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Inorganica Chimica Acta 247 (1996) 203-207

Inorganica Chimica Acta

4-Amino-6-methoxy-2-methylthiopyrimidine and Hg(II) system: solution and solid state studies on metalated and N-coordinated species. Crystal structure of $[Hg_2(HL)_2(\mu\text{-}Cl)_2Cl_2]$

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Received 25 May 1995; revised 3 October 1995

Abstract

The acid–base behaviour of the pyrimidine analogue 4-amino-6-methoxy-2-methylthiopyrimidine (HL) and the reactivity with Hg(II) ion have been studied by potentiometric methods at 25 °C and 0.1 M KCl ionic strength. By fixing the appropriate pH conditions, solid species with stoichiometries $HgLCl\cdot H_2O$ and $Hg_2(HL)_2Cl_4$ have been isolated. The spectroscopic study of the solids shows that $HgLCl\cdot H_2O$ is a C(5)-organomercurial species, whereas the structure of $Hg_2(HL)_2Cl_4$ has been determined by single crystal X-ray diffraction methods. $Hg_2(HL)_2Cl_4$ is a binuclear complex with two Hg(II) ions tetrahedrally coordinated by a terminal chloride ion, a HL molecule and two bridging chloride ions. The Hg(II) ion is coordinated to HL via the N(3) endocyclic atom.

Keywords: Crystal structures; Mercury complexes; Thiopyrimidine complexes; Dinuclear complexes

1. Introduction

Mercuric ion is highly toxic to many organisms. This toxicity derives from the high affinity of this ion for thiols in a variety of proteins and enzymes, given that the stability of the adducts formed inactivate these essential thiols in many biological processes [1–3]. Furthermore, many species resulting from metabolic processes react with mercuric ion forming adducts which are also toxic. Detoxification mechanisms of the last species in bacterial systems, imply the use of enzymes that catalyze hydrolytic reactions of metal ion–molecules bonds [1]. In order to a good understanding of the nature of these hydrolytic processes, the study of the reactivity of Hg(II) with biological analogue molecules, including the nature of the bonds formed, the stability of the adducts and their structure, seems very interesting. Concerning that in the present paper, we report on the reactions of the pyrimidine analogue 4-amino-6-methoxy-2-methylthio pyrimidine (HL) with Hg(II) metal ion. The study of the reactivity in solution lets us identify two species, with $(HgL)^+$ and $[Hg_2(HL)_2]^{4+}$ stoichiometries, depending on the pH conditions. Whereas at physiological pH values it exists as the HgL^+ species, $[Hg_2(HL)_2]^{4+}$ exits only at acidic pH values. By fixing the appropriate pH conditions, solid species with stoichiometries $HgLCl\cdot H_2O$ and $Hg_2(HL)_2Cl_4$ have been isolated.

2. Experimental

2.1. Reagents

Anhydrous ligand HL ($C_6H_9N_3OS$) was obtained as previously reported [4] and recrystallized in water. *Anal.* Found: C, 41.87; H, 5.33; N, 24.29. Calc.: C, 42.11; H, 5.26; N, 24.56%. Hg(II) chloride was purchased from Aldrich and used without further purification.

In the potentiometric measurements CO_2-free double distilled water was used as solvent. CO_2-free KOH solutions (Merck) were prepared by dilution and standardized with hydrogenphthalate and then used to standardize HCl solutions. $HgCl_2$ 5×10^{-3} N standardized solutions (Merck) were also used. All the potentiometric measurements were carried out in 0.1 M KCl as background electrolyte.

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SSDI 0020-1693(95)04969-8

2.2. Preparation of the complexes

2.2.1. $HgLCl\cdot H_2O$ (1)

To a stirred solution of HL (1 mmol) in 100 ml of hot water (60 °C), $HgCl_2$ (1 mmol) was added. From the resulting solution ($pH = 6.5$) a white microcrystalline precipitate appeared and the pH of the remaining solution decreased to 3.5. Different attemps to obtain crystals suitable for X-ray diffration were unsuccessfull. The precipitate was filtered off and washed with water, ethanol and diethyl ether, and dried over P_4O_{10}. *Anal.* Found: C, 17.03; H, 2.36; N, 9.80. Calc. for $C_6H_{10}N_3O_2SClHg$: C, 17.12; H, 2.25; N, 9.90%.

2.2.2. $Hg_2(HL)_2(\mu\text{-}Cl)_2Cl_2$ (2)

The solution ($pH = 3.5$) resulting from the synthesis of **1** was left to concentrate at room temperature. When the volume was reduced to ~50 ml, pale yellow crystals precipitated. These were filtered off, washed with ethanol and diethyl ether, and dried over P_4O_{10}. *Anal.* Found: C, 16.32; H, 2.06; N, 9.44. Calc. for $C_{12}H_{18}N_6O_2S_2Cl_4Hg_2$: C, 16.27; H, 2.03; N, 9.49%.

2.3. Apparatus

Microanalyses of C, H and N, IR and NMR spectra were performed as previously reported [5]. Electronic spectra of aqueous $HL/HgCl_2$ mixtures in 1/1 molar ratio were obtained in a Perkin-Elmer Lambda19 spectrophotometer, in the 200–400 nm range.

2.4. Procedures

Calibration of the electrodes (Gran method [6]), ionic product of the medium ($\log K_w$) [7] and processing of data [8] were carried out as already reported [5].

The protonation equilibria of the HL ligand were studied at 25 °C, in 0.1 mol l^{-1} KCl ionic strength and ligand concentration of 10^{-3} mol l^{-1}. The complex formation equilibria were obtained in aqueous solutions at [HL]/[Hg(II)] ratios varying between 4:1 to 1:1 ($[HL] = 10^{-3}$ mol l^{-1}), at 25 °C, in 0.1 mol l^{-1} KCl ionic strength.

The electronic spectra of HL/Hg(II) mixtures in aqueous media, were obtained from samples containing HL and Hg(II) in 1/1 molar ratios ($[HL] = 10^{-4}$ mol l^{-1}), in 0.1 mol l^{-1} KCl ionic strength, using as reference an aqueous HL solution (10^{-4} mol l^{-1}), in 0.1 M KCl ionic strength. In all cases the pH of the solutions were adjusted by adding 0.1 mol l^{-1} HCl.

2.5. X-ray data collection and structure determination

Single crystal data collection was performed at 293 K with a Siemens R3 m/V diffractometer using graphite monochromatized Mo Kα ($\lambda = 0.71069$ Å) radiation. A prismatic pale yellow crystal was used with dimensions 0.20 × 0.15 × 0.15 mm. The complex crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14) with $a = 10.744(2)$, $b = 15.135(3)$, $c = 7.297(2)$ Å and $\beta = 108.25(3)°$, $V = 1126.8(4)$ Å^3, $Z = 4$, $D_c = 2.610$ g cm^{-3}, $F(000) = 816$, μ(Mo Kα) = 14.290 mm^{-1}.

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 $2 < 2\theta < 60°$. Intensities of four check reflections measured after every 120 min showed only statistical variation. A total of 3606 reflections was collected ($R_{int} = 0.042$) from which 1571 (with 127 parameters) were considered as observed with $I > 3\sigma(I_o)$. The data were corrected for Lorentz and polarization effects. Absorption correction was applied via an empirical Ψ scan. Minimum and maximum transmission factors were 0.052 and 0.118, respectively.

The structure of $[Hg_2(HL)_2(\mu\text{-}Cl)_2(Cl)_2]$ was solved by direct methods and subsequent Fourier syntheses with the SHELXTL PLUS program [9]. All non-hydrogen atoms were refined anisotropically in the final refinements. The position of hydrogen atoms were calculated with isotropic temperature factors ($U = 0.08$) and were not refined. The maximum residual peak in the ΔF map was 2.78 e Å^{-3} located in the neighborhood of the mercury atom. 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 $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ value of 0.057 and $R_w = [(\Sigma w|F_o - F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ value of 0.077, with $S = 2.0$.

3. Results and discussion

3.1. Protonation equilibria

The protonation equilibria of HL have been studied potentiometrically by titration of acidified aqueous solutions (HCl) of HL at 25 °C and 0.1 mol l^{-1} ionic strength, with KOH 0.1 mol l^{-1}. Protonation constants were obtained from 63 experimental points in the 2.8–10.5 pH range. The protonation processes are those corresponding to Eqs. (1) and (2) given below. The $\log\beta$ values for processes (1) and (2) are given in Table 1 ($\sigma_{fit} = 0.0082$). The species formed are labelled by the (pqr) parameters which define the number of metal ions, deprotonated ligands and protons, forming the species.

Table 1

Equilibrium data for protonation of L and complex formation of Hg(II) with protonated and unprotonated species (25 °C in 0.1 M KCl) [a]

Species (pqr)	Process	$\log\beta$
(011)	$H^+ + L^- \rightleftarrows HL$	11.24(5)
(012)	$2H^+ + L^- \rightleftarrows H_2L^+$	14.73(1)
(110)	$Hg^{2+} + L^- \rightleftarrows HgL^+$	13.76(9)
(222)	$2Hg^{2+} + 2L^- + 2H^+ \rightleftarrows [Hg_2(HL)_2]^{4+}$	38.4 (3)

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

$$H^+ + L^- \rightleftarrows HL \quad (\beta_{011}) \qquad (1)$$

$$HL + L^- \rightleftarrows H_2L^+ \quad (\beta_{012}) \qquad (2)$$

The first protonation constant ($\log \beta_{011} = 11.24$) corresponds to the protonation of the deprotonated exocyclic amino group. This has been confirmed by the ^{1}H NMR spectrum of NaL, which shows the loss of one proton belonging to the NH_2 group. The signals of the remaining hydrogen atoms appear unaffected except that of the deprotonated amino group (4.10 ppm) which is strongly shielded with respect to the NH_2 group (6.65 ppm) in HL spectrum.

The second process has a value for log K of 3.49 ($\log \beta_{012}$–$\log \beta_{011}$) and likely corresponds with the protonation of a nitrogen atom of the pyrimidine ring. This value is higher than those obtained for related pyrimidine derivatives without electron donating exocyclic substituents, such as 4,6-dimethyl-2-thiopyrimidine ($\log \beta_{012}$–$\log \beta_{011} = 2.48$) [5], which highlight the influence of these substituents on the basicity of the N_{cyclic} atoms.

The species distribution diagram shows that deprotonation of neutral HL starts at pH 9.5. HL is the predominant species (100%) from pH 5.5 to 9.5, whereas H_2L^+ species predominates in the 2.0–3.7 pH range.

3.2. *Hg(II) complexation equilibria*

Solutions of Hg(II) chloride and HL with $C_{HL}/C_{Hg(II)}$ varying from 1/1 to 4/1 ($C_{HL} = 10^{-3}$ mol l^{-1}) were acidified with HCl and then titrated with 0.1 mol l^{-1} KOH at 0.1 mol l^{-1} KCl ionic strength. Equilibrium constants, obtained from 53 experimental points in the 2.8–9.0 pH range, are summarized in Table 1. The distribution plots as a function of the pH for the Hg(II)/HL system appear in Fig. 1.

The best fit of the experimental data points out the existence of HgL^+ and $[Hg_2(HL)_2]^{4+}$ species ($\sigma_{fit} = 0.0063$) formed in the overall processes (3) and (4), respectively;

$$Hg^{2+} + L^- \rightleftarrows HgL^+ \quad (\beta_{110}) \qquad (3)$$

$$2Hg^{2+} + 2L^- + 2H^+ \rightleftarrows [Hg_2(HL)_2]^{4+} \quad (\beta_{222}) \qquad (4)$$

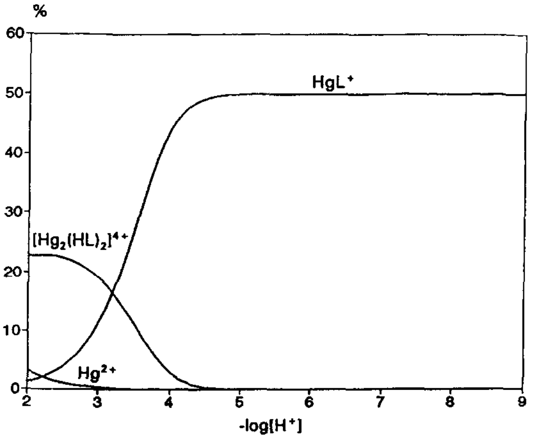

Fig. 1. Distribution diagram for the Hg(II)/HL system as a function of pH.

Fig. 1 shows that at pH values below 3.2 the major species existing is the binuclear complex with HL, whereas HgL^+ species with deprotonated HL is the only species existing at pH > 4. Taking into account that deprotonation of the exocyclic amino group (1) occurs at pH values over 9, it seems that (1) does not occur in the formation of the HgL^+ adduct. Thus, HgL^+ is rather an organomercurial species formed via a π-aromatic electrophilic substitution of Hg^{2+} on the endocyclic C(5) atom (which does not implie the previous deprotonation of this group) which is in accordance with the great affinity of Hg^{2+} for electron-rich C atoms; the high π-electron density of C(5) position being favoured by the existence in HL of suitable electron donating exosubstituents (OCH_3–C(6); SCH_3–C(2) and NH_2–C(4)) existing in *ortho* and *para* positions. The stability constant of the HgL^+ is comparable to those reported for Hg(II) adducts, of the same stoichiometry, with S-containing biological ligands [2].

The electronic difference spectrum of an aqueous HL/Hg(II) mixture, in 1/1 molar ratio at pH = 2.5, shows an asymmetric band at 290 nm, assignable to a metal–to–ligand charge transfer, which, in accordance to literature data [10], is a hallmark of tetrahedral coordination of Hg(II) in the $[Hg_2(HL)_2]^{4+}$ complex. Beside this, the spectrum of the same mixture at pH 5.5 does not present any absorption bands, suggesting a linear environment of Hg(II) in HgL^+ species, as can be expected.

The high formation constants values of the species detected in solution interestingly indicate that, besides mercury(II)–carbon and mercury(II)–sulfur, mercury(II)–nitrogen interactions in pyrimidine derivatives could generate competing species, in appropriate conditions, in biological systems. In the case of the ligand studied here, the steric hindrance of the CH_3 group is linked to the sulfur atom which probably favors the coordination to N(3).

3.3. *Spectroscopic study*

The IR spectrum of **1** shows the same ν(N–H) bands as HL, at 3439 cm^{-1} ($\nu(N\text{–}H)_{asym}$) and 3341 cm^{-1} ($\nu(N\text{–}H)_{sym}$), which are partially hidden by a wide ν(O–H) stretching vibration band due to a H_2O molecule; the existence of a water molecule in this complex was proved by TG methods. Furthermore, $\delta(NH_2)$ of the free ligand, shows a band at 1632 cm^{-1} (a band at 1638 cm^{-1} in the IR spectrum of **1**); this band could be assigned unambiguously due to the fact that it remains in the IR spectrum of **1** when this compound becomes dehydrated at 150 °C. On the contrary, the lack of an in-plane C–H bend in the spectrum of the complex (which appears in that of HL at 1210 cm^{-1} [11]) together with the shift and splitting of the strong ν(C=C) + ν(C=N) band from 1568 cm^{-1} in HL to 1520 + 1549 cm^{-1}, strongly suggests interaction of Hg(II) with a deprotonated C(5) endocyclic atom. A new strong band appears in the low frequency range, at 333 cm^{-1}, assigned to ν(Hg–Cl) in a HgLCl organometallic species [12].

^{1}H NMR and ^{13}C NMR spectral data of **1** also support the C(5)–Hg bonding. ^{1}H NMR signals of SCH_3 (32.39 ppm), OCH_3 (3.76 ppm) and NH_2 (6.65 ppm) appear at the same field values as in HL spectrum, a new signal at 3.23 ppm is due to the H_2O molecule; but the most highlighted is the lack of the sharp C(5)–H signal existing at 5.39 ppm in HL spectrum, due to deprotonation of the C(5) position.

On the other hand, ^{13}C NMR signals of SCH_3 (13.00 ppm), OCH_3 (52.97 ppm) and C(2) (169.28 ppm) groups of **1** are at the same field as in free ligand spectrum, whereas C(4) and C(6) (at 167.53 and 171.01 ppm in HL) are slightly shifted (2.5 and 1.5 ppm, respectively) to lower field values, due to the deshielding of the ring upon coordination to Hg(II). Nevertheless, the most significant feature is a 20.76 ppm shift to lower field values of C(5) signal (at 81.11 ppm in HL), which clearly indicates the existence of a Hg–C(5) bond. All these spectroscopic data strongly suggest a linear structure for **1** similar to those found in the literature for related compounds [13].

IR spectra of HL and **2** are very similar except in the fact that the single $\nu(C{=}C) + \nu(C{=}N)$ band of HL, at 1568 cm^{-1}, splits into two, at 1572 and 1614 cm^{-1}, indicating a direct Hg(II)-cycle interaction. In the low frequency range, the spectrum of the complex shows two new strong bands, at 278 and 182 cm^{-1}. The first one is assigned to a ν(Hg–Cl) of a terminal chloride ion, while the second corresponds to a ν(Hg–Cl) of bridging chloride ions [12], in accordance with the structural data for this complex, see below. ^{1}H and ^{13}C NMR spectra of **2** are equal to those of free HL in dmso-d_6 medium, due to the dissociation of **2** in dmso solutions.

3.4. Description of the structure of 2

The structure consists in dinuclear $[Hg_2(HL)_2(\mu\text{-}Cl)_2Cl_2]$ units in which the metal ions are bridged by chloride anions. The dinuclear unit is formed by two asymmetric units related by an inversion centre. Fractional atomic coordinates are listed in Table 2. A perspective view of the dinuclear unit together with the atomic labelling scheme is given in Fig. 2. Bond distances and angles are listed in Table 3.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq}

Atom	x	y	z	U_{eq}
Hg(1)	1686(1)	284(1)	1319(1)	54(1)
Cl(1)	−529(4)	140(3)	2203(7)	50(2)
Cl(2)	2849(4)	−926(3)	3216(8)	62(2)
N(1)	4072(12)	2639(9)	1218(20)	43(5)
C(2)	3614(14)	1855(10)	1269(21)	35(5)
S(2)	4628(4)	930(3)	1362(8)	53(2)
C(21)	6125(16)	1444(14)	1389(28)	59(7)
N(3)	2365(11)	1636(8)	1117(17)	34(4)
C(4)	1544(12)	2337(10)	984(20)	36(5)
O(4)	333(10)	2060(7)	782(17)	44(4)
C(41)	−663(16)	2741(13)	552(34)	67(8)
C(5)	1960(15)	3186(12)	847(23)	43(6)
C(6)	3252(15)	3316(10)	1038(20)	36(5)
N(6)	3744(15)	4116(10)	994(24)	60(6)

The Hg(II) ions are tetra-coordinated within each dinuclear unit, showing a Hg···Hg distance of 3.633 Å. Two of these bonds are formed by two asymmetric chloride bridges, while the remaining two bonds are formed by a terminal chloride ion and the N(3) atom of the pyrimidine ring. This tetra-coordination mode is compatible with two idealized geometries: square-planar and tetrahedral. The procedure proposed by Muetterties and Guggenberg [14] locates the coordination polyhedron at 11% towards D_{4h} of the $T_d \rightarrow D_{4h}$ deformation pathway. In this tetrahedral description, bond lengths and angles within the $ClHg(\mu\text{-}Cl)_2HgCl$ core are well in the range of those reported in the literature for related Hg(II) dimers [15–18]. However, the coordination mode of the pyrimidine derivative deserves further analysis. Two nitrogen atoms, N(1) and N(3), belonging to the pyrimidine ring are available for coordination, N(1) being the position with less steric crowding in a hypothetical coordination to the metal atom. Even though coordination through N(3) would present more steric hindrance because of the two bulky groups in *ortho* positions, this effect could be balanced by the existence of two long intramolecular interactions between

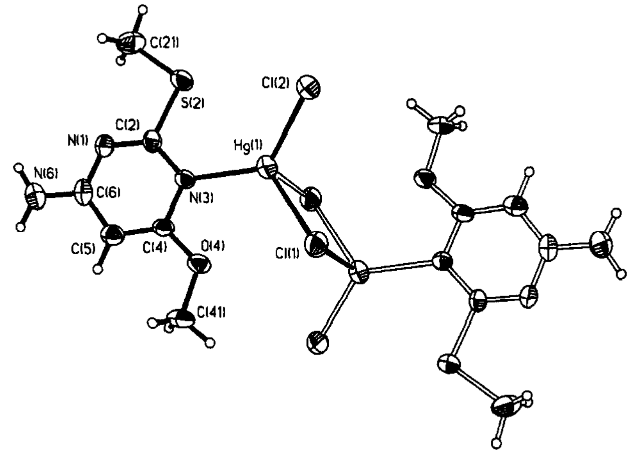

Fig. 2. A perspective view of the dinuclear unit, (40% thermal ellipsoids). Black sticks represent the asymmetric unit.

Table 3
Selected bond lengths (Å) and angles (°)

Hg–Cl(1)	2.662 (5)	Hg–N(3)	2.193 (12)
Hg–Cl(2)	2.397 (5)	Hg–Cl(1)$^{\mathrm{I}}$	2.562 (4)
Cl(1)–Hg(1)$^{\mathrm{I}}$	2.562 (4)	N(1)–C(2)	1.290 (21)
N(1)–C(6)	1.330 (21)	C(4)–O(4)	1.330 (17)
C(2)–S(2)	1.761 (16)	C(4)–C(5)	1.374 (24)
C(2)–N(3)	1.353 (19)	O(4)–C(41)	1.458 (22)
S(2)–C(21)	1.781 (19)	C(5)–C(6)	1.365 (23)
N(3)–C(4)	1.363 (19)	C(6)–N(6)	1.325 (22)
Cl(1)–Hg–Cl(2)	98.1(2)	Cl(2)–Hg–Cl(1)$^{\mathrm{I}}$	113.0(2)
Cl(1)–Hg–N(3)	115.7(4)	N(3)–Hg–Cl(1)$^{\mathrm{I}}$	103.5(3)
Cl(1)–Hg–Cl(1)$^{\mathrm{I}}$	91.9(2)	Hg–Cl(1)–Hg$^{\mathrm{I}}$	88.1(2)
Cl(2)–Hg–N(3)	128.8(3)	Hg(1)–N(3)–C(2)	124.4(10)
Hg(1)–N(3)–C(4)	120.6(10)	C(2)–N(3)–C(4)	114.8(12)

$^{\mathrm{I}} = -x, -y, -z$.

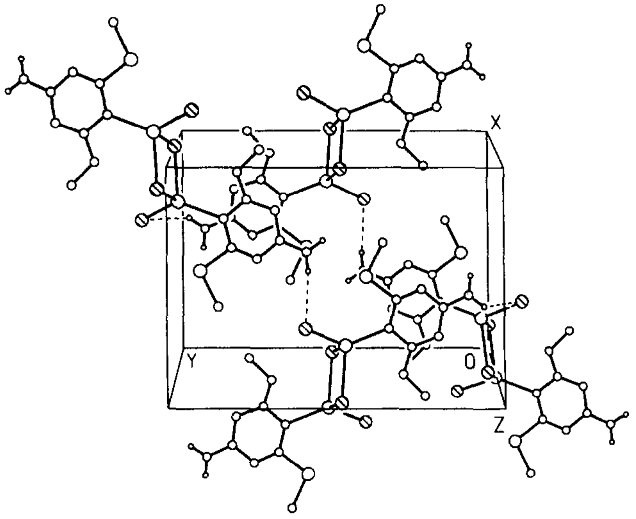

Fig. 3. A perspective view of the columnar stacking of the dinuclear units.

S(2) and O(4) atoms with the Hg(II) ion (3.300 and 3.023 Å, respectively). Both distances are at the limits of the sum of their respective van der Waals radii, by which very weak, at the best, interactions can be expected. Nevertheless, since similar long contacts have been reported [19], these may well favoure N(3) over N(1) as coordination point.

As usual pyrimidine ring is planar with a maximum deviation from the mean-squares plane of 0.0279 Å for C(4). Remaining bond distances and angles within the pyrimidine derivative are well in the range of those reported for related coordinated pyrimidine derivatives [13,15,20].

A view of the crystal packing is given in Fig. 3. The dinuclear units stack parallel to the z-axis, resulting two different columns of dimers. The columns are related in pairs which interpenetrate to each other, yielding a stacking of pyrimidine ring with an interplanar ring···ring distance of 3.649 Å. Finally these arrangements of interpenetrating pairs of columns are linked by intra and inter-columns hydrogen bonds formed by the amino group and the Cl(2) ions, with the following values N–H(6a)···Cl(2)^{I} = 2.708 Å and N–H(6b)···Cl(2)^{II} = 2.632 Å ($^{I} = x, 1/2-y, z-1/2$; $^{II} = 1-x, 1/2+y, 1/2-z$).

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