1/T_\alpha$ plot, the corresponding E_α value is derived as a function of α.

4. Results and discussion

4.1. Crystal structure analysis

Refinement parameters and details of the crystal data for the cadmium(II) complex investigated are shown in Table 1. As it can be seen the complex $[Cd(1\text{-}AIm)_3(NO_3)_2]$ crystallizes in the monoclinic system, in the $P2_1$ space group, with the parameters of the unit cell: a = 10.596(2), b = 14.379(3), c = 15.252(3) Å, β = 99.35(3)°, Z = 4, T = 100(2) K.