Zn(II) and Hg(II) Complexes of 4,6-Diamino-2-thiopyrimidine and 4,6-Diamino-2-methylthiopyrimidine. Crystal Structure of 4,6-Diamino-2-methylthiopyrimidinium Hemitetrachlorozincate(II)

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Abstract

Reaction of Zn(II) and Hg(II) with 4,6-diamino-2-thiopyrimidine (DATP) and 4,6-diamino-2-methylthiopyrimidine (DAMTP) in aqueous medium gave six new compounds which have been characterized by elemental analysis, IR and ^{1}H NMR spectroscopic techniques. The crystal structure of the Zn(II) complex of DAMTP has been determined by X-ray diffraction. It crystallizes in the trigonal space group $P3_121$ (or $P3_221$), $a = 8.725(2)$, $c = 24.288(4)$ Å, $C_5H_9Cl_2N_4SZn_{0.5}$, $Z = 6$, $D_{calc} = 1.616$ g cm^{-3} and $R = 0.045$ for 1056 unique reflections. The compound forms a salt structure composed of a 4,6-diamino-2-methylthiopyrimidinium cation with the ring nitrogen N1 protonated and a hemitetrachlorozincate anion. The crystal packing is dominated by a three-dimensional network of N–H...Cl hydrogen bonds.

Introduction

Purines and pyrimidines are the main constituents of nucleic acids and play important roles in many biological systems. Substituted purines and pyrimidines are also biologically important [1–4]. Among pyrimidine derivatives, thiopyrimidines are of great interest because of their wide biological activities. Some of these derivatives can act as inhibitors and antimetabolites [5–8]. 2-Thiopyrimidine shows a strong bacteriostatic activity *in vitro* on *E. coli* [9]. Likewise, 6-amino-2-thiouracil is well known as an antiviral [10] or a chemotherapeutic [10–12] agent. Also because of the biological importance of the metal complex formation processes of these pyrimidine derivatives, their interactions with metal ions have been widely investigated [13].

As the continuation of our works on metal interactions with thiopyrimidine and thiopurine derivatives [14], we report here the synthesis of six new compounds, formed from Zn(II) or Hg(II) and 4,6-diamino-1,2-dihydro-2-thiopyrimidine (DATP) or 4,6-diamino-2-methylthiopyrimidine (DAMTP), and the crystal structure of $[HDAMTP]_2[ZnCl_4]$. Although X-ray [15] as well as solution [16] studies of Zn(II) or Hg(II) complexes with nucleic acid constituents are numerous, only a limited number of investigations of Zn(II) or Hg(II) complexes with thiopyrimidines, which are all X-ray works, are available [17].

Experimental

Preparations

DATP and DAMTP

Thiopyrimidine derivatives were synthesized using methods previously described [18, 19].

Zn(DATP)$_2$Cl$_2$ (1), Hg$_3$(DATP)$_2$Cl$_6$ (5) and Hg$_3$(DAMTP)$_2$Cl$_6$ (6)

The corresponding thiopyrimidine derivative (2 mmol) was added to a hot solution (60 °C) of $ZnCl_2$ or $HgCl_2$ (6 mmol) dissolved in the minimum amount of water. Both Hg(II) complexes precipitated immediately. Zn(II) complex formed after one day by slow

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evaporation of the solution at 40 °C. The complexes were washed with cold water, ethanol and ether, and dried over P_4O_{10}. *Anal.* Calc. for $C_8H_{12}Cl_2N_8S_2Zn$ (1): C, 22.84; H, 2.85; Cl, 16.88; N, 26.67; Zn, 15.55. Found: C, 22.86; H, 2.97; Cl, 16.89; N, 26.68; Zn, 14.9%. Calc. for $C_8H_{12}Cl_6Hg_3N_8S_2$ (5): C, 8.74; H, 1.09; Hg, 54.77; N, 10.19. Found: C, 8.96; H, 1.07; Hg, 54.5; N, 10.20%. Calc. for $C_{10}H_{16}Cl_6Hg_3N_8S_2$ (6): C, 10.65; H, 1.42; Hg, 53.41; N, 9.94. Found: C, 11.08; H, 1.38; Hg, 55.0; N, 9.85%.

Zn(DATP)(DATP⁻)Br (2) and Zn(HDAMTP)(DAMTP)Br₃ (3)

These compounds were obtained by the same method as that of the above compounds using a $ZnCl_2$–Kbr (1:3 molar ratio) aqueous solution as solvent. *Anal.* Calc. for $C_8H_{11}BrN_8S_2Zn$ (2): C, 22.42; H, 2.57; N, 26.15. Found: C, 22.21; H, 2.63; N, 25.83%. Calc. for $C_{10}H_{17}Br_3S_2Zn$ (3): C, 18.45; H, 2.75; N, 18.15. Found: C, 18.98; H, 2.79; N, 17.53%.

[HDAMTP]₂[ZnCl₄] (4)

$ZnCl_2$ (20 mmol) was added to a solution of DAMTP (2 mmol) dissolved in 100 ml of water. The resulting solution was kept in a thermostatic bath at 40 °C until the colour of the solution turned to yellow. Pale yellow crystals suitable for X-ray analysis precipitated after several days by evaporating the solution at room temperature. *Anal.* Calc. for $C_{10}H_{18}Cl_4N_8S_2Zn$: C, 23.06; H, 3.46; N, 21.52. Found: C, 23.17; H, 3.56; N, 21.23%.

Methods

Microanalyses were carried out at the Technical Services of University of Granada, using a Perkin-Elmer Microanalyzer model 240C.

The IR spectra of the complexes were obtained from KBr pellets in the range of 4000–600 cm^{-1} and polyethylene pellets in the range of 600–180 cm^{-1} using a Perkin-Elmer 983G spectrophotometer.

^1H NMR spectra were recorded on a Hitachi Perkin-Elmer R-600 FT NMR spectrometer using DMSO-d_6 and D_2O as solvents, and TMS as internal standard.

Thermal measurements were made in Mettler TA 3000 equipment. TG curves were obtained by heating the samples in a pure air atmosphere (100 ml min^{-1}) at a heating rate of 10 °C min^{-1}; likewise, DSC plots were carried out at static conditions and the same heating rate.

X-ray Structure Determination of [HDAMTP]₂[ZnCl₄] (4)

The cell constants were obtained by least-squares fit of 20 high-order reflections ($20 < 2\theta < 35°$) on a Rigaku four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å): trigonal, space group $P3_121$ (or $P3_221$), $a = 8.725(2)$, $c = 24.288(4)$ Å, $V = 1601.2(5)$ Å^3; crystal size 0.28 × 0.35 × 0.38 mm, μ(Mo Kα) = 18.8 cm^{-1}, T = 296 K. Three standard reflections monitored after every 200 reflections did not show any appreciable intensity variation during the whole data collection; ω–2θ scan method, 2θ limits = 3.0–55.0°, data collected = ($0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 9$, $0 \leqslant l \leqslant 31$), scan range (°) = 1.6 + 0.5 tan θ, scan speed (°/min) = 4.0. Lorentz and polarization corrections were applied to the data, but not absorption correction.

The structure was solved by Patterson method using SHELX-86. The zinc atom is located on a special position. The refinement was carried out by full matrix least-squares method using VAX11/730 (SDP Package) computer system. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms, which were located from a difference-Fourier map, isotropically. The final R and R_w values were 0.045 and 0.051, respectively, for 150 variables and 1056 unique reflections with $I_o > 2\sigma(I_o)$; $w = \sigma(F_o)^{-2}$, $S = 1.57$, $(\Delta/\sigma)_{max} = 0.08$, $\Delta\rho_{max}$ and $\Delta\rho_{min}$ in the final difference-Fourier map = 0.69 and −0.65 e Å^{-3}, respectively.

Results and Discussion

Spectroscopic Results

The most significant IR data of the ligands and their complexes are summarized in Table 1. The corresponding assignment has been made from literature data concerning both 2-thiopyrimidine derivatives and their metal complexes [20]. The ^1H NMR data of the compounds are collected in Table 2.

Among the new isolated complexes, only Zn(HDAMTP)(DAMTP)Br_3 (3) and $[HDAMTP]_2[ZnCl_4]$ (4) contain the protonated HDAMTP ligand. The protonation of the ligand introduces two prominent spectral features: the presence of new IR bands in the 3200–2800 cm^{-1} region, which correspond to ν(N–H) stretching vibrations and the displacement to higher wavenumber of the bands corresponding to ν(C=C) + ν(C=N). Both features are due to a protonation process in the pyrimidine ring [21] at N1 or N3 (protonation on the ring nitrogen was confirmed by X-ray analysis for 4, as described later). On the other hand, the far infrared spectra of both compounds show a new band in the 220–240 cm^{-1} region, which is attributed to ν(Zn–X). Introduction of a positive charge on the ring in both the compounds should induce a general downfield shift of the hydrogen atoms near the protonation site. In fact, the signals corresponding to C5–H and NH_2 groups in the ^1H NMR spectra of 3 and 4 are shifted to downfield values (slightly for C5–H) arising from the lowering in electronic density of the aromatic ring.

TABLE 1. Infrared data (cm^{-1})

Compound	$\nu(N-H) + \nu(C-H)$	$\nu(NH_2) + \nu(C=)$ $+ \nu(C=N)$	$\nu(N-C=S)$ [a]	$\nu(N-C) + \nu(C-S)$ $+ \nu(N-C=S)$ [b]	$\nu(M-X)$
DATP	3410–3100	1635, 1615, 1565	1510	1315, 1240, 1195[c]	
DAMTP	3440–3170	1625, 1565, 1540, 1465		1285, 1235	
$Zn(DATP)_2Cl_2$ (1)	3480–3000	1650, 1625, 1565	1540	1340, 1225, 1205[c]	265
$Zn(DATP)(DATP^-)Br$ (2)	3400–3100	1655, 1625, 1570	1540	1310, 1255, 1210[c]	220
$Zn(HDAMTP)(DAMTP)Br_3$ (3)	3430–3130	1640, 1627, 1578		1260, 1214	220
$(HDAMTP)_2(ZnCl_4)$ (4)	3440–3120	1660, 1630, 1580		1255, 1210	240
$Hg_3(DATP)_2Cl_6$ (5)	3480–2940	1655, 1625, 1605, 1555	1535	1355, 1270, 1225 [c]	338, 280
$Hg_3(DAMTP)_2Cl_6$ (6)	3580–3170	1625, 1567, 1540		1320, 1290, 1235	355

[a]Thioamide I. [b]Thioamide III. [c]C=S component.

TABLE 2. ^1H NMR data

Compound	$S-CH_3$	C5–H	NH_2	N1–H
DATP		5.00	6.60	11.00
DAMTP	2.50	5.30	6.20	
$Zn(DATP)_2Cl_2$ (1)		5.10	6.70	
$Zn(DATP)(DATP^-)Br$ (2)		5.10	6.80	
$Zn(HDAMTP)(DAMTP)Br_3$ (3)	2.50	5.40	7.45	
$(HDAMTP)_2(ZnCl_4)$ (4)	2.65	5.55	7.00	
$Hg_3(DATP)_2Cl_6$ (5)		5.40	7.10	
$Hg_3(DAMTP)_2Cl_6$ (6)	2.50d [a] (J = 10 Hz)	5.75	6.35	

[a]d = doublet.

On the other hand, IR spectra of $Zn(DATP)_2Cl_2$ (1), $Zn(DATP)(DATP^-)Br$ (2) and $Hg_3(DATP)_2Cl_6$ (5) show positive shifts in the thioamide I and $\nu(C=S)$ bands which are displaced by 25–30 and 10–30 cm^{-1}, respectively, from their positions in the IR spectrum of the free ligand. Both features can be associated with the metal ligation to the ring nitrogen and the sulfur, respectively [22]. ^1H NMR spectrum of $Zn(DATP)_2Cl_2$ (1) shows two signals at 5.10 and 6.70 ppm, assigned to C5–H and NH_2 resonances, respectively, with the four hydrogen atoms being equivalent. Both signals are downfield shifted, which is probably due to the lowering in electronic density of the aromatic ring originated by the coordination to the metal ion. The same behaviour has also been observed in 2 and 5. Thus bidentate coordination via N3 and S2 can be proposed for 1, 2 and 5. This coordination mode has been found widely in analogous complexes such as dichloro(4,6-diamino-2-thiopyrimidine)cadmium(II) monohydrate [14a], (4-amino-2-mercapto-6-pyrimidinonato)methylmercury(II) monohydrate [17c], (4-amino-5-methyl-2-pyrimidinethiolato)methylmercury(II) [17c], tris-(4,6-dimethylpyrimidine-2-thiolato)cobalt(III) [23], and tetrakis(2-mercapto-6-pyrimidinato)tungsten(IV) [24], whose structures have been solved by X-ray analysis or proposed on the basis of spectroscopic data for several metal complexes of 2-thiopyrimidine [3] and 6-methyl-2-thiouracil [25].

For $Hg_3(DATP)_2Cl_6$ (5) and $Hg_3(DAMTP)_2Cl_6$ (6), an ionic constitution may be excluded on the basis of their molar conductivities, since both complexes behave as non-electrolytes in DMF solution. The same behaviour has been observed by Battistuzzi and Peyronel in their studies on $Hg_3L_2Cl_6$ complexes (L = 4,6-dimethylpyrimidine-2(1H)one) [26]. Infrared spectra of these compounds show a great modification in the 1350–1200 cm^{-1} region and the presence of new bands at 338 and 280 cm^{-1} for 5 and 355 cm^{-1} for 6, which are due to $\nu(Hg-Cl)$, in relation to the IR spectra of the free ligands.

Thermal Behaviour

From the TG and DSC curves of the six complexes two different steps can be clearly established: (i) dehalogenation processes and (ii) pyrolitic decomposition, ending at temperatures varying from 250–800 °C. In Table 3, the principal thermal data are listed. For $Hg_3(DATP)_2Cl_6$ (5) and $Hg_3(DAMTP)_2Cl_6$ (6), the dehalogenation process overlaps with the beginning of pyrolitic decomposition. All DAMTP complexes melt before decomposition showing an endothermic effect in the 180–250 °C temperature range; likewise, during thermal decomposition, a

TABLE 3. Thermoanalytical data for the isolated compounds

Compound	Process	Temperature (°C)	Accumulated weight loss	
			Found	Calc.
$Zn(DATP)_2Cl_2$ (1)	dehalogenation	289 (endo)	17.5	16.88
	pyrolysis	380–800 (exo)	81.5	80.64
$Zn(DATP)(DATP^-)Br$ (2)	partial dehalogenation	160–250 (endo)		
	pyrolysis	250–800 (exo)	90.0	81.04
$Zn(HDAMTP)(DAMTP)Br_3$ (3)	melting	251.3 (endo)		
	partial dehalogenation	283 (endo)		
	pyrolysis	283–800 (exo)		
$(HDAMTP)_2(ZnCl_4)$ (4)	melting	264.9 (endo)		
	partial dehalogenation	300.8 (endo)		
	pyrolysis	300.8–750 (exo)	98.4	89.42
$Hg_3(DATP)_2Cl_6$ (5)	partial dehalogenation	180–290 (endo)		
	melting of intermediate compound	248.2 (endo)		
	pyrolysis	290–600 (exo)	100	100
$Hg_3(DAMTP)_2Cl_6$ (6)	melting	185.1 (endo)		
	pyrolysis	200–700 (exo)	100	100

TABLE 4. Positional parameters and equivalent isotropic temperature factors[a] for $[HDAMTP][ZnCl_4]_{0.5}$

Atom	x	y	z	B_{eq} (Å^2)
Zn	0.000	0.8508(1)	0.167	3.9
Cl1	−0.1792(1)	0.9218(2)	0.11471(5)	4.4
Cl2	0.1867(2)	0.8064(2)	0.11482(5)	4.6
N1	0.6175(5)	0.4558(5)	−0.0635(2)	4.4
C2	0.6221(6)	0.3884(5)	−0.0130(2)	4.1
N3	0.4973(4)	0.2384(4)	0.0054(1)	4.1
C4	0.3510(6)	0.1464(5)	−0.0284(2)	4.0
C5	0.3394(6)	0.2049(5)	−0.0809(2)	4.3
C6	0.4775(6)	0.3654(6)	−0.0989(2)	4.0
S2	0.8143(2)	0.5200(2)	0.02447(6)	5.4
C21	0.7737(7)	0.3807(8)	0.0841(2)	6.0
N4	0.2206(5)	−0.0029(4)	−0.0060(2)	4.6
N6	0.4808(6)	0.4375(5)	−0.1479(2)	5.6

[a] $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

partial sublimation of mercury halide has been observed. The final residues of pyrolytic decomposition of the Zn(II) complexes were characterized by IR spectroscopy; they are ZnO in all cases. The great variations between theoretical and experimental values are due to a partial elimination of ZnX_2 during pyrolytic decomposition

Description of the Structure of $[HDAMTP]_2[ZnCl_4]$ (4)

The final atomic parameters for the non-hydrogen atoms are listed in Table 4. The molecular dimensions with the numbering scheme are shown in Fig. 1.

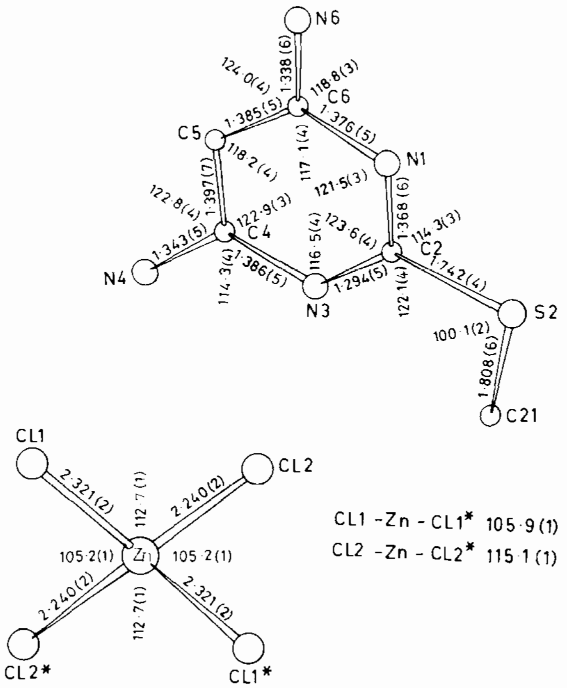


Fig. 1. The numbering scheme of $[HDAMTP][ZnCl_4]_{0.5}$ (4) with the molecular dimensions.

The compound forms a salt, that is, there is no direct metal–base bond. The pyrimidine base is protonated at N1, in accordance with the hydrogen-bonding system (described below) and the internal bond angle C2–N1–C6 of 121.5(3)°, the value being in sharp contrast to the angle at the non-protonated N3, C2–N3–C4 = 116.5(4)°; it is well documented that in six-membered nitrogen heterocycles the angle

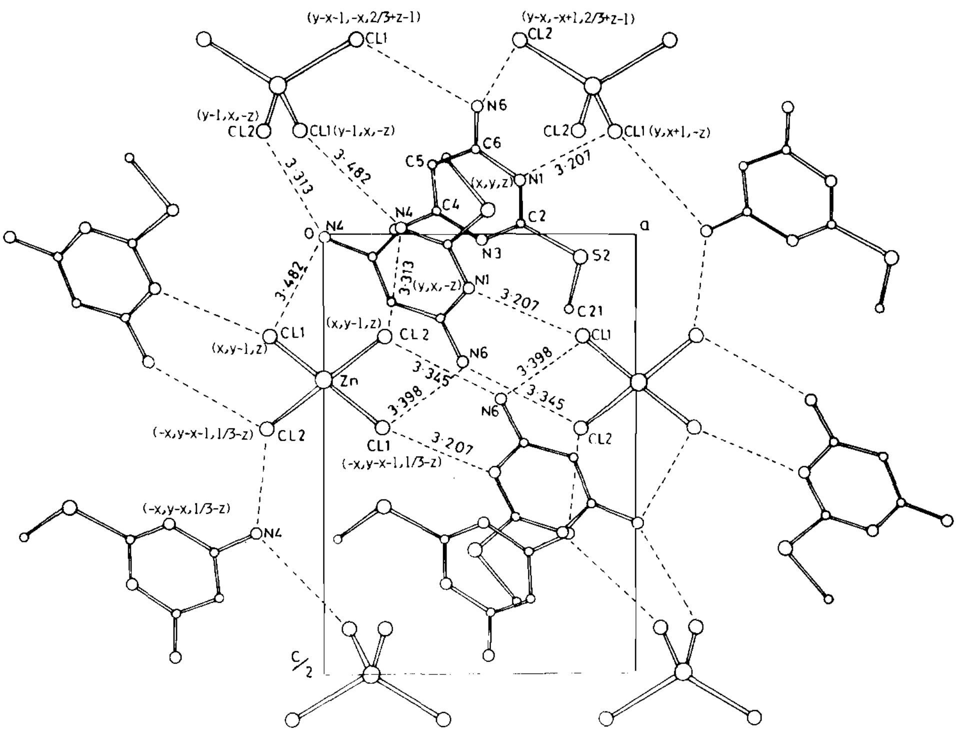


Fig. 2. Crystal packing of the molecules in $[HDAMTP][ZnCl_4]_{0.5}$ (**4**).

around a nitrogen atom falls into the range 125 ± 3° if there is a proton on the nitrogen atom and in the range 116 ± 3° if there is no proton [27]. Indeed, the hydrogen atom attached to the N1 could be located in a difference-Fourier map.

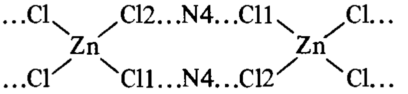
The bond lengths and angles of the pyrimidinium moiety involving the 4,6-diamino groups compare well with those found in the Cd(II) complex of 4,6-diamino-2-thiopyrimidine [14a], where the metal ion binds to the base through the S2 atom, and the molecular dimensions of the methylthio group are also normal [28]. The methylthio group rotates away from N1, possibly due to steric hindrance with the N1 proton. The pyrimidine ring is planar; the methylthio group also lies nearly in this plane with the methyl C21 deviated by 0.15(1) Å and the torsional angle N3–C2–S2–C1 of 2.2(5)°. The bond lengths and angles of the $[ZnCl_4]^{2-}$ anion, where two of the four Cl atoms are crystallographically independent since the Zn atom locates on a two-fold axis along b through $x = 0, z = 1/6$, fall into the range of values reported for a tetrahedral $ZnCl_4{}^{2-}$ ion, e.g. Zn–Cl bond distances and Cl–Zn–Cl angles = 2.245(2)–2.312(2) Å and 104.9(1)–113.3(1)° in xanthinium hemitetrachlorozincate [29] and 2.246(3)–2.321(3) Å and 104.8(1)–112.8(1)° in dicytosinium tetrachlorozincate [30].

The crystal packing is stabilized by a three dimensional network of N–H...Cl hydrogen bonds (Fig. 2 and Table 5). The protonated N1 is hydrogen bonded to the chlorine atom Cl1 (at $y, x + 1, -z$). The amino nitrogen N4 donates a proton to Cl2 (at $x, y - 1, z$) and another to Cl1 (at $y - 1, x, -z$), thus forming a doubly hydrogen-bonded molecular chain along the three-fold screw axis c.

TABLE 5. Hydrogen bonding scheme

D–H	A	Symmetry code[a]	D...A (Å)	H...A (Å)	D–H...A (°)
N1–H	Cl1	1	3.207(3)	2.13(4)	170(3)
N4–H1	Cl2	2	3.313(4)	2.61(5)	143(5)
N4–H2	Cl1	3	3.482(4)	2.82(5)	138(4)
N6–H1	Cl2	4	3.345(4)	2.48(6)	135(5)
N6–H2	Cl1	5	3.398(4)	2.43(5)	145(5)

[a] 1, $y, x + 1, -z$; 2, $x, y - 1, z$; 3, $y - 1, x, -z$; 4, $y - x, -x + 1, \frac{2}{3} + z - 1$; 5, $y - x - 1, -x, \frac{2}{3} + z - 1$.



The N6 amino group connects these two helical chains, which are crystallographically related to each other by a translation along $a + b$ (i.e. $x + 1, y + 1, z$), by bridging between them via two hydrogen bonds, one to Cl1 (at $y - x - 1, -x, z - \frac{1}{3}$) and another to Cl2 (at $y - x, -x + 1, z - \frac{1}{3}$).

Supplementary Material

Listings of the thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates, bond distances and angles involving hydrogen atoms, torsional angles, least-squares planes, and observed and calculated structure factors are available from the authors on request.

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