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# Mercury(II) complexes of heterocyclic thiones. Part 1. Preparation of 1:2 complexes of mercury(II) halides and pseudohalides with 3,4,5,6-tetrahydropyrimidine-2-thione. X-ray, thermal analysis and NMR studies

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#### Abstract

A series of complexes  $HgX_2(H_4pymtH)_2$  (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup>, CN<sup>-</sup>;  $H_4pymtH = 3,4,5,6$ -tetrahydropyrimidine-2-thione) has been obtained by the reaction of  $H_4pymtH$  with mercury(II) halides and pseudohalides in the molar ratio 2:1. X-ray diffraction studies revealed tetrahedral coordination of mercury with S-bound  $H_4pymtH$ . The exception is  $Hg(CN)_2(H_4pymtH)_2$  where the coordination is 2 + 2 with two strongly bound  $CN^-$  ligands and weaker H–S bonds with  $H_4pymtH$ . One- and two-dimensional <sup>1</sup>H and <sup>13</sup>C NMR measurements in dimethylsulfoxide solution confirmed the complexation of mercury to sulfur. The greatest complexation effects on chemical shifts were detected for the C-2, C-5 and H-1,3 atoms, i.e. two, four and five bonds away from mercury atom. The complexation effects in  $Hg(SCN)_2(H_4pymtH)_2$  and  $Hg(CN)_2(H_4pymtH)_2$  are in agreement with the strongest intramolecular H-bonding in the former and the weakest Hg–S bonds in the latter as compared to other complexes here. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Thermal analysis; Mercury complexes; Heterocyclic thione complexes; NMR studies

# 1. Introduction

Mercury(II) is in neutral mercury(II) halides a typical soft electron pair acceptor which forms strong bonds of a covalent character to soft donor atoms. In the past few decades many papers have dealt with solvated mercury(II) halides in solvents with different coordinating properties [1-6]. The solvation of the involved species plays an important role for all complex formation reactions in solutions. If the metal ion or the ligand is strongly solvated, their ability to form complexes is hampered. The complex formation thermodynamics, kinetic and structural properties of mercury(II) halide and pseudohalide systems in non-aqueous and aqueous solutions are available [1,7-11]. These data have to be taken into account while planing the reaction. The fact that mercury(II) ions interact with many biological molecules through coordination with deprotonated thiol, imidazole, disulfide, thioether, amino or carboxylate groups is well known and a great deal of effort has been devoted to the characterisation of these interactions in model molecules and in proteins [12]. The complexes of HgCl<sub>2</sub> with L-cysteine show an interesting example where a complex with covalently bonded chlorine atoms can be easily converted into an

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essentially ionic chloride which is the more stable complex at physiological pH [13]. There are also evidences pointing to the significance of mercury-halide complexation in biological systems. Both neutral mercuric halides and halogenomercurate anions have been used as probes of biological activity in proteins since intact mercurates can interact electrostatically with the protein in a specific site [14]. As a part of a more general program designed to prove certain aspects of mercury-halide binding in competition with other ligand s particularly heterocyclic thiones [15-17] we have investigated the reactions of mercury(II) halides and pseudohalides with 3,4,5,6-tetrahydropyrimidine-2thione under various conditions. There are no reports on the donor characteristics of H<sub>4</sub>pymtH toward mercury in solid or in solution, although the metal complexes of the related ligands, namely ethylene thiourea [18,19], pyrimidine-2-thione and its derivatives, have been reported [20-33]. On the contrary, the structure of the ligand itself has been known for many years [34].

We report here the synthesis of the 1:2 complexes of mercury(II) halides and pseudohalides with  $H_4$ pymtH and spectroscopic, thermal and X-ray diffraction studies.

# 2. Experimental

# 2.1. Materials and measurements

Mercury(II) halides and cyanide as well as the  $H_4$ pymtH ligand were obtained from Aldrich and used without further purification. Mercury(II) thiocyanate was prepared by the reaction of mercury(II) nitrate monohydrate and ammonium thiocyanate. The IR spectra were recorded as KBr pellets on the Perkin–Elmer FTIR 1600 spectrometer over the range 4000–450 cm<sup>-1</sup>.

The <sup>1</sup>H and <sup>13</sup>C NMR measurements were performed with a Varian Gemini 300 spectrometer, operating at 75.46 MHz for the <sup>13</sup>C nucleus. Concentrations of samples, dissolved in DMSO- $d_6$  in 5 mm tubes, were 0.05 and 0.25 M in <sup>1</sup>H and <sup>13</sup>C measurements, respectively. Spectra were recorded at 20°C. All chemical shifts, in parts per million (ppm), are referred to TMS. Digital resolution was 0.32 Hz per point in <sup>1</sup>H and 0.70 Hz per point in <sup>13</sup>C one-dimensional spectra. The following spectra were measured: standard <sup>1</sup>H, <sup>13</sup>C broadband proton decoupled, <sup>13</sup>C gated decoupled, COSY45 and NOESY. For proton decoupling the Waltz-16 sequence was used. The COSY45 spectra were measured in the magnitude mode with 1024 points in F2 dimension and 256 increments in F1 dimension, latter zerofilled to 1024 points. Each increment was taken with 16 scans, 5000 Hz spectral width and a relaxation delay of 0.8 s. The corresponding digital resolution was 9.8 and

19.5 Hz per point in F2 and F1 dimensions, respectively. The NOESY spectra were recorded in phase-sensitive mode with mixing time 0.5 s. All other measurement parameters were as for COSY spectra. The thermal measurements were performed using a simultaneous TGA–DTA analyzer (TA Instruments, SDT model 2960). The samples were placed in small aluminium oxide sample pans. The TGA and DTA curves were obtained by placing the samples of about 5 mg in mass, in open sample pans, with a heating rate of  $10^{\circ}$ C min<sup>-1</sup> and nitrogen (purity above 99.996%) pouring at a flow rate of 50 ml min<sup>-1</sup>. The SDT was calibrated with indium.

## 2.2. Preparation of the complexes

In solvents with strong donor properties, the mercury(II) halides react immediately with the solvent forming adduct compounds in the solid phase. Therefore we have chosen methanol as the media for preparing these complexes. Mercury(II) complexes 1-5 were prepared by reacting 1 equiv. of the corresponding mercury(II) salt and 2 equiv. of the H<sub>4</sub>pymtH ligand in methanol. The crystalline solids, which formed on standing for several days, were filtered off, washed with methanol and dried. The isolated complexes are crystalline and colourless substances, except for the iodo complex which is yellow. The thiocyanato complex is photosensitive and should be kept in the dark. All of the complexes are generally insoluble in common organic solvents, but soluble in solvents with pronounced donor properties such as DMSO, DMF, y-picoline or pyridine.

# 2.2.1. Preparation of $HgCl_2(H_4pymtH)_2$ (1)

Yield: 71%. Anal. Calc. for  $C_8H_{16}Cl_2HgN_4S_2$ : Hg, 39.81; N, 11.12; S, 12.73. Found: Hg, 40.02; N, 11.22; S, 12.65%.

## 2.2.2. Preparation of $HgBr_2(H_4pymtH)_2$ (2)

Yield: 92%. Anal. Calc. for  $C_8H_{16}Br_2HgN_4S_2$ : Hg, 33.84; N, 9.45; S, 10.82. Found: Hg, 34.09; N, 9.54; S, 10.72%.

# 2.2.3. Preparation of $HgI_2(H_4pymtH)_2$ (3)

Yield: 69%. Anal. Calc. for  $C_8H_{16}HgI_2N_4S_2$ : C, 13.99; H, 2.34; N, 8.16. Found: C, 14.07; H, 2.60; N, 8.12%.

## 2.2.4. Preparation of $Hg(SCN)_2(H_4pymtH)_2$ (4)

Yield: 67%. Anal. Calc. for  $C_{10}H_{16}HgN_6S_4$ : Hg, 36.53; N, 15.30; S, 23.36. Found: Hg, 36.77; N, 15.32; S, 23.46%.

## 2.2.5. Preparation of $Hg(CN)_2(H_4pymtH)_2$ (5)

Yield: 81%. Anal. Calc. for  $C_{10}H_{16}HgN_6S_2$ : N, 17.33; S, 13.22; Hg, 41.36. Found: Hg, 41.50; N, 17.55; S, 13.09%.

## 2.3. Crystal structure studies

Crystal data, experimental conditions, details of structure determination and final refinement parameters are given in Table 1. Data were collected at room temperature on a four-circle PW 1100 diffractometer (Stoe upgraded) with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Lattice constants were obtained by least-squares refinement from the settings of 46 reflections ( $10.3 \le \theta \le 18.7^{\circ}$ ) for 1, 29 reflections ( $8.9 \le \theta \le 16.5^{\circ}$ ) for 2, 58 reflections ( $10.0 \le \theta \le 18.4^{\circ}$ ) for 3, 64 reflections ( $10.2 \le \theta \le 16.5^{\circ}$ ) for 4 and 55

Table 1

General and crystal data and summary of intensity data collection and structure refinement

Compound	1	2	3	4	5
Formula Formula weight	C <sub>8</sub> H <sub>16</sub> Cl <sub>2</sub> HgN <sub>4</sub> S <sub>2</sub> 503.86	$C_8H_{16}Br_2HgN_4S_2$ 592.78	C <sub>8</sub> H <sub>16</sub> I <sub>2</sub> HgN <sub>4</sub> S <sub>2</sub> 686.76	C <sub>10</sub> H <sub>16</sub> HgN <sub>6</sub> S <sub>4</sub> 549.12	$C_{10}H_{16}HgN_6S_2$ 485.00
Crystal system and habit	orthorhombic,	monoclinic, prism	monoclinic, prism	triclinic, prism	monoclinic, prism
Space group Crystal dimensions (mm <sup>3</sup> )	$Pbca$ $0.53 \times 0.51 \times 0.50$	$P2_1/c$ 0.30 × 0.22 × 0.08	I2/a 0.26 × 0.15 × 0.12	$P\overline{1}$ 0.65 × 0.50 × 0.35	$P2_1/a$ 0.60 × 0.20 × 0.12
Unit cell parameters	0.55 × 0.51 × 0.50	0.30 × 0.22 × 0.08	0.20 × 0.15 × 0.12	0.05 × 0.50 × 0.55	0.00 × 0.20 × 0.12
a (Å)	14.8340(7)	7.8698(7)	14.7371(17)	7.6508(7)	12.5082(7)
b (Å)	12.8340(3)	15.644(2)	7.8550(5)	8.4976(7)	9.0302(5)
c (A) $\alpha$ (°)	16.8530(5)	12.8821(10)	15.0797(11)	14.175(2) 105.968(10)	14.0857(10)
$\beta$ (°) $\gamma$ (°)		98.79(2)	96.345(8)	89.941(9) 92.003(10)	95.583(6)
$V(\dot{A})$	3208.47(19)	1567.4(3)	1734.9(3)	885.44(18)	1583.45(17)
Z	8	4	4	2	4
$D_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	2.086	2.512	2.629	2.060	2.034
$\mu  ({\rm mm^{-1}})$	10.173	15.170	12.659	9.164	9.980
F(000)	1904	1096	1240	524	920
$2\theta$ Range for data collection	4–56	4-60	4–60	4–54	4–54
Range $h, k, l$	-12 to 0,	-11 to 0,	-20 to 20,	−9 to 9,	-15 to 15,
	-1 to 10,	0 to 21,	-4 to 11,	-10 to 10,	0 to 11,
	0 to 10	0 to 18	0 to 21	0 to 18	0 to 17
Scan type	$\omega/ heta$	ω	$\omega/ heta$	ω	$\omega/ heta$
Measured reflections	2006	4635	2613	3977	3509
Independent reflections $(R_{int})$	898 (0.006)	4456 (0.0554)	2437 (0.0366)	3825 (0.0231)	3374 (0.0790)
Refined parameters	155	156	89	202	173
Observed reflections, $I \ge 2\sigma(I)$	797	2142	1168	3160	2150
Range of transmission factors, min., max. <sup>a</sup>	0.0301, 0.0627	0.0785, 0.3353	0.0252, 0.0808	0.0265, 0.1359	0.1303, 0.3500
Face indices from centroid (mm)		(-110) 0.109		(1 0 0) 0.173	(1 0 0) 0.300
		(1 - 1 0) 0.109		(-100) 0.173	(-100) 0.300
		(0 1 1) 0.038		(0 0 1) 0.250	(0 0 1) 0.060
		(0 - 1 - 1) 0.038		$(0\ 0\ -1)\ 0.250$	$(0\ 0\ -1)\ 0.060$
		(-101)0.150		$(0\ 1\ -1)\ 0.323$	(0 - 1 1) 0.090
		(10 - 1) 0.150		(0 - 1 1) 0.323	(0 1 1) 0.098
		$(0\ 1\ -1)\ 0.150$ $(0\ -1\ 1)\ 0.150$		(0 2 1) 0.113	(0 -1 1) 0.150
$g_1, g_2$ in $w^b$	0.0710, 8.1007	0.0465, 0	0.0318, 0	0.0950, 0	0.0795, 0
$R^{c}$ , $wR^{d}$ $[I \ge 2\sigma(I)]$	0.0380, 0.0955	0.0397, 0.0802	0.0297, 0.0634	0.0512, 0.1221	0.0464, 0.1069
R, wR [all data]	0.0443, 0.1020	0.1255, 0.1007	0.0931, 0.0768	0.0640, 0.1300	0.0767, 0.1216
Goodness-of-fit on $F^2$ , S <sup>e</sup>	1.178	0.870	0.854	1.059	0.983
Max., min/ electron density (e $Å^{-3}$ ) <sup>f</sup>	0.758, -1.294	0.784, -1.525	0.633, -0.509	2.680, -2.933	1.694, -3.321
Extinction coefficients	0.0025(2)	0.0035(2)	0.00086(9)	0.0030(10)	0.0209(9)
Maximum $\Delta/\sigma$	0.001	0.001	0.001	0.001	0.001

<sup>a</sup> Absorption correction type: numerical Gaussian for 2, 4 and 5 and  $\psi$ -scan semi-empirical for 1 and 3.

<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + [g_1P + g_2P]$  where  $P = (F_o^2 + 2F_o^2)/3$ .

<sup>c</sup>  $\mathbf{R} = \Sigma ||F_o| - |F_c|| / \Sigma w |F_o|.$ 

<sup>d</sup> 
$$wR = [\Sigma (F_{0}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{0}^{2})^{2}]^{1/2}$$

<sup>e</sup>  $S = \Sigma [w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$ .

f In all structures the maximum electron density in the last difference Fourier map is near Hg.

Table 2 Characteristic frequencies (cm<sup>-1</sup>)<sup>a</sup> of the -NHCSNH- moiety and their assignment<sup>b</sup>

	vNH	$v_{0}C-N+\delta NH$	$\delta NH + v_{0}C - N$	$\delta NH + v_{c}C - N$	wCH <sub>2</sub>	πNH	vC=S
H.nymtH	3158s br 3099s	1563vs	1554vs	1208vs	11938	768s br	644s
$H_{4}pymtH$ $HgCl_{2}(H_{4}pymtH)_{2}$	3229s,br 3143m	1593vs	1561vs	1228s	11995 1199m-s	706m,br	624m
$HgBr_2(H_4pymtH)_2$ $HgI_2(H_4pymtH)_2$	3239vs,br 3146s 3300s,br 3125m	1595vs 1586vs	1561vs 1553vs	1229vs 1207s	1208s 1207s	704s,br 679m-s,br	607m °
$Hg(SCN)_2(H_4pymtH)_2$ $Hg(CN)_2(H_4pymtH)_2$	3236vs,br 3145vs 3371s 3204s,br	1589vs 1580vs,br	1564vs 1556vs,br	1224vs 1222s	1190S 1208vs	741s,br 749s,br	634s 625m
0 /2 41 /2							

<sup>a</sup> Abbreviations:  $v_a$ , asymmetric stretching;  $v_a$ , symmetric stretching;  $\delta$ , in plane bending;  $\pi$ , out of plane bending; w, wagging; vs, very strong; s, strong; m, medium; br, broad.

<sup>b</sup> The assignment according to Ref. [39].

<sup>c</sup> Very broad band ( $\sim 100 \text{ cm}^{-1}$ ) centred at 607 cm<sup>-1</sup>.

reflections (9.3  $\leq \theta \leq 14.7^{\circ}$ ) for 5. Reference reflections were monitored periodically (every 60 min in 1 or every 90 min in all others) during intensity collection to check crystal stability. The intensity variation of standard reflections was as follows:  $\pm 1.4$  in 1,  $\pm 2.2$  in 2,  $\pm 1.6$ in 3, +1.4 in 4, +6.5% in 5. The data were corrected for Lorentz-polarisation and absorption effects by the X-RED [35] program. The Gaussian numerical integration based on regular shapes of crystals was performed for 2, 4 and 5 and the  $\psi$ -scan semi-empirical method for 1 and 3 [35]. The absorption correction significantly improved the crystal structure parameters in all structures (lower R values, e.s.d. values and residual density near Hg in last difference Fourier maps). Heavy atoms were located by Patterson (1) or direct methods (2-5). The remaining non-hydrogen atoms were found in subsequent difference Fourier maps. Refinement in which non-hydrogen atoms were treated anisotropically was performed by full-matrix least-squares methods based on  $F^2$  values against all reflections. Positional disorder of the methylene C3 atom was found in 3 and 4. The disordered atoms were refined anisotropically with restraints on the  $U_{ii}$  components to have the same values as the neighbouring C atoms. The sum of the occupancy factors of the split C atoms was restrained to unit and resulted in a value of 0.67 for the major component in 3 and 0.72 in 4. All methylene H atoms were constrained to ride at C-H 0.97 Å with the temperature factor  $U_{ii} = 1.2 U_{eq}$  (Csp<sup>3</sup>). The last Fourier maps revealed positions of all H atoms bonded to N atoms but mostly with poor geometry. Their positions were therefore geometrically optimised (only in 2 the found coordinates had good geometry and were fixed during refinement, while the thermal isotropic parameters were allowed to refine) assuming sp<sup>2</sup> hybridisation of N atoms and applying the riding model with N-H 0.86 Å and  $U_{ij} = 1.2U_{eq}$ . Calculations were done by SHELXS-97 [36] and SHELXL-97 [37], and the molecular graphics with PLATON-98 [38].

#### 3. Results and discussion

## 3.1. IR spectra

The most significant IR data of the H<sub>4</sub>pymtH ligand and its mercury(II) complexes 1-5 are summarised in Table 2. In the spectrum of  $H_4$ pymtH the in-phase and out-of-phase N-H stretching modes are assigned to a strong band at 3099 cm<sup>-1</sup> and a broad one centred at  $3158 \text{ cm}^{-1}$ . In the region  $1500-1600 \text{ cm}^{-1}$  there is a very strong broad band, split at the bottom (1563, 1554  $cm^{-1}$ ), which can be assigned to coupled modes of asymmetric C-N stretching and N-H bending. The contribution from N-H groups is confirmed by deuteration studies [39]. The broad absorption bands of strong intensity at 768 cm<sup>-1</sup> are assigned to the out-ofplane NH bending, while symmetric C-N stretching coupled with NH bending can be associated with strong bands at 1361 and 1208 cm<sup>-1</sup>, respectively. The present band of strong intensity at 644 cm<sup>-1</sup> in the spectrum of free H<sub>4</sub>pymtH is assigned to C=S stretching on the basis of its sensitivity to S-methylation (in its S-methyl derivative this band is shifted to 596 cm<sup>-1</sup>) [39]. In the spectra of investigated complexes 1-5, C-S stretching is shifted to lower frequencies due to Hg-S bonding. From the structural studies of H<sub>4</sub>pymtH the predominance of the thione form over thiol was revealed in solid and solution phases although a weak band at 2658  $cm^{-1}$  in the IR spectrum of solid H<sub>4</sub>pymtH is observed. In the complexes the NH stretching frequency increases by approximately 70-200 cm<sup>-1</sup> on going from chloro to cyano complex. This displacement of the NH modes can be explained by means of different hydrogen bonding present in complexes. The ligand bands at 1563 and 1554 cm<sup>-1</sup> shifted to higher frequencies due to an increase in the C-N bond order in the complexes. The bands assigned to the NH out-of-plane vibrations shifted to lower frequencies by approximately 90 cm $^{-1}$  confirming the coordination through

the exocyclic sulfur atom as revealed by NMR and X-ray structure analysis. The lowest shift is observed for the cyano complex, which is consistent with the weakest mercury–sulfur bonds in complexes 1-5.

# 3.2. Description of the crystal structures

The stereochemistry of mercury in the solid state is characterised by a few typical modes of ligand binding, i.e. characteristic coordination (m) which is formed by covalent Hg–L bonds with m ligands, and effective coordination (m+n) with n additional ligands at distances shorter than the sum of the van der Waals radii of Hg and L [40]. In a tetrahedral environment the extension of coordination number is usually not accomplished, but the deviation from regular tetrahedral geometry occurs.

The deformation from regular polyhedral geometry can be influenced by crystal packing forces in the crystalline state, mostly by hydrogen bonds that involve ligand-donor atoms. In this work we examined by single-crystal X-ray analysis the influence of the X ligand on the length of the Hg–S bond in the 1:2 mercury complexes  $HgX_2(H_4pymtH)_2$ .

The values of selected bond distances and angles are listed in Table 3 and the hydrogen bonding geometry in Table 4.

## 3.2.1. $HgX_2(H_4pymtH)_2$ , X = Cl (1), Br (2) and I (3)

The mean H–S distances are similar in the chloro (2.450 Å) and bromo complex (2.449) and are by 0.07 Å shorter than the sum of the covalent radii of S (1.04 Å [41]) and tetrahedral Hg (1.48 Å [40]). The longest Hg–S bond is found in the iodo complex (2.612(2) Å) being significantly longer than the calculated covalent bond. The molecular structures of **1**, **2** and **3** are shown in Figs. 1–3, respectively.

The sum of the covalent radius of Hg with Cl, Br and I amounts to 2.52, 2.62 and 2.81 Å, respectively. It can, therefore, be calculated that the mean Hg–X bond length (Hg–Cl 2.640 Å) in 1 and (Hg–Br 2.733 Å) in 2 is by 0.12 and 0.11 Å longer than the calculated sum.

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

	HgCl <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	HgBr <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	HgI <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	Hg(SCN) <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	Hg(CN) <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>
Hg–X1 <sup>a</sup>	2.647(4)	2.7336(10)	2.7123(5)	2.556(2)	2.046(7)
Hg–X2 <sup>b</sup>	2.633(4)	2.7315(8)		2.608(2)	2.065(7)
Hg–S1	2.414(4)	2.431(2)	2.6119(16)	2.5260(19)	2.8558(18)
Hg–S2	2.485(4)	2.4674(19)		2.487(2)	2.9742(17)
S1–C1 (S–C1 in 3)	1.746(15)	1.756(8)	1.729(5)	1.753(8)	1.723(6)
S2-C21	1.748(15)	1.752(8)		1.730(9)	1.710(7)
C11–N11 (C1–N1 in 3)	1.296(6)	1.312(10)	1.303(7)	1.303(10)	1.331(8)
C11-N12 (C1-N2 in 3)	1.353(15)	1.315(9)	1.323(7)	1.311(10)	1.309(8)
N11-C12 (N1-C2 in 3)	1.465(16)	1.482(10)	1.461(8)	1.449(13)	1.471(9)
C12–C13 (C2–C3 in 3) °	1.506(19)	1.475(12)	1.457(12), 1.501(12)	1.456(18)	1.493(13)
C13–C14 (C3–C4 in 3)	1.472(17)	1.527(12)	1.428(10), 1.455(12)	1.458(17)	1.495(14)
C14-N12 (C4-N2 in 3)	1.502(16)	1.451(10)	1.453(8)	1.469(11)	1.470(10)
C21-N21	1.308(16)	1.311(9)		1.318(11)	1.328(8)
C21-N22	1.331(16)	1.297(9)		1.315(10)	1.321(8)
N21-C22	1.444(16)	1.448(9)		1.458(12)	1.454(9)
C22–C23	1.51(2)	1.430(6)		1.479(13), 1.474(17)	1.448(15)
C23–C24	1.43(2)	1.467(12)		1.467(17), 1.457(13)	1.456(15)
C24–N22	1.481(17)	1.436(11)		1.467(12)	1.459(8)
S3-C3				1.659(10)	
C3–N3				1.139(13)	1.151(8)
S4-N4				1.656(10)	
C4–N4				1.150(13)	1.119(8)
S1-Hg-S2	128.31(12)	138.82(8)	98.67(9)	112.45(7)	98.02(5)
S1–Hg–X1 <sup>a</sup>	107.66(13)	93.38(5)	108.56(4)	114.01(9)	97.46(19)
S1-Hg-X2 <sup>b</sup>	110.97(13)	105.93(6)	108.56(4)	103.39(9)	93.35(19)
S2-Hg-X1	107.11(12)	103.44(6)	107.64(3)	112.34(9)	96.43(19)
S2–Hg–X2	104.28(11)	101.28(5)	107.64(3)	112.97(8)	91.5(2)
X2–Hg–X1	92.71(14)	105.56(3)	123.06(3)	100.80(9)	165.6(3)

<sup>a</sup> X1 = C1 in 1, Br in 2, I in 3, S3 (from SCN) in 4 and C3 (from CN) in 5.

<sup>b</sup> X2 = C1 in 1, Br in 2, S4 (from SCN) in 4 and C4 (from CN) in 5.

<sup>c</sup> Values in the second column in **3** are for the disordered C3 atom of smaller occupancy; the same is for C23 in **4**. Symmetry transformations used to generate equivalent atoms: (i) -x-1/2, y, -z.

Table 4				
Hydrogen	bond	geometry	(Å,	°) a

D–H…A	D–H	d(D–H)	d(H···A)	∠DHA	d(D…A)
$HgCl_2(H_4pymtH)_2$					
N11-H11····C12 <sup>i</sup>	N11-H11	0.86	2.43	170.4	3.278(14)
N12-H12…C11	N12-H12	0.86	2.39	165.8	3.227(11)
N21-H21…C11	N21-H21	0.86	2.41	175.5	3.264(13)
N22-H22C12 <sup>ii</sup>	N22-H22	0.86	2.55	146.1	3.300(13)
$HgBr_2(H_4pymtH)_2$					
N11-H11···S2 <sup>iii</sup>	N11-H11	1.07	2.69	155.2	3.691(7)
N12-H12····Br2 iv	N12-H12	0.95	2.52	175.9	3.466(6)
N21-H21…Br1	N21-H21	1.00	2.50	150.5	3.403(6)
N22–H22····Br <sub>2</sub> $^{v}$	N22-H22	1.01	2.55	148.7	3.454(6)
$HgI_{2}(H_{4}pymtH)_{2}$					
N2–H2····S <sup>vi</sup>	N2-H2	0.86	2.89	141.1	3.599(6)
NI–H1…I <sup>vii</sup>	N1-H1	0.86	2.89	164.2	3.725(5)
$Hg(SCN)_{2}(H_{4}pymtH)_{2}$					
N11-H11····N3 viii	N11-H11	0.86	2.06	172.6	2.918(13)
N21-H21····N4 <sup>iii</sup>	N21-H21	0.86	2.12	158.9	2.933(13)
N12-H12···S1 ix	N12-H12	0.86	2.59	165.2	3.424(8)
N22-H22…N4	N22-H22	0.86	2.39	157.3	3.199(13)
$Hg(CN)_2(H_4pymtH)_2$					
N11–H11····N4 ×	N11-H11	0.86	2.36	134.2	3.020(9)
N22–R22…N3 <sup>xi</sup>	N22-H22	0.86	2.29	146.6	3.041(9)
N12-H12····S2 xii	N12-H12	0.86	2.49	168.9	3.335(6)
N21-H21···S1 xiii	N21-H21	0.86	2.55	170.6	3.399(6)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (i) 0.5-x, 0.5-y; -z; (ii) 0.5-x, 0.5+y, z; (iii) 1+x, y, z; (iv) x, 0.5-y, 0.5+z; (v) 1-x, 1-y, -z; (vi) -x-0.5, y, -z; (vii) -0.5+x, 1-y, z; (viii) x, -1+y, z; (ix) -x, 1-y, 1-z; (x) 0.5-x, -0.5+y, -z; (xi) 0.5-x, 0.5+y, 1-z; (xii) -0.5+x, 0.5-y, z; (xiii) 0.5+x, 0.5-y, z.

On the contrary, the bond length Hg–I in **3** is even shorter than Hg–Br in **2** and is 0.10 Å shorter than the length of the corresponding calculated bond. Therefore the strongest bond, Hg–I, is formed by elements having the smallest electronegativity difference.

Mercury has a strong tendency to preserve linear coordination and the largest angle will always be the one with the strongest bonds. This is in agreement with the experimental values since the I–Hg–I angle of 123.06(3) is the greatest X–Hg–X angle in complexes 1-3 [Br–Hg–Br 105.56(3), Cl–Hg–Cl 92.71(14)]. Correspondingly, the weakest Hg–S bond and the smallest S–Hg–S angle of 98.67(9) is in 3. It is interesting, however, that the tetrahedron in 2 is the one with greatest distortions — the S–Hg–S angle is 138.82(8) in 2 and 128.31(12) in 1 whereas the Hg–S bonds are of similar strength. This could be influenced by crystal packing and a hydrogen bond to sulfur in 2.

There is only one type of tetrahedral HgX<sub>2</sub>L<sub>2</sub> complex (L being a S bound monodentate ligand) where crystal structures of all three halide complexes (X = Cl, Br, I) have been determined up to now: the structures with L = N,N-dimethylthioformamide [42]. In these complexes the Hg–S bonds are weaker than in 1 and 2 and stronger than in 3. The mean value increases from the chloro to the iodo complex, 2.532, 2.542 and 2.578

Å, respectively, with a corresponding increase in the S–Hg–S angle [103.3(1), 107.2(2) and 109.1(2)] and a decrease in the X–Hg–X angle [113.2(1), 112.4(1) and 111.8(2)]. The mean Hg–Cl (2.481 Å) and Hg–Br (2.592 Å) bond lengths are shorter than in 1 and 2 but Hg–I (2.743 Å) is longer than in 3. These three complexes show a much smaller distortion of the tetrahedron and we suppose that it could be explained by hydrogen bonding which is much stronger in 1–3 than in the mentioned complexes where only weak C–H···X hydrogen bonds exist. In 1–3 both nitrogen atoms from both H<sub>4</sub>pymtH ligands are involved in extensive hydrogen bonding which interconnects the molecules. The hydrogen bonds are both intra- and intermolecular (1 and 2)



Fig. 1. PLATON-98 drawing of  $HgCl_2(H_4pymtH)_2$  (1) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii.



Fig. 2. PLATON-98 drawing of  $HgBr_2(H_4pymtH)_2$  (2) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii.



Fig. 3. PLATON-98 drawing of HgI<sub>2</sub>(H<sub>4</sub>pymtH)<sub>2</sub> (3) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii. The two possible orientations of C3 atom are shown with the major component labelled. The symmetry transformation used to generate equivalent atoms: (i) -x - 1/2, y, -z.



Fig. 4. PLATON-98 drawing of  $Hg(SCN)_2(H_4pymtH)_2$  (4) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii. The positional disorder of C23 atom is shown with the major component labelled.

or only intermolecular as in 3. In all complexes they are of the type  $N-H\cdots X$  while in 1 and 3 bonds of the type  $N-H\cdots S$  are also formed (Table 4).

# 3.2.2. $Hg(SCN)_2(H_4pymtH)_2$ (4)

In the crystal structure of  $Hg(SCN)_2(H_4pymtH)_2$  the mercury atom is tetrahedrally surrounded with four sulfur atoms. Two stronger Hg-S bonds are formed with the H<sub>4</sub>pymtH ligands [Hg–S1 2.526(2) and Hg–S2 2.487(2) Å] and two weaker ones with thiocyanate anions [Hg-S3 2.556(2) and Hg-S4 2.608(2) Å] (Fig. 4). The bond angles vary between S3-Hg-S4 of 100.80(9)° and S1-Hg-S3 of 114.01(9)° and have the smallest deviation from a regular tetrahedron in all complexes 1-4. The Hg-S(thiocyanate) bond lengths are slightly longer than the sum of covalent radii for Hg and S, while those from the H<sub>4</sub>pymtH ligand, are equal to or shorter than 2.52 Å. The Hg-S(thiocyanate) bond values are among the larger ones in tetrahedral  $[Hg(SCN)_4]^{2-}$  which are in the range from 2.496 to 2.610 Å according to the Cambridge Structural Database (CSD) [43]. The analogous bond model [shorter Hg-S(thione) and longer Hg-S(thiocyanate)] is found in the structures of two polymorphs of Hg(SCN)<sub>2</sub>-(C<sub>5</sub>H<sub>5</sub>NS)<sub>2</sub> [16] containing Hg–S(thiocyanate) bonds in the range 2.568(1)-2.685(2) Å, while the Hg–S(thione) distances are in the range 2.4580(12)-2.5123(12) Å. A survey of the CSD retrieved only one other monomeric complex with mercury in the tetrahedral surrounding built up of S atoms (two from SCN- anions and two from any other ligand): (dithiocyanato-S)-(N,N'-dicyclohexyldithio - oxamide)mercury(II) (YUBZOK [44]). In this structure the Hg-SCN bond lengths are the shorter ones (2.494(2) and 2.500(2) Å) whereas the Hg-S values are longer (2.577(2) and 2.551(2) Å) since the ligand is chelating and forms a very small angle S-Hg-S of 86.27(6)°.

The crystal structure is stabilised by N–H···N and N–H···S hydrogen bonds (Table 4). Interestingly, atom N3 from the SCN<sup>-</sup> anion is involved in only one linear intermolecular hydrogen bond, but atom N4 takes part as a proton acceptor forming two hydrogen bonds which depart from linearity. Such a hydrogen bond pattern is not unexpected, i.e. a statistical analysis of the hydrogen bonding geometry at the thiocyanate nitrogen acceptor atom showed that the SCN<sup>-</sup> anion usually accepts more than one non-linear hydrogen bond [45].

# 3.2.3. $Hg(CN)_2(H_4pymtH)_2$ (5)

This structure is quite different from the previous ones since two strong linear Hg–C bonds are formed with the CN<sup>-</sup> ligands [Hg–C3 2.046(7), Hg–C4 2.065(7) Å, C3–Hg–C4 165.6(3)°] (Fig. 5). The Hg–S distances [Hg–S1 2.8558(18) and Hg–S2 2.9742(17) Å] are the longest ones in 1–5. They are longer than covalent Hg–S bond but shorter than the sum of van der Waals radii for Hg (1.55, 1.54 or 1.55–1.65 Å [46–48]) and S (1.60–2.03 Å [49]). Therefore, the effective coordination is 2 + 2 [40]. The Hg–C values relate to strong covalent



Fig. 5. PLATON-98 drawing of  $Hg(CN)_2(H_4pymtH)_2$  (5) with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii. The Hg···S contacts are shown by dashed lines indicating the 2 + 2 coordination of Hg.

mercury to carbon bonds and according to the X-ray crystallographic criterion could be regarded only as slightly longer than in the structure of Hg(CN)<sub>2</sub> where they are 2.015(3) Å [50]. The review of the CSD revealed no structures containing such a HgS<sub>2</sub>(CN)<sub>2</sub> coordination moiety as in **5**.



All available N–H protons are included in intermolecular hydrogen bond formation. There are no intramolecular hydrogen bonds. Two N–H groups are involved in hydrogen bonding with the cyano N atoms. Two others form N–H···S hydrogen bonds with thione S atoms.

# 3.3. <sup>1</sup>H and <sup>13</sup>C NMR spectra

NMR data of parent H<sub>4</sub>pymtH and its complexes with mercury(II) halides and pseudohalides 1–5 are collected in Table 5. <sup>1</sup>H and <sup>13</sup>C NMR spectra show that in dimethylsulfoxide (DMSO) solution the H<sub>4</sub>pymtH molecule exists in the thione form as previously found in the solid phase [34,39]. The thione and thiol tautomers of H<sub>4</sub>pymtH and the enumeration of carbon atoms are displayed in Scheme 1. In <sup>1</sup>H spectra the greatest complexation effect ( $\Delta\delta$ ) was observed at

Table 5

<sup>1</sup>H and <sup>13</sup>C NMR data for the ligand H<sub>4</sub>pymtH and its mercury(II) complexes 1–5. Chemical shifts ( $\delta$ /ppm)<sup>a</sup>, H–H spin–spin coupling constants ( $J_{\rm HH}/\rm Hz$ )<sup>b</sup>, mercury induced <sup>1</sup>H shifts ( $\Delta\delta$ /ppm)<sup>c</sup> and mercury induced <sup>13</sup>C shifts ( $\Delta\delta$ /ppm)<sup>d</sup>

Compound		H <sub>4</sub> pymtH	HgCl <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	HgBr <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	HgI <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	Hg(SCN) <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub> °	Hg(CN) <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub> <sup>f</sup>
H-1,3	$ \begin{array}{c} \delta \\ J_{\rm HH} \ ({\rm s}) \\ \Delta \delta \end{array} $	7.86 (2H) (s)	8.97 (2H) (s) 1.11	8.72 (2H) (s) 0.86	8.59 (2H) (s) 0.73	9.01 (2H) (s) 1.15	8.22 (2H) 0.36
H-4,6	$\delta J_{\rm HH} \ \Delta \delta \ \delta$	3.09 (4H) (m) 1.71 (2H)	3.26 (4H) (m) 0.17 1.82 (2H)	3.25 (4H) (m) 0.16 1.82 (2H)	3.25 (4H) (m) 0.16 1.83 (2H)	3.29 (4H) (m) 0.20 1.84 (2H)	3.18 (4H) 0.09 1.77 (21-1)
H-5	$J_{ m HH} \Delta \delta$	5.70 (qn)	5.22 (t) <sup>g</sup> 0.11	4.78 (t) <sup>g</sup> 0.11	4.98 (t) <sup>g</sup> 0.12	5.07 (t) <sup>g</sup> 0.13	5.41 (qn) 0.06
C-2	$\delta \Delta \delta$	175.95	168.66 -7.29	168.90 -7.05	169.74 -6.21	167.10 - 8.85	172.99 -2.96
C-4,6	$\delta \Delta \delta$	39.88	40.06 0.18	40.10 0.22	40.11 0.23	40.21 0.33	39.99 0.11
C-5	$\delta \Delta \delta$	19.29	18.25 -1.04	18.30 - 0.99	18.50 - 0.79	18.03 -1.26	18.79 -0.50

<sup>a</sup> Measured in DMSO-d<sub>6</sub> solution. Referred to TMS. Number of protons in brackets.

<sup>b</sup> Digital resolution  $\pm 0.32$  Hz; (s) singlet, (t) triplet, (qn) quintet, (m) multiplet splitting.

<sup>c</sup> Mercury-induced <sup>1</sup>H shifts are defined as the difference of proton chemical shifts in mercurated and parent molecule. Minus sign denotes shielding.

<sup>d</sup> Mercury-induced <sup>13</sup>C shifts are defined as the difference of carbon chemical shifts in mercurated and parent molecule. Minus sign denotes shielding. Digital resolution  $\pm 0.70$  Hz.

<sup>e</sup> In Hg(SCN)<sub>2</sub>(H<sub>4</sub>pymtH)<sub>2</sub> the <sup>13</sup>C chemical shift of SCN is 122.79 ppm.  $\Delta\delta$  is 6.91 ppm as referred to Hg(SCN)<sub>2</sub> in DMSO-*d*<sub>6</sub>,  $\delta$  = 115.88 ppm. <sup>f</sup> In Hg(CN)<sub>2</sub>(H<sub>4</sub>pymtH)<sub>2</sub> <sup>13</sup>C chemical shift of CN is 144.50 ppm. It is somewhat broadened.  $\Delta\delta$  is -0.25 ppm as referred to Hg(CN)<sub>2</sub> in DMSO-*d*<sub>6</sub>,  $\delta$  = 144.75 ppm.

<sup>g</sup> Signal appears as a triplet, since quintet splitting is not completely resolved.

the H-1, 3 similarly as in the mercury(II) complexes with 1,3-imidazole-2-thione [17]. These NH protons, four bonds away from the mercury atom, are 0.36-1.15 ppm more deshielded in the complexes than in the free H<sub>4</sub>pymtH molecule. This is due to delocalization of  $\pi$ -electrons between N-atoms and accompanies shortening of the C-N and lengthening of the C-S bonds in the complexes. In addition, deshielding of NH protons is also caused by differences of H-bonding in complexes and in free H<sub>4</sub>pymtH, which was supported by variable temperature measurements.  $\Delta\delta$  at the H-1, 3 is related to the strength of the Hg-S bond, which is influenced by the character of the Hg-X bond [40,51]. Thus, shielding of the H-1, 3 is greater in the iodo than in the bromo and chloro complexes. The greatest complexation <sup>1</sup>H shift (1.15 ppm) in a series of complexes 1-5was found at the H-1, 3 in the thiocyanato complex, due to strong intramolecular H-bonding of these protons with the nitrogen atoms of the SCN groups. Contrary to this, in the cyano complex the smallest complexation effect at H-1, 3 (0.36 ppm) was observed (Table 5) suggesting that in the cyano complex the H<sub>4</sub>pymtH ligand is bound much weaker (longest Hg-S bonds) than in the other complexes. Deshielding complexation effects at the H-5 in 1-5 are the smallest ones observed (0.06-0.13 ppm). This is due to six-bond separation between Hg and the H-5 protons, but also because of considerable distance from the nitrogen positive charge. The greatest change on complexation in <sup>13</sup>C chemical shifts was observed for the thione carbon atom (C-2). This confirms that mercury is

Table 6

Thermoanalytical	data	for	thermal	analysis	of 1	the	mercury(II)	com-
plexes								

Complex	Process	Temperature of peak (°C)
HgCl <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	melting (endo) I endo II endo	179.43 328.42 386.29
$HgBr_2(H_4pymtH)_2$	melting (endo) I endo II endo	147.78 370.85 426.86
$HgI_2(H_4pymtH)_2$	melting (endo) I endo II endo	134.81 368.07 430.88
Hg(SCN) <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	melting (endo) I II endo III exo	133.43 243.89 369.70 407.21
Hg(CN) <sub>2</sub> (H <sub>4</sub> pymtH) <sub>2</sub>	melting (endo) I II endo III exo	147.02 206.84 304.63 407.08

bonded to sulfur, since the C-2 is the closest carbon to the complexation site. This is in agreement with lengthening of the C-S bond in complexes as also obtained by PM3 calculation [52]. In 1-5 the C-2 is shielded from -2.96 to -8.85 ppm, as compared to the C-2 in the parent H<sub>4</sub>pymtH. The difference in shielding at the C-2 is consistent with the difference of the Hg-S bond strength which arises from the back donation of mercury to sulfur and is influenced by the degree of covalency of the Hg-X bonds. As a consequence, the shielding at the C-2 is lowered from the chloro to the iodo complex, while deshielding at the H-1, 3 is lowered in same sequence. The large downfield shift (6.91 ppm) of the C(thiocyanate) in 4, relative to the chemical shift of this C-atom in free mercuric thiocyanate is in agreement with intramolecular H-bonding and the tetrahedral coordination of the mercury atom. The decrease in shielding at the C-2 in 5 is connected with the 2+2coordination. This means that due to longer Hg-S bonds, the influence of the Hg(CN)<sub>2</sub> moiety on the electron distribution in the ligand is small. Therefore, among all complexes investigated here, the <sup>13</sup>C chemical shifts in 5 are the most similar to those of the free H<sub>4</sub>pymtH molecule. The smallest complexation <sup>13</sup>C shift at C-2, amounting to -2.96 ppm, was detected in 5 while the greatest one (-8.85 ppm) was found in 4 (Table 5). Although the C-4, 6 are four bonds and the C-5 are even five bonds away from mercury, the complexation effects at the latter carbon (-0.50 to -1.26ppm) are approximately five times greater than at the former one. In addition,  $\Delta \delta$  at the C-5 is a shielding effect (as at the C-2), while that at the C-4, 6 is a deshielding one. The subtle deshielding in the latter is related to an increase of the  $\pi$ -electron density in the C–N bond.  $\Delta\delta$  at C-2 and C-5 are different by an order of magnitude, which arises from a different throughbond distance between mercury and these carbons. The complexation effects at C-5 show that even long-range effects on chemical shifts (through five bonds), might be used as a complexation probe.

One has to mention that the conformational flexibility of the ring system might also be important for the long-range transmission. Satellite <sup>199</sup>Hg–<sup>1</sup>H and <sup>199</sup>Hg–<sup>13</sup>C couplings were not observed. This is usually encountered when the Hg–C coupling pathway includes heteroatoms like S, N or O [16,17].

# 3.4. Thermal analysis (TGA and DTA)

The samples of mercury complexes 1-5 were heated from room temperature up to 700°C (see thermoanalytical data shown in Table 6). In each DTA curve there is a typical endothermic minimum, which corresponds to the melting process of the complex. It is represented by the first single endothermic peak at a temperature between 130 and 180°C. The endothermic peak of melting of the halide complexes progressively decreases with increasing formula weight. Two overlapping endothermic peaks, the first one being small and broad and the second one larger and sharper, represent the decomposition of the halide complexes. The DTA curve contains endothermic minima at 368.07 and 430.88°C in 3, at 370.85 and 426.86°C in 2, and at 328.42 and 386.29°C in 1. Two different decomposition steps can be classified as decomposition of the ligand and dehalogenation of the residue. From the first decomposition peak in the DTA curve the following order of complex stability can be established: iodo  $\approx$  bromo > chloro. From the temperature of the second decomposition step, the following order of dehalogenation processes is established: iodo > bromo > chloro. The shapes of the DTA curves of the halide complexes suggest an analogy in the decomposition steps due to their similar structures. The decomposition of the thiocyanato complex is represented by a broad exothermic peak at 243.89°C, an endothermic minimum at 369.70°C, and a broad exothermic peak at 407.21°C. The DTA curve of  $Hg(CN)_2(H_4pymtH)_2$  is characterised by three peaks, two exothermic ones, a sharp one at 206.84°C and a small, broad one at 407.08°C, and the third one being a broad endothermic peak at 304.63°C. The first step of decomposition, determined by exo(I) and endo(II) peaks, represents elimination of the ligand. One can conclude from the TGA-DTA curves of the reactants that the second step, exo(III), is connected with degradation of the corresponding mercury(II) pseudohalides. Parallel occurrence of different steps of the decomposition process, resulting in the overlapping of DTA peaks, makes partial determination of the weight loss of particular elimination compounds impossible.

## 4. Supplementary material

Structure factor tables are available from the authors. Atomic coordinates and equivalent isotropic displacement parameters, calculated hydrogen atom parameters, anisotropic thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (deposition Nos. 137430–1374334). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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