

Study of the reactivity of Cd(II) with 4,6-dimethyl-2-thiopyrimidine. Crystal structure of 4,6-dimethyl-2-thiopyrimidinium trichlorocadmium(II)

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Abstract

The distribution species and stability constants of the 4,6-dimethyl-2-thiopyrimidine (HL)/CdCl₂ system have been determined by potentiometric measurements at 25 °C and 0.1 M KCl ionic strength. The solid complexes CdL(OH) and {[H₂L]CdCl₃}_n were obtained and characterized by IR, ¹H and ¹³C NMR spectroscopic and thermal techniques. In addition, the structure of the complex {[H₂L]CdCl₃]_n has been established by single-crystal X-ray diffraction. Crystals of the compound are orthorhombic, space group *Pbca* (No. 61) with cell constants *a* = 6.723(1), *b* = 17.624(4), *c* = 19.401(4) Å, *Z* = 8, *D_c* = 2.080 g cm⁻³. The structure was solved and refined to *R* = 0.055 (*R_w* = 0.079) and consists of Cd(II) centres hexacoordinated by chloride ions in an octahedral arrangement. These octahedra are linked by opposite faces giving rise to infinite [CdCl₃]_n chains which are bridged by H₂L units through hydrogen bonds.

Keywords: Crystal structures; Cadmium complexes; Thiopyrimidine ligand complexes; Electrochemistry; Spectroelectrochemistry

1. Introduction

Among the heterocyclic derivatives containing sulfur, thiopyrimidine derivatives are very important because of their biological activity [1–4]. On the other hand, cadmium is an environmental pollutant which inhibits RNA polymerase activity *in vivo* [5] and reacts readily with proteins and other biological molecules. Further, the chemical similarity of Cd(II) and Zn(II) suggests the hypothesis that in many cases such reactions may displace Zn(II) from a critical site in Zn enzymes [6,7].

In previous papers we have published the study of the interaction between the pyrimidinic derivative 4,6-dimethyl-2-thiopyrimidine (HL) and the Zn(II) ion in aqueous media [8,9]. In the present paper we report on the study of the reactivity of the Cd(II)/HL system in aqueous media. This study has been carried out in order to establish the complex formation processes by using potentiometric techniques at 0.1 M ionic strength KCl and 25 °C. From this study, we have selected the pH conditions to obtain the solid species CdL(OH)

and {[H₂L]CdCl₃]_n, which were characterized by IR, ¹H and ¹³C NMR spectroscopic techniques. The structure of the latter compound has been determined by single crystal X-ray diffraction and the thermal decomposition mechanisms of the complexes have been established. It should be noted that even though no evidence of Cd(HL)₂Cl₂ formation has been obtained from the solution study, this compound has previously been isolated in the solid phase and its crystal structure reported by us [8]. Further, the thermal treatment of both CdL(OH) and {[H₂L]CdCl₃]_n leads to CdL₂ as intermediate before the pyrolytic decomposition starts.

2. Experimental

2.1. Reagents

Standardized Cd(II) chloride solution (Merck) was used. The ligand HL (99%) was obtained from Aldrich and used as provided. Potentiometric measurements were carried out using CO₂-free double distilled water as solvent. CO₂-free KOH solutions (Merck) were pre-

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pared by dilution and standardized with potassium hydrogen phthalate. HCl solutions were also standardized using CO₂-free KOH as titrating agent. The potentiometric measurements were carried out in 0.1 M KCl as background electrolyte.

2.2. Preparation of the complexes

CdL(OH). To a mixture of HL (1 mmol) and KOH (1 mmol) in 20 ml of H₂O, CdCl₂ (3 mmol) was added under stirring, resulting in a solution with a pH equal to 7. The white powder that precipitated almost immediately was filtered off, washed with water/ethanol (4:1) and ether, and dried over P₄O₁₀. *Anal.* Calc. for C₄H₇N₂OCd: C, 26.8; H, 3.0; N, 10.4. Found: C, 27.2; H, 3.2; N, 10.8%.

{[H₂L]CdCl₃}_n. To a solution of HL (1 mmol) in the minimum amount of water a 0.1 M HCl solution was added until the pH was equal to one. To the resulting mixture, CdCl₂ (1 mmol) was added and the solution concentrated in a water bath at 60 °C until a crystalline pale-yellow solid appeared. This was filtered off, washed with ethanol and ether, and dried over P₄O₁₀. *Anal.* Calc. for C₄H₈N₂Cl₃Cd: C, 20.0; H, 2.5; N, 7.8. Found: C, 19.8; H, 2.5; N, 7.8%.

2.3. Apparatus

Microanalyses of C, H and N were performed with a Perkin-Elmer 240 C instrument. IR spectra were obtained using a Perkin-Elmer 983 G spectrophotometer in KBr pellets in the 4000–250 cm⁻¹ range. ¹H and ¹³C NMR spectra were recorded with a Bruker AM-300 spectrometer, using DMSO-d₆ as solvent and TMS as internal standard. The TG, DTG and DSC diagrams were obtained with a Mettler TG-50 thermobalance in a dynamic pure air atmosphere (100 ml min⁻¹) and a heating rate of 20 °C min⁻¹.

The potentiometric assembly was described in a previous work [9]. For the pH and e.m.f. measurements, calomel K4040 and glass G2040B Radiometer electrodes were used. The sample solutions were titrated at 25.0 ± 0.1 °C under a continuous flow of nitrogen previously bubbled through ascarite (NaOH-coated silica).

2.4. Procedure

Calibration of the electrodes [10] and the ionic product of the medium [11] was through the titration of HCl with KOH; the liquid junction potential was negligible in the pH working range.

The complex formation equilibria were studied using solutions with [HL] = 1 × 10⁻³ M and [HL]/[Cd(II)] ratios varying from 4:1 to 1:1 and 0.1 M KCl ionic strength. The computer program BEST [12] was used to process the titration data and to calculate the stability

constants of the complexes; this program minimizes the parameter $U = \sum w_i ([pH]_{obs} - [pH]_{calc})^2$ where w_i is defined by $w_i = 1/([pH]_{i+1} - [pH]_{i-1})^2$. The standard deviation in pH units is given by $\sigma_{fit} = (U/N)^{1/2}$, where $N = \sum w_i$. In the calculations, previously reported values of protonation constants of the ligand L were used [9].

2.5. X-ray data collection and structure determination

Single crystal data collection was performed at 293 K with a Siemens R3m/V diffractometer using graphite monochromatized Mo K α ($\lambda = 0.71069$ Å) radiation. A plated pale-yellow crystal of dimensions 0.68 × 0.46 × 0.04 mm was used. The complex crystallizes in the orthorhombic system, space group *Pbca* (No. 61) with cell constants: $a = 6.723(1)$, $b = 17.624(4)$, $c = 19.401(4)$ Å, $V = 2298.7(5)$ Å³, $Z = 8$, $D_c = 2.080$ g cm⁻³, $F(000) = 1392.0$, $\mu(\text{Mo K}\alpha) = 2.74$ mm⁻¹.

The unit cell parameters were calculated by least-squares refinement of 25 well centred reflections in the range $15 < 2\theta < 45^\circ$. The data were collected by $\omega/2\theta$ scan mode in the range $3 < 2\theta < 65^\circ$. Intensities of three check reflections measured after every 120 min showed no significant variation. A total of 2595 reflections was considered as observed with $I > 3\sigma(I_o)$. The data were corrected for Lorentz and polarization effects and for absorption.

The structure was solved by Patterson methods and subsequent Fourier syntheses with the SHELXTL PLUS program [13]. All non-hydrogen atoms were refined anisotropically in the final refinements. The positions of the hydrogen atoms were calculated with isotropic temperature factors ($U = 0.08$) and were not refined. Neutral atomic scattering and dispersion factors were those included in the SHELXTL package. The function minimized was $\sum w(\Delta F)^2$ ($1/w = \sigma^2(F_o)$), resulting in a final $R = \sum |F_c - F_o| / \sum |F_o|$ value of 0.055 and $R_w = [(\sum w|F - F_o|)^2 / \sum w|F_o|^2]^{1/2}$ value of 0.079, with $S = 0.16$ for 118 parameters. Maximum and minimum transmission factors were 0.5741 and 0.1819, respectively. Atomic fractional coordinates are listed in Table 1.

3. Results and discussion

3.1. Solution study

Previously acidified solutions (HCl) containing HL/Cd(II) mixtures with [HL]/[Cd(II)] varying from 4:1 to 1:1 ([HL] = 1.10 × 10⁻³ M) were titrated with 0.1 M KOH at 25 °C and 0.1 M KCl ionic strength to study the complex formation processes. Each titration was extended between the pH values of 2.8 and 6.6, before the precipitation of a white solid CdL(OH) complex occurred. The experimental points obtained from the

Table 1

Atomic coordinates ($\times 10^{-4}$) and U_{eq} ($\times 10^{-3}$) for $\{[H_2L][CdCl_3]\}_n$

Atom	x	y	z	U_{eq}
Cd(1)	929(1)	1807(1)	2508(1)	33(1)
Cl(1)	-1567(2)	832(1)	1900(1)	33(1)
Cl(2)	-1544(2)	2804(1)	2042(1)	38(1)
Cl(3)	-1595(2)	1645(1)	3573(1)	34(1)
N(1)	2310(6)	5753(2)	4724(2)	31(1)
C(2)	2491(5)	5038(2)	5000(2)	28(1)
N(3)	2640(6)	5035(2)	5707(2)	32(1)
C(4)	2663(7)	5666(2)	6109(2)	34(1)
C(5)	2442(7)	6364(2)	5802(2)	33(1)
C(6)	2250(6)	6404(2)	5083(2)	31(1)
S(2)	2530(2)	4257(1)	4532(1)	38(1)
C(41)	2929(10)	5550(3)	6854(3)	54(2)
C(61)	1957(9)	7106(3)	4691(3)	45(1)

Table 2

Equilibrium data for the complex formation of Cd(II) with the deprotonated ligand L^- (25 °C in 0.1 M KCl) ^a

Species (<i>pqr</i>)	Process	Log β
(110)	$Cd^{2+} + L^- \rightleftharpoons [CdL]^+$	5.54(4)
(11-1)	$Cd^{2+} + L^- \rightleftharpoons CdLOH + H^+$	-1.34(3)

^a Values in parentheses are the standard deviation corresponding to the last significant digit.

valoration curves in each experiment were 74. The best fit to the data has been found with the model corresponding to the existence of the processes given in Table 2.

The species formed in the equilibria are labelled by the *pqr* parameters, which define the number of metal ions, deprotonated ligands (L) and protons, respectively, forming the species. The *pqr* values included in Table 2 have been calculated from solutions with an $[HL]/[Cd(II)]$ ratio of 2:1. The experimental data indicate the existence of CdL^+ and $CdL(OH)$ species ($\sigma_{fit}=0.0041$). It should be noted that the inclusion of the (0,2,-1), (0,4,-4) and (0,4,-5) species [12] in the postulated model for the treatment of the data results in an increase of the σ_{fit} to a value of 0.087. Moreover, these species are found to be formed only to a maximum of 1 ppm, therefore they were not considered further. This behaviour is similar to that found by other authors in the study of uracil and uridine with Zn(II) ions [14]. The 111 and 112 species, corresponding to the complexes formed between the metal ion and the neutral ligand, and which obviously must be formed in solutions of slight acidity, have not been detected in these systems, probably because they exist in a lower concentration range than that observable by the technique used. Nevertheless, a complex of $Cd(HL)_2Cl_2$ stoichiometry has previously been obtained and characterized by X-ray diffraction methods, starting

from slightly acidified solutions containing the $HL/CdCl_2$ mixture in a 1/2 molar ratio [8].

The stability of the CdL^+ species ($\log \beta_{110}=5.54$) is similar to that of the homologous Zn(II) species, ZnL^+ ($\log \beta=5.06$), suggesting a similar coordination pattern in both complexes. This means that the anion L is bidentately coordinated to the Cd(II) ion through an S–N bridge.

The distribution plot as a function of the pH for the species formed in the $HL/Cd(II)$ system is given in Fig. 1, from which it became evident that the free metal ion predominates at pH values below 5, whereas the complex species existing in the 5–6 pH range is the CdL^+ one. In the 6–7 pH range the CdL^+ and $CdL(OH)$ species coexist, the latter predominating at pH=7.

As previously noted, at pH values below 2 a species with $(H_2L)CdCl_3$ stoichiometry was isolated in the solid state, whereas solutions with the pH adjusted to 7 yielded a white solid complex of empirical formula $CdL(OH)$.

3.2. Spectroscopic study

The IR spectrum of $CdL(OH)$ shows a sharp new band at 3469 cm^{-1} characteristic of hydroxy complexes. In accordance with the literature, this band usually can be seen even in the presence of water absorption [15]. The lack of the $\nu(NH)$ stretching vibration band, which in the free ligands appears at 2913 cm^{-1} , is indicative of a monoanionic coordination mode for the ligand. The IR spectral range between 1700 and 600 cm^{-1} is quite similar to that of the $[ZnL_2]_n$ compound indicating coordination of L through the S–N bridge [9]. Thus the strong $\nu(C=C)$ and $\nu(C=N)$ stretching vibration bands of the ligand are shifted from 1624 and 1568 cm^{-1} to 1583 and 1537 cm^{-1} , respectively, suggesting a Cd–N_{cyclic} interaction.

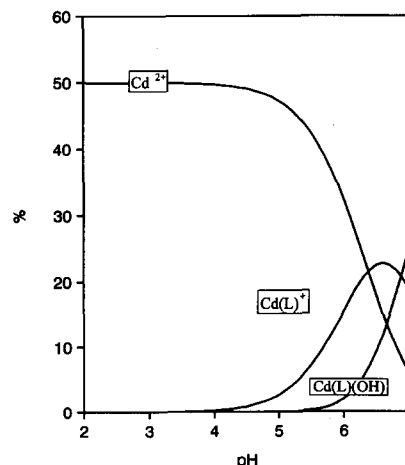


Fig. 1. Distribution diagram for the Cd(II)/HL system as a function of pH.

Table 3
NMR data (δ in ppm)

Compound	^1H NMR				^{13}C NMR			
	CH_3	OH	$\text{C}(5)\text{--H}$	NH	$\text{C}(2)$	$\text{C}(5)$	$\text{C}(4)$ and $\text{C}(6)$	CH_3
HL	2.23		6.60	13.46	180.90(s)	109.60(s)	157.00 vb	18.40 b 24.00 b
CdLOH	2.18	3.87	6.67		180.00(s)	114.07(s)	167.08(s)	22.89(s)
H_2LCdCl_3	2.49		7.12	8.04	173.50(s)	111.49(s)	167.11(s)	20.01(s)

s=singlet; b=broad; vb=very broad.

On the other hand, Thioamide I and Thioamide III bands of free HL at 1437 and 1180 cm^{-1} , respectively, weakly appear at 1428 and 1176 cm^{-1} in the complex indicating the existence of a Cd–S interaction, in accordance with previous observations [8]. Finally, a new strong wide band at 554 cm^{-1} , is assigned to a $\nu(\text{Cd--O})$ band, supporting the existence of a coordinated hydroxy group in the complex.

The IR spectrum of $\{[\text{H}_2\text{L}]\text{CdCl}_3\}_n$ shows two sharp bands at 3085 and 2917 cm^{-1} assignable to a $\nu(\text{N--H})$ band belonging to the doubly protonated species, H_2L . The aforementioned $\nu(\text{C=C})$ and $\nu(\text{C=N})$ bands of the free ligand are strongly modified and appear in this spectrum as a double band with peaks at 1618 and 1592 cm^{-1} which indicate that the protonation of HL takes place on the free N_{cyclic} atom. In the low frequency range two new strong wide bands, at 242 and 188 cm^{-1} , typical of a metal ion in an O_h environment of halide ions [15], have been detected.

The ^1H and ^{13}C NMR spectral data of the complexes, together with that of HL, are summarized in Table 3.

In the ^{13}C NMR spectrum of $\text{CdL}(\text{OH})$ the $\text{C}(2)$ signal of the pyrimidine ring is at a similar field value to that of free HL. Given that in the free ligand an S–H–N hydrogen bond interaction exists [8], this means that in this complex there is a similar interaction for the S atom, but likely with the metal ion Cd(II). In addition, the signal corresponding to both the $\text{C}(4)$ and $\text{C}(6)$ atoms and that of $\text{C}(5)$ are widely shifted to lower field values as can be expected due to the existence of an $\text{N}_{\text{cyclic}}\text{--Cd}$ interaction which results in a deshielding of the ring atoms. Moreover, this spectrum shows the same values for the chemical shifts of the signals as in the spectrum of the compound $[\text{ZnL}_2]_n$ [9], which has been structurally characterized by X-ray diffraction methods and in which L is S–N' coordinated to the Zn(II) ion.

The most noticeable features of the ^1H NMR spectrum of this compound are the absence of the NH signal, in accordance with the anionic character of the ligand, and the display of a sharp new signal, at 3.87 ppm , corresponding to the hydroxy group linked to the metal ion Zn(II).

In the ^{13}C NMR spectrum of $\{[\text{H}_2\text{L}]\text{CdCl}_3\}_n$ the $\text{C}(2)$ signal is significantly shifted to higher field values (7.40 ppm higher) which means that the S–H–N hydrogen bond interaction existing in the free ligand disappears. The $\text{C}(5)$ and $\text{C}(4)+\text{C}(6)$ signals are shifted to lower field values than in the free ligand thus indicating the deshielding caused by the interaction between a proton and the N_{cyclic} atom.

In the ^1H NMR spectrum of this compound the NH signal corresponds to two protons, which is in accordance with the protonated character of the ligand. The shielding of this signal compared to that of the free ligand points to the existence of free H_2L species in solution.

3.3. Crystal structure of $\{[\text{H}_2\text{L}][\text{CdCl}_3]\}_n$

The asymmetric unit consists of a protonated ligand and a trichlorocadmiate(II) anion. The Cd(II) centres are hexacoordinated by chloride ions giving a distorted octahedral arrangement. The octahedra are linked by two opposite shared faces giving rise to infinite chains $[\text{CdCl}_3]_n$ parallel to the b axis. A perspective view of the asymmetric unit together with the atomic labelling scheme is given in Fig. 2. A tridimensional view of the packing is shown in Fig. 3. Selected bond distances and angles are listed in Table 4.

Within each $[\text{CdCl}_6]$ entity the Cd(II) ion is hexacoordinated. Four long bonds of $\sim 2.7\text{ \AA}$ are formed with $\text{Cl}(1)$, $\text{Cl}(3)$, $\text{Cl}(1)^{\text{I}}$ and $\text{Cl}(3)^{\text{I}}$ ($\text{I} = x - \frac{1}{2}, y, -z - \frac{1}{2}$) while the two remaining bonds, shorter than the former, are formed with the $\text{Cl}(2)$ and $\text{Cl}(2)^{\text{I}}$ ions, giving a $\text{Cd} \cdots \text{Cd}^{\text{I}}$ intrachain distance of $3.362(1)\text{ \AA}$. It should

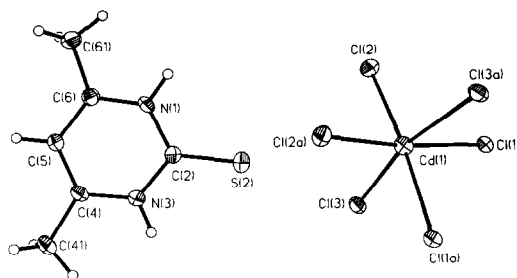
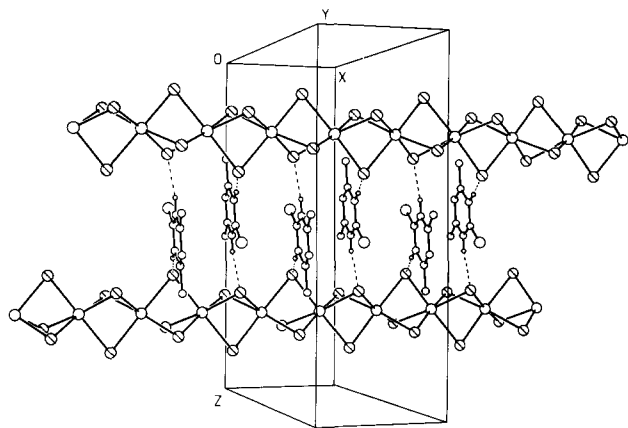


Fig. 2. Labelling scheme of the asymmetric unit of the structure.

Fig. 3. Tridimensional view of the packing in $\{[H_2L]CdCl_3\}_n$.

be noted that this columnar arrangement is found frequently in ABX_3 compounds [16–19], which have been extensively studied because numerous crystal structures containing methylammonium cations exhibit phase transitions related to the dynamics of the organic cations and inorganic anions [17]. In these monodimensional compounds the distortions of the $[CdCl_6]$ octahedra are less important than those exhibited by our compound. This fact is likely related to the formation of hydrogen bonds between the chloride ions and the protonated ligand, which is not possible for the majority of the organic ammonium cations mentioned above [16–19]. As can be observed in Fig. 2, the two hydrogen bonds are formed with the Cl(1) and Cl(3) ions, $N(1)-H \cdots Cl(1)^{II}$ ($II = -x, y + \frac{1}{2}, \frac{1}{2} - z$) and $N(3)-H \cdots Cl(3)^{III}$ ($III = x + \frac{1}{2}, \frac{1}{2} - y, 1 - z$) with bond distances and angles of 3.190 Å and 172° and 3.299 Å and 173.0°, respectively. Thus it is not surprising that the most important distortions from an idealized octahedral geometry are those involving the Cl(1) and Cl(3) ions [20].

On the other hand, the protonation of 4,6-dimethyl-2-thiopyrimidine can lead to the $N(3)=C-S(2)H \rightleftharpoons HN(3)-C=S(2)$ tautomeric equilibrium. Comparison of the bond lengths in the title and related compounds

[8,9,21] as well as the spectroscopic study, have made us assign the protonation position to a nitrogen atom of the pyrimidine ring instead of the exocyclic sulfur atom. Further, this assignation is supported by the existence of the aforementioned hydrogen bonds.

Finally, it should be noted that the pyrimidine rings bridge the $[CdCl_3]_n$ chains by hydrogen bonds. This results in a stacking of the pyrimidine bases parallel to the cadmium chains in which each base is related to the neighbouring one by an inversion centre ($-x, 1-y, 1-z$). Within this stacking the rings have a separation of 3.360 Å, therefore interaction between the π -clouds cannot be disregarded.

3.4. Thermal study

The TG curve of $CdL(OH)$ shows a first weight loss, with two well differentiated steps, which finishes at 160 °C and is accompanied by two well differentiated endothermic effects in the DSC ($\Delta H = 49.1 \text{ kJ mol}^{-1}$). The first weight loss corresponds to a negligible amount of non-stoichiometric water while the second, with a 3.4% weight loss, is in agreement with that calculated for the dehydration of anhydrous $CdL(OH)$ (3.35%), according to the following process: $2CdLOH \rightarrow CdL_2 + CdO + H_2O$. The resulting CdL_2 shows a thermal behaviour similar to that of the $[ZnL_2]_n$, which confirms the above hypothesis. Then, CdL_2 decomposes in a long step in the 300–700 °C temperature range giving a final residue of CdO (43.0%, found; 44.12%, calc.).

The compound $\{[H_2L]CdCl_3\}_n$ starts its pyrolytic decomposition at 180 °C through a first weight loss which takes place in two clearly differentiated steps, as can be seen in the DTG, which are accompanied in the DSC curve by two partially overlapped endothermic effects. Once the first step has taken place, the TG and DSC plots of $\{[H_2L]CdCl_3\}_n$ are very similar to those of $Cd(HL)_2Cl_2$ [22]. Moreover, this step is accompanied by the release of HCl and the IR spectrum of the resulting sample, in the 4000–600 cm^{-1} range, is that corresponding to $Cd(HL)_2Cl_2$. Thus the onset

Table 4
Selected bond distances (Å) and angles (°) for $\{[H_2L]CdCl_3\}_n$

Cd(1)–Cl(1)	2.676(1)	Cd(1)–Cl(3) ^I	2.694(1)
Cd(1)–Cl(2)	2.583(1)	Cd(1)–Cd(1) ^I	3.362(1)
Cd(1)–Cl(3)	2.688(1)	N(1)–C(2)	1.373(5)
Cd(1)–Cl(1) ^I	2.666(1)	C(2)–N(3)	1.376(5)
Cd(1)–Cl(2) ^I	2.595(1)	C(2)–S(2)	1.648(4)
Cl(1)–Cd(1)–Cl(2)	83.0(1)	Cl(1)–Cd(1)–Cl(2) ^I	173.5(1)
Cl(1)–Cd(1)–Cl(3)	82.8(1)	Cl(2)–Cd(1)–Cl(2) ^I	94.5(1)
Cl(2)–Cd(1)–Cl(3)	86.3(1)	Cl(3)–Cd(1)–Cl(2) ^I	103.1(1)
Cl(1)–Cd(1)–Cl(1) ^I	99.9(1)	Cl(1)–Cd(1)–Cl(3) ^I	88.6(1)
Cl(2)–Cd(1)–Cl(1) ^I	174.9(1)	Cl(2)–Cd(1)–Cl(3) ^I	101.4(1)
Cl(3)–Cd(1)–Cl(1) ^I	89.9(1)	Cl(3)–Cd(1)–Cl(3) ^I	167.7(1)

$$I = x - \frac{1}{2}, y, -z - \frac{1}{2}.$$

of the thermal decomposition of this compound corresponds to the following process: $[\text{H}_2\text{L}]\text{CdCl}_3 \rightarrow \text{HCl} \uparrow + 1/2\text{CdCl}_2 + 1/2\text{Cd}(\text{HL})_2\text{Cl}_2$. The second step in the above cited weight loss, finishing at 380 °C, consists of the sublimation of one of the two HL coordinated molecules in $\text{Cd}(\text{HL})_2\text{Cl}_2$ as was proved by IR spectroscopy of the sublimate [22]. Moreover, the IR spectrum of the sample heated up to 380 °C shows the disappearance of the $\nu(\text{Cd}-\text{Cl})$ band at 206 cm^{-1} , characteristic of the compound $\text{Cd}(\text{HL})_2\text{Cl}_2$, and the arising of a new $\nu(\text{Cd}-\text{Cl})$ band, at 249 cm^{-1} , due to the CdCl_2 formed. All these data demonstrate that the above second step is due to the following process: $\text{Cd}(\text{HL})_2\text{Cl}_2 \rightarrow \text{HCl} \uparrow + 1/2\text{CdCl}_2 + \text{HL}(\text{sublim.}) + 1/2\text{CdL}_2$. At the end of this process, the total accumulated weight loss (33.2%) is in good agreement with that calculated for the loss of 1.5 mol of HCl and 0.5 mol of HL per mole of complex (34.66%). It should be stressed at this point that thermal treatment of the $\{[\text{H}_2\text{L}]\text{CdCl}_3\}_n$ complex leads to $\text{Cd}(\text{HL})_2\text{Cl}_2$ and CdL_2 as intermediates, neither of which were detected in the solution study.

Finally, the pyrolysis of the remaining sample ($\text{CdCl}_2 + \text{CdL}_2$) in the 380–700 °C temperature range, consists of the total combustion of the organic part of CdL_2 with formation of CdO and partial sublimation of CdCl_2 .

4. Supplementary material

Atoms coordinates, anisotropic thermal parameters, full listing of bond lengths and angles, and observed and calculated structure factors are available from the authors on request.

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