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Note

Synthesis, spectroscopic study and crystal structure of bis(4,6-dimethyl-2-thiopyrimidinium) tetrachlorozincatum(II) monohydrate and its solid state transformations

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Abstract

The solid complex $[H_2L]_2[ZnCl_4]\cdot H_2O$ (HL = 4,6-dimethyl-2-thiopyrimidine) has been obtained and characterized by IR, ^1H and ^{13}C NMR spectroscopies and thermal techniques. The molecular structure of this complex has been established by single crystal X-ray diffraction. Crystals of the compound are orthorhombic, of space group $P2_12_12_1$ with cell constants $a = 7.153(2)$, $b = 14.624(3)$, $c = 20.499(4)$ Å, $Z = 6$ and $D_c = 1.572$ g cm^{-3}. The structure was solved and refined to $R = 0.049$ ($R_w = 0.029$). The asymmetric complex unit consists of two 4,6-dimethyl-2-thiopyrimidinium cations, a $[ZnCl_4]^{2-}$ anion and a water molecule. The Zn(II) centres are tetracoordinated by chloride ions giving a tetrahedral arrangement. This asymmetric unit is stacked along the *b* axis giving rise to a packing of pyrimidine rings and $[ZnCl_4]^{2-}$ anions which are linked by hydrogen bonds involving chlorine atoms, NH groups and water molecules. The thermal treatment of $[H_2L]_2[ZnCl_4]\cdot H_2O$ leads to two different solid complexes $[Zn(HL)_2Cl_2]$ and $[ZnL_2]$ which have been previously obtained and characterized by us.

Keywords: Crystal structures; Zinc complexes; Thiopyrimidine ligand complexes

1. Introduction

Because of the important roles that thiopyrimidine derivatives [1–5] and the Zn(II) ion have in living systems [6,7], we have carried out a detailed study of the interaction between the thiopyrimidinic derivative 4,6-dimethyl-2-thiopyrimidine (HL) and the Zn(II) ion. Thus we have recently reported the study of the acid–base properties of the HL ligand and its complexation with the Zn(II) ion in aqueous medium. From this study, and by selecting suitable pH conditions, we synthesized and characterized by spectroscopic and X-ray diffraction techniques the $[Zn(HL)_2Cl_2]$ and $[ZnL_2]_n$ complexes [8,9], Fig. 1, in which the ligand acts in its molecular and anionic form, respectively.

The present paper is devoted to completing this work by reporting the synthesis, spectroscopic study and crystal structure of the $[H_2L]_2[ZnCl_4]\cdot H_2O$ complex, which was obtained in acidic medium with the pyrimidine derivative acting in its protonated form. Furthermore, this compound can be transformed in the solid state into the above-mentioned complexes [8,9] by thermal treatment. This fact gives rise to an unusual parallelism between the solid species isolated either in the solid state or in solution. We wish to point out that these processes by which mononuclear complexes are converted in the solid state into a polynuclear complex are not new but rather scantly reported [10,11].

2. Experimental

2.1. Preparation of $[H_2L]_2[ZnCl_4]\cdot H_2O$

To a solution of HL (1 mmol) (Aldrich 99%) in the minimum amount of water, an HCl 0.1 M solution was added until the pH was equal to 1.5. To the resulting mixture, $ZnCl_2$ (1 mmol) was added. This solution was 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 P_4O_{10}. *Anal.* Found: C, 28.05; H, 3.88; N, 10.92. Calc. for $C_{12}H_{20}N_4OS_2Cl_4Zn$: C, 28.37; H, 3.94; N, 11.03%

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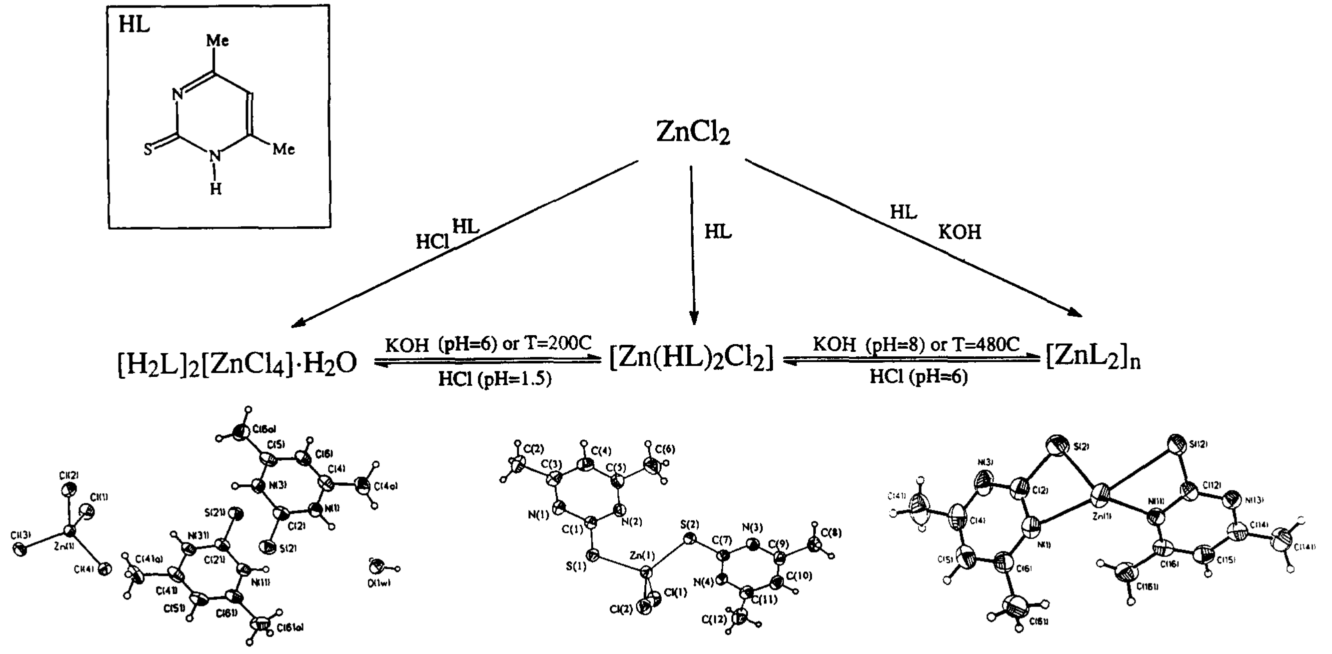

Fig. 1. Parallelism of the reactions in the solid state and in solution.

2.2. Apparatus

Microanalyses of C, H and N, and IR and NMR spectra were carried out as already described [8]. 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}, using samples weighing 11.910 (TG) and 2.393 (DSC) mg.

2.3. 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 Kα ($\lambda = 0.71069$ Å) radiation. A needle-shaped pale yellow crystal was used with dimensions 0.30 × 0.30 × 0.27 mm. The complex crystallizes in the orthorhombic system, space group $P2_12_12_1$ with cell constants $a = 7.153(2)$, $b = 14.624(3)$, $c = 20.499(4)$ Å, $V = 2298.7(5)$ Å^3, $Z = 6$ and $D_c = 1.572$ g cm^{-3}.

The unit cell parameters were calculated by least-squares refinement of 25 well centred reflections in the range $15 < 2\theta < 45°$. The data were collected by $\omega/2\theta$ scan mode in the range $3 < 2\theta < 63°$. The intensities of three check reflections measured after 120 min showed no significant variation. A total of 3213 reflections (with 277 parameters) was considered as observed with $I < 4\sigma(I_o)$. 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 [12]. 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 $\Sigma w(\Delta F)^2(1/w = \sigma^2(F_o))$, resulting in a final $R = \Sigma|F_c - F_o|/\Sigma|F_o|$ value of 0.049 and $R_w = [(\Sigma w|F - F_o|)^2/\Sigma w|F_o|^2]^{1/2}$ value of 0.029. Atomic fractional coordinates are listed in Table 1.

3. Results and discussion

3.1. Spectroscopic study

The IR spectrum of $[H_2L]_2[ZnCl_4]\cdot H_2O$ shows a new band at 3400 cm^{-1} assignable to the ν(OH) mode, due to the presence of a water molecule in the complex. Two sharp bands at 3079 and 2917 cm^{-1} correspond to ν(N–H) stretching vibration bands of the protonated HL. The ν(C=C) and ν(C=N) bands of the free ligand have been strongly modified, appearing as a broad band at 1602 cm^{-1}. This suggests that the protonation on HL takes place on the free N_{cyclic} atom rather than on the S atom.

On the other hand, the spectrum shows minor variations in the frequencies of the thioamide I and thioamide III bands (1431 and 1193 cm^{-1}, respectively) relative to HL (1437 and 1221 + 1187 cm^{-1}, respectively). In the low frequency range a strong wide band at 275 cm^{-1}, typical of a Zn(II) ion in a tetrahedral environment of chloride ions, has been detected, see below.

In the ^{1}H and ^{13}C NMR spectra of $[H_2L]_2[ZnCl_4]\cdot H_2O$ (Table 2) each expected signal appears as a doublet, except those assigned to the NH groups in the ^{1}H NMR spectrum and that assigned to C(2) in the ^{13}C NMR spectrum. This fact could be explained by the existence of two species in solution, which, at present, have not been identified. In the ^{13}C NMR spectrum the C(2) signal is significantly shifted to higher field values (7.68 ppm) than in the spectrum of HL. This indicates that the S–H–N hydrogen bond interactions in the free HL solutions are somehow quenched by the protonation at the N_{cyclic} atom. Additionally the C(5) and C(4) + C(6) signals are shifted to lower field values, which points out the deshielding of the ring caused by the protonation of the N_{cyclic} atom.

3.2. Crystal structure of $[H_2L]_2[ZnCl_4] \cdot H_2O$

The asymmetric unit consists of two protonated H_2L molecules, a tetrachlorozincate(II) anion and a water molecule. The Zn(II) centres are tetracoordinated by chloride ions giving a tetrahedral arrangement. This asymmetric unit is stacked along the *b* axis giving rise to a packing of pyrimidine rings and $[ZnCl_4]^{2-}$ anions, which are linked by hydrogen bonds involving chlorine atoms, NH groups and water molecules.

Table 1
Atomic coordinates (× 10^4) and U_{eq} (× 10^3) for $[H_2L]_2[ZnCl_4] \cdot H_2O$

Atom	*x*	*y*	*z*	U_{eq}
Zn(1)	921(1)	9718(1)	8817(1)	50(1)
Cl(1)	2442(2)	8416(1)	8593(1)	77(1)
Cl(2)	−1877(2)	9371(1)	9285(1)	71(1)
Cl(3)	2532(2)	10602(1)	9533(1)	68(1)
Cl(4)	321(2)	10501(1)	7886(1)	63(1)
N(1)	−11647(5)	9473(3)	5500(2)	48(2)
C(2)	−11302(7)	9959(3)	6058(3)	46(2)
N(3)	−10920(6)	9407(3)	6589(2)	45(1)
C(4)	−11654(8)	8557(4)	5451(3)	54(2)
C(5)	−10869(8)	8490(3)	6586(3)	52(2)
C(6)	−11265(8)	8055(3)	5997(3)	56(2)
S(2)	−11364(2)	11085(1)	6108(1)	55(1)
C(4a)	−12093(9)	8204(3)	4802(2)	73(2)
C(6a)	−10482(9)	8027(3)	7209(2)	71(3)
N(11)	−6470(5)	10486(3)	5873(2)	48(2)
C(21)	−5988(8)	9925(3)	6382(2)	48(2)
N(31)	−5470(5)	10385(3)	6937(2)	48(2)
C(41)	−5561(8)	11309(4)	6998(3)	61(2)
C(51)	−6115(9)	11815(3)	6473(3)	62(2)
C(61)	−6596(8)	11403(4)	5897(3)	58(2)
S(21)	−5981(2)	8796(1)	6332(1)	57(1)
C(41a)	−4859(9)	11679(4)	7630(3)	76(3)
C(61a)	−7104(9)	11896(3)	5299(3)	73(3)
O(1w)	807(6)	5673(3)	2063(2)	86(2)

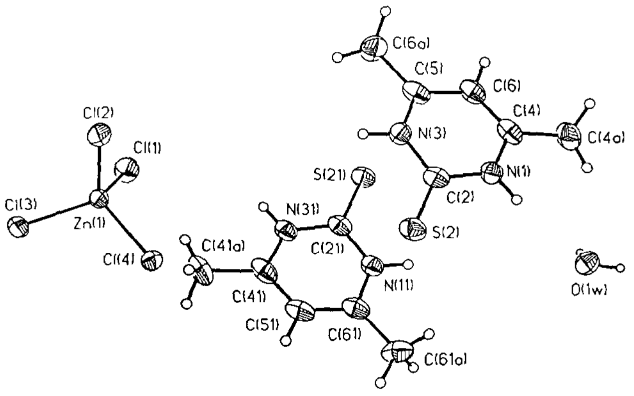

Fig. 2. Labelling scheme of the asymmetric unit of the structure.

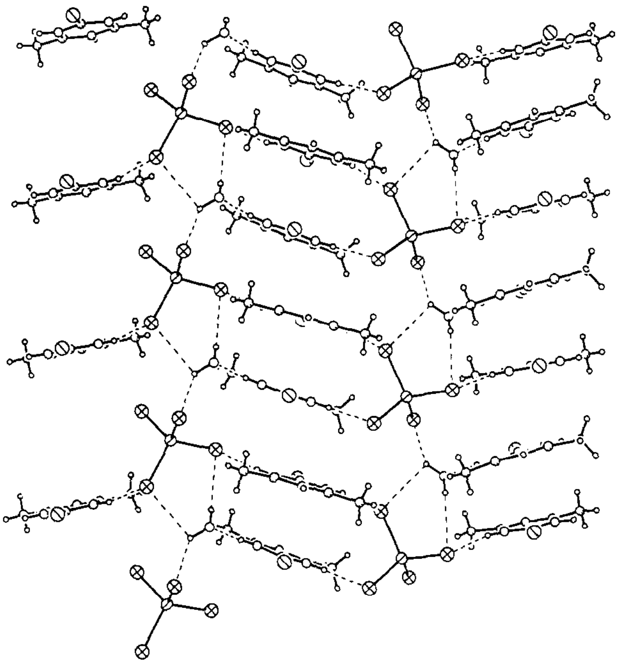

Fig. 3. Tridimensional view of the packing in $[H_2L]_2[ZnCl_4] \cdot H_2O$.

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 3.

The Zn(II) ion is tetracoordinated within each $[ZnCl_4]^{2-}$ anion. Three of the Zn–Cl bond distances are in the range between 2.266(1) and 2.277(2) Å while the fourth one, Zn–

Table 2
NMR data (δ in ppm)

Compound	^{1}H NMR			^{13}C NMR			
	CH_3	C(5)–H	NH	C(2)	C(5)	C(4) and C(6)	CH_3
HL	2.23(s)	6.60(s)	13.46(s)	180.90(s)	109.60(s)	157.00(vb)	18.40(b) 4.00(b)
$[H_2L]_2[ZnCl_4] \cdot H_2O$	2.30(s) 2.50(s)	7.04(s) 7.11(s)	8.30(vb)	173.22(s)	111.49(s) 117.92(s)	167.11(s) 168.00(s)	19.95(s) 23.38(s)

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

Table 3
Selected bond distances (Å) and angles (°) for $[H_2L]_2[ZnCl_4]\cdot H_2O$

Zn(1)–Cl(1)	2.241 (2)	C(2)–N(3)	1.384 (6)
Zn(1)–Cl(2)	2.277 (2)	C(2)–S(2)	1.650 (5)
Zn(1)–Cl(3)	2.270 (2)	N(11)–C(21)	1.371 (6)
Zn(1)–Cl(4)	2.266 (1)	C(21)–N(31)	1.373 (6)
N(1)–C(2)	1.368 (6)	C(21)–S(21)	1.654 (5)
Cl(1)–Zn(1)–Cl(2)	108.9 (1)	Cl(1)–Zn(1)–Cl(4)	110.4 (1)
Cl(1)–Zn(1)–Cl(3)	111.7 (1)	Cl(2)–Zn(1)–Cl(4)	107.5 (1)
Cl(2)–Zn(1)–Cl(3)	107.5 (1)	Cl(3)–Zn(1)–Cl(4)	110.7 (1)
O(1w)–H···Cl(1)	3.062	123.7	$-\frac{1}{2}+x, 1\frac{1}{2}-y, 1\frac{1}{2}-z$
O(1w)···H–N(31)	2.726	175.8	$\frac{1}{2}+x, 1\frac{1}{2}-y, 1\frac{1}{2}-z$
N(1)–H···Cl(2)	3.189	168.8	$-1\frac{1}{2}-x, 2-y, -\frac{1}{2}+z$
N(3)–H···Cl(4)	3.227	171.7	$x-1, y, z$
N(11)–H···Cl(3)	3.264	175.7	$-\frac{1}{2}-x, 2-y, -\frac{1}{2}+z$
O(1w)–H···Cl(4) [a]	3.659	155.5	$\frac{1}{2}+x, 1\frac{1}{2}-y, 1\frac{1}{2}-z$

[a] Very weak interaction.

Cl(1), is slightly shorter, 2.241(2) Å. This tetracoordinated mode is compatible with two idealized geometries: square-planar and tetrahedral. The procedure proposed by Muetterties and Guggenberg [13] locates the coordination polyhedron at 99% towards T_d of the $D_{4h} \rightarrow T_d$ deformation pathway. This quantitative result is not surprising because the Cl–Zn–Cl angles are in the range between 107.5(1) and 111.7(1)°, in the neighbourhood of the value of an ideal T_d geometry, 109.47°.

Although quantitatively these deviations are somewhat less than the majority of those described in the literature [14–17], qualitatively they are similar to those observed for this sort of anion. Thus, the α angle is bigger than the expected one for an ideal tetrahedral geometry, while the β angle is slightly smaller than the theoretical one. The Zn–Cl bond distances are in accordance with those described in the bibliography for other examples of $[ZnCl_4]^{2-}$ ions [14–17].

The two 4,6-dimethyl-2-thiopyrimidine rings are protonated. This protonation can lead to the N(3)=C–S(2)H ⇄ HN(3)–C=S(2) tautomeric equilibrium. Comparison of the bond lengths in the title and related compounds [8,9] 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 hydrogen bonds that implicate the afore-mentioned nitrogen atom. Planarity characterizes both pyrimidine rings, the maximum deviations from the mean-squares planes being 0.007 Å for the C(5) atom and 0.024 Å for the C(21) atom.

Finally, it should be noted that the tridimensional structure of the complex consists of stacking of pyrimidine rings and $[ZnCl_4]^{2-}$ anions, parallel to the *b* axis. The mean distance between two adjacent pyrimidine planes in the stacking is 3.418 Å. $[ZnCl_4]^{2-}$ ions are linked by hydrogen bonds involving water molecules to give chains. Furthermore $[ZnCl_4]^{2-}$ and water chains and pyrimidine rings are linked by hydrogen bonds involving chlorine atoms, NH groups of the pyrimidine rings and the water molecules (see Fig. 3). Significant hydrogen bond lengths and angles are collected in Table 3.

3.3. *Solid state transformations*

As was cited above the title compound undergoes solid state transformations to give rise to the related complexes $[Zn(HL)_2Cl_2]$ and $[ZnL_2]_n$ [8,9]. Interestingly the species isolated in the solid state and in solution are identical which represents an unusual parallelism between the reactions carried out in both phases, as reflected in Fig. 1. This behaviour in the solid state by which mononuclear complexes are transformed into a polynuclear complex by thermal treatment is only rarely reported for two main reasons [10,11]. First, because a linear temperature range in which the compound will be stable is needed in order to stop the thermal process. Second, because an appropriate disposition of the monomeric units of the starting complex in the crystal packing is needed in order to allow the molecular rearrangements in the solid state.

The TG plot of $[H_2L]_2[ZnCl_4]\cdot H_2O$ shows two weight losses in the 40–200 °C temperature range which are accompanied in the DSC diagram by two partially overlapped endothermic effects ($\Delta H = 267.5$ kJ mol^{-1}). The IR spectrum of the sample remaining at 200 °C is superimposable to that corresponding to the compound $[Zn(HL)_2Cl_2]$ [8]. In addition, the vapour given off by the compound during heating was shown to be acidic. All these data point out that the onset of the pyrolytic decomposition of the compound corresponds to the following process:

$$[H_2L]_2[ZnCl_4]\cdot H_2O \longrightarrow 2HCl\uparrow + Zn(HL)_2Cl_2 + H_2O\uparrow$$

The thermal decomposition of the compound $[Zn(HL)_2Cl_2]$ consists of a step characterized by two weight losses in the 200–480 °C temperature range which are accompanied in the DSC by a wide asymmetric endothermic effect ($\Delta H = 127$ kJ mol^{-1}) corresponding to the sublimation of HL and the solid state transformation into $ZnCl_2$ and $[ZnL_2]_n$, which was proved by IR spectroscopy. Thus, the IR spectra of the sublimate and the sample in the 400–600 cm^{-1} region are identical to those corresponding to HL and $[ZnL_2]_n$, respectively. Moreover, the IR spectrum of the sample at 480 °C in the 600–200 cm^{-1} range shows the disappearance of the strong ν(Zn–Cl) band at 269 cm^{-1}, characteristic of $[Zn(HL)_2Cl_2]$, and the appearance of a strong new band, at 298 cm^{-1}, due to the formation of $ZnCl_2$. All these data indicate that the decomposition of $[Zn(HL)_2Cl_2]$ takes place in accordance with the following process:

$$Zn(HL)_2Cl_2 \longrightarrow \tfrac{1}{2}ZnCl_2 + \tfrac{1}{2}ZnL_2 + HCl\uparrow + HL(\text{sublimate})$$

At the end of this process (480 °C), the total accumulated weight loss, 50.97%, is in good agreement with that calculated for the loss of 1 mol of H_2O, 3 mol of HCl and 1 mol of HL per mole of compound (52.72%). Finally, pyrolysis of $[ZnL_2]_n$ and sublimation of $ZnCl_2$ formed take place in the 480–740 °C range yielding 8.8% of ZnO as final residue, which is in good agreement with that calculated (8.01%).

4. Supplementary material

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

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