X-Ray Structural Studies † on Free and Co-ordinated 6-Amino-8-mercaptopurinium Cation in Bismuth(III) Complexes

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Reaction of $BiCl_3$ with 6-amino-8-mercaptopurine (amp) in HCl solution results in the formation of $[Hamp]_2[BiCl_5(Hamp)]Cl\cdot5H_2O$ (2) and $[Hamp][BiCl_5(Hamp)]\cdot2H_2O$ (3). These complexes, together with the free ligand as a chloride, (1), have been characterized structurally by single-crystal *X*-ray diffraction showing that both the structures of (2) and (3) consist of $[BiCl_5(Hamp)]^-$ anions, protonated ligand, and water molecules in different ratios; in addition, in (2) a Cl^- is present. In the complex anions the bismuth atom is octahedrally surrounded by five chlorines and one ligand molecule co-ordinated *via* sulphur; in each of the three structures base stacking is present. All data were collected using Mo-K_α radiation. The space groups are $C2/c$ for (1), $P2_1$ for (2), and $P\bar{1}$ for (3). The final *R* indices were 0.031, 0.047, and 0.038 respectively.

Research on metal complexes of purines and related derivatives has only recently developed in view of their relevant biological interest, some of these being known as anticarcinogenic. As far as we know at the present time, structural studies on complexes of Hg^{II},[1] Cu^{I},[2] Cu^{II},[3] and Pd^{II} [4] only with mercaptopurines have been considered; we have now synthesized and determined the crystal and molecular structures of two complexes between $BiCl_3$ and $Hamp^+$ (amp = 6-amino-8-mercaptopurine) with the resulting formulae $[Hamp]_2[BiCl_5(Hamp)]Cl\cdot5H_2O$ (2) and $[Hamp][BiCl_5(Hamp)]\cdot2H_2O$ (3). The structure of 6-amino-8-mercaptopurinium chloride (1) provides their accurate molecular dimensions, while in the bismuth complexes these structural parameters are affected by large estimated standard deviations (e.s.d.s) because of the dominance of the bismuth scattering.

Experimental

Colourless crystals of 6-amino-8-mercaptopurinium chloride (1) were obtained by dissolving neutral amp in 50% aqueous HCl; the two complexes were synthesized by reacting $BiCl_3$ and the ligand (1 : 3 molar ratio) in 50% aqueous HCl. Two preparations gave at first yellow crystals of (2) and subsequently orange-yellow crystals of (3), but in spite of several attempts we were not able to obtain complex (2) again. The compounds were characterized by elemental analyses [Found for (1): C, 29.1; H, 3.50; Cl, 17.5; N, 34.1; S, 15.75. Calc. for $C_5H_6ClN_5S$: C, 29.35; H, 3.45; Cl, 17.3; N, 34.2; S, 15.65%. Found for (2): C, 17.85; H, 2.75; Bi, 20.6; Cl, 21.0; N, 20.8; S, 9.55. Calc. for $C_{15}H_{28}BiCl_6N_{15}O_5S_3$: C ,17.7; H, 2.75; Bi, 20.55; Cl, 20.95; N, 20.65; S, 9.45%. Found for (3): C, 15.9; H, 2.15; Bi, 27.6; Cl, 23.45; N, 18.5; S, 8.45. Calc. for $C_{10}H_{16}BiCl_5N_{10}O_2S_2$: C, 15.85; H, 2.10; Bi, 27.5; Cl, 23.35; N, 18.45; S, 8.45%].

Cell parameters were obtained by single-crystal diffractometry using Mo-K_α radiation (λ = 0.710 69 Å); the final accurate values were determined by a least-squares refinement of 2θ values for some high-angle reflections. Relevant crystal and diffraction data are summarized in Table 1.

The intensity data were collected using the ω–2θ scan technique on a Siemens AED single-crystal automated diffractometer; in all cases a standard reflection was monitored every 50 reflections, and showed no significant variation. The data were corrected for Lorentz and polarization effects. In addition, the data of (2) were corrected for absorption: the transmission factors were in the range 1.02—1.80. For (3) an attempted correction for absorption did not improve the results of the structural analysis.

The structure of (1) was solved by direct methods; the heavy-atom technique was employed for (2) and (3), using Patterson and Fourier methods. All structures were refined by full-matrix least-squares methods using isotropic and anisotropic thermal parameters. In (2) and (3), only Bi, Cl, and S were treated anisotropically and the hydrogens were not located; in (1) a ΔF map revealed all the hydrogen atoms which were included isotropically in the final refinements. The final *R* values were 0.031, 0.047, and 0.038 for (1), (2), and (3) respectively. Scattering factors were taken from International Tables;[5] all the calculations were made using SHELX 76 [6] on the CDC 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, Casalecchio, Bologna with the financial support of University of Parma. Atomic co-ordinates are listed in Tables 2—4.

Results and Discussion

Structures of the Complex Anions.—Both structures (2) and (3) (Figures 1 and 2) consist of $[BiCl_5(Hamp)]^-$ complex anions, organic cations, water molecules and, in addition, in (2), chloride ions. In the complex anions, the bismuth atoms co-ordinate octahedrally five chlorines and one ligand molecule *via* sulphur as expected for a 'soft' metal; these polyhedra show considerable displacements from the ideal geometry [Table 5: Bi–Cl 2.536(6)—2.825(6) Å, *cis* angles 86.2(2)—94.2(2)°, *trans* angles 172.8(2)—178.6(3)° for (2); Bi–Cl 2.575(3)—2.883(3) Å, *cis* angles 83.2(1)—102.7(1)°, *trans* angles 166.8(1)—170.5(1)° for (3)]. The values for the Bi–Cl bonds agree well with those found in the literature [7] and it is noteworthy that the chlorines, which have shorter bonds to Bi, are not involved in hydrogen bonding: *e.g.* Cl(1) and Cl(2) in (2); Cl(1) and Cl(4) in (3). The Bi–S bond distances are comparable with the longer ones reported for this type, particularly in (3), and this can be partially explained by the crowding of the ligand whose arrangement also allows several hydrogen bonds.

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† *Supplementary data available* (No. SUP 56029, 6 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystal data and collection, solution, and refinement details

	(1)	(2)	(3)
Formula	$C_5H_6ClN_5S$	$C_{15}H_{28}BiCl_6N_{15}O_5S_3$	$C_{10}H_{16}BiCl_5N_{10}O_2S_2$
M	203.7	1 016.3	758.7
Z	8	2	2
Space group	$C2/c$	$P2_1$	$P\bar{1}$
Crystal system	Monoclinic	Monoclinic	Triclinic
a/Å	15.251(6)	8.465(2)	7.255(2)
b/Å	7.982(2)	27.669(7)	9.260(2)
c/Å	15.215(6)	7.399(1)	18.220(5)
α/°	—	—	100.33(2)
β/°	120.99(8)	96.19(1)	91.86(2)
γ/°	—	—	84.84(2)
U/Å^3	1 588(1)	1 722(1)	1 199(1)
D_m/g cm^{-3}	1.70	1.98	2.10
D_c/g cm^{-3}	1.711	1.959	2.095
F(000)	832	992	724
μ/cm^{-1}	6.8	57.9	80.8
Crystal dimensions (mm)	0.33 × 0.75 × 0.58	0.23 × 0.39 × 0.36	0.26 × 0.29 × 0.20
Measured reflections	1 318	3 349	5 060
Independent reflections	994	2 339	3 598
Observed reflections, $I > 2\sigma(I)$	1 040	2 532	3 911
Final R, R' [a]	0.031, 0.036	0.047, 0.050	0.038, 0.041
g [b]	47×10^{-4}	37×10^{-1}	57×10^{-4}
Calculated transmission factors	—	1.02—1.80	—
Number of variables	133	230	161
θ range (°)	3—24	3—25	3—26

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma(w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] In the expression for weight, $w = 1/[\Sigma^2(F) + |g|F^2]$.

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for (1)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cl	599(1)	3 198(1)	6 791(1)	C(2)	3 432(2)	5 848(3)	5 148(2)
S	−505(1)	1 936(1)	3 527(1)	C(6)	2 630(2)	5 402(3)	6 139(0)
N(9)	1 166(1)	3 513(3)	3 717(2)	C(5)	1 887(2)	4 553(3)	5 272(2)
N(3)	2 749(1)	5 056(3)	4 327(2)	H(N9)	969(19)	3 148(31)	3 074(25)
N(1)	3 390(1)	6 051(3)	6 012(2)	H(N1)	4 018(24)	6 627(44)	6 596(28)
N(6)	2 651(2)	5 575(3)	7 008(2)	H(C2)	4 020(19)	6 377(35)	5 158(19)
N(7)	1 011(1)	3 712(3)	5 058(2)	H1(N6)	2 213(24)	5 017(38)	7 091(25)
C(8)	559(2)	3 069(3)	4 106(2)	H2(N6)	3 255(24)	6 293(52)	7 594(28)
C(4)	1 985(2)	4 428(3)	4 425(2)	H(N7)	767(22)	3 460(38)	5 482(27)

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for (2)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Bi	1 155(1)	0(0)	2 676(1)	N(63)	8 123(28)	1 164(8)	1 343(32)
Cl(1)	4 313(6)	−5(4)	3 436(8)	N(73)	7 577(23)	2 263(7)	1 386(25)
Cl(2)	1 297(8)	−742(2)	688(10)	C(81)	−803(29)	−325(8)	6 529(32)
Cl(3)	−2 072(5)	28(4)	1 912(7)	C(41)	−2 753(25)	227(8)	7 122(28)
Cl(4)	1 537(8)	612(2)	−104(9)	C(21)	−5 046(31)	550(10)	7 807(36)
Cl(5)	1 067(8)	836(2)	4 856(9)	C(61)	−4 710(28)	−313(9)	8 049(32)
Cl(6)	2 941(8)	3 380(2)	2 602(12)	C(51)	−3 229(33)	−231(9)	7 535(35)
S(1)	813(7)	−537(2)	5 864(8)	C(82)	3 857(28)	2 314(9)	−2 278(31)
S(2)	3 109(8)	1 741(2)	−1 868(11)	C(42)	5 361(27)	2 884(8)	−3 104(31)
S(3)	7 370(9)	3 242(2)	1 199(11)	C(22)	6 371(35)	3 603(10)	−3 760(38)
N(91)	−1 214(20)	178(6)	6 588(24)	C(62)	3 883(26)	3 600(7)	−2 636(29)
N(31)	−3 516(24)	637(7)	7 238(27)	C(52)	4 022(29)	3 077(8)	−2 547(30)
N(11)	−5 521(20)	115(6)	8 246(22)	C(83)	6 669(25)	2 696(7)	1 590(29)
N(61)	−5 403(25)	−720(8)	8 418(28)	C(43)	5 176(32)	2 060(9)	2 382(36)
N(71)	−2 103(21)	−556(6)	7 092(23)	C(23)	4 361(31)	1 321(8)	3 076(33)
N(92)	5 172(25)	2 396(7)	−2 907(28)	C(63)	6 765(29)	1 374(8)	1 883(32)
N(32)	6 550(27)	3 139(9)	−3 816(31)	C(53)	6 627(26)	1 878(7)	1 910(29)
N(12)	4 994(29)	3 837(8)	−3 201(32)	O(1)	102(27)	3 027(9)	4 610(31)
N(62)	2 591(28)	3 835(8)	−2 140(30)	O(2)	0(29)	2 009(9)	4 920(35)
N(72)	3 041(21)	2 724(6)	−2 075(24)	O(3)	441(25)	1 925(8)	997(29)
N(93)	5 272(23)	2 559(7)	2 192(27)	O(4)	179(29)	3 101(9)	−1 475(31)
N(33)	4 106(24)	1 809(7)	3 027(29)	O(5)	2 657(28)	6 693(9)	3 479(31)
N(13)	5 705(24)	1 130(7)	2 468(26)				

Table 4. Fractional atomic co-ordinates (× 10^4) for (3)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Bi	6 680(1)	−140(0)	7 503(0)	N(12)	8 384(12)	−1 188(10)	3 714(5)
Cl(1)	6 342(4)	1 794(3)	6 641(2)	N(62)	7 459(13)	−163(11)	4 930(6)
Cl(2)	9 913(4)	−1 638(3)	6 736(2)	N(72)	7 413(11)	−3 488(9)	5 076(5)
Cl(3)	7 546(4)	−2 120(3)	8 512(2)	C(81)	6 519(13)	3 248(10)	8 703(5)
Cl(4)	3 522(4)	603(3)	8 130(2)	C(41)	3 768(14)	4 331(11)	9 131(6)
Cl(5)	4 871(4)	−1 779(3)	6 393(1)	C(21)	1 065(19)	5 637(15)	9 268(8)
S(1)	8 461(4)	2 063(3)	8 591(2)	C(61)	2 992(16)	5 980(13)	8 264(7)
S(2)	7 349(4)	−6 268(8)	5 362(1)	C(51)	4 226(14)	4 905(11)	8 524(6)
N(91)	5 219(12)	3 318(9)	9 257(5)	C(82)	7 634(12)	−4 981(10)	4 853(5)
N(31)	2 226(13)	4 664(11)	9 539(6)	C(42)	8 232(13)	−3 909(10)	3 888(5)
N(11)	1 376(13)	6 269(11)	8 668(6)	C(22)	8 827(15)	−2 343(12)	3 157(6)
N(61)	3 243(13)	6 638(10)	7 697(5)	C(62)	7 841(14)	−1 370(11)	4 394(6)
N(71)	5 912(12)	4 212(10)	8 263(5)	C(52)	7 771(13)	−2 806(10)	4 488(5)
N(92)	8 113(11)	−5 226(8)	4 117(4)	O(1)	6 936(10)	5 343(8)	7 082(4)
N(32)	8 732(12)	−3 727(9)	3 200(5)	O(2)	4 261(10)	8 311(8)	9 656(4)

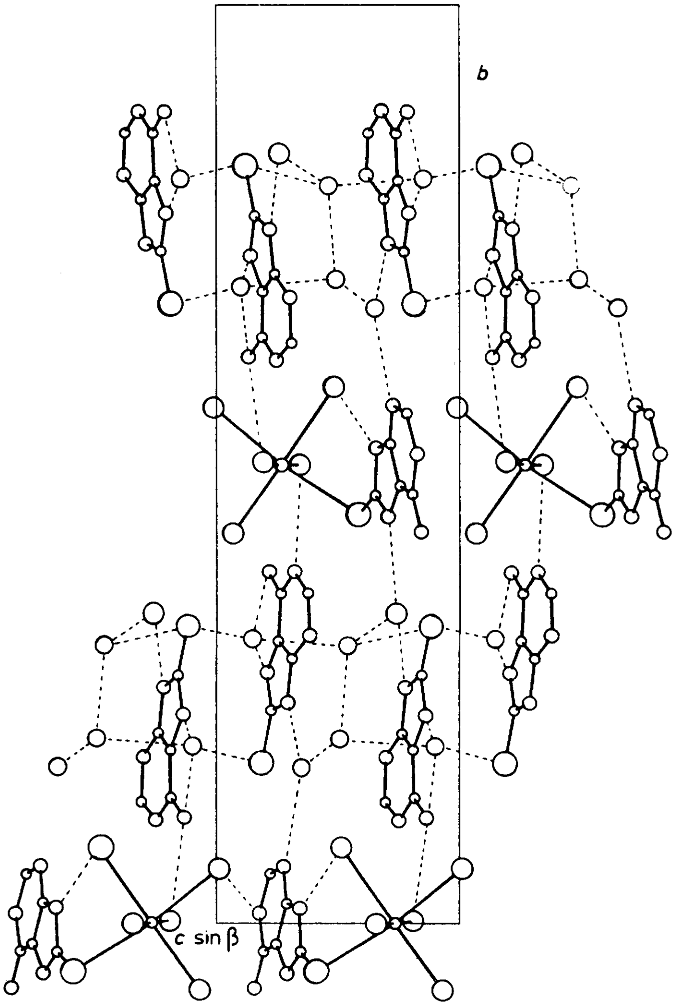


Figure 1. Structure of (2) projected along the *a* axis

Structure of the Ligand Molecules.—Bond distances and angles for 6-amino-8-mercaptopurinium chloride (1), and for the ligand molecules of the complexes (2) and (3), are reported in Table 6. Only the data of (1), which are comparable with the values found in 6-mercaptopurine monohydrate,[8] are of high accuracy, while for (2) and (3), because of the dominance of the bismuth atom scattering, the e.s.d.s in the light-atom positions are rather large. In view of this some differences (sometimes considerable) are not judged as significant: *e.g.* C–N distance 9, 1.23(3)—1.38(3); C–N distance 11, 1.29(3)—1.42(3) Å. The values of the bond angles at the nitrogen atoms, together with the hydrogen-bond

Table 5. Bond distances (Å) and angles (°) in the co-ordination polyhedra of (2) and (3)

	(2)	(3)		(2)	(3)		(2)	(3)
Bi–Cl(1)	2.671(5)	2.576(3)	Cl(1)–Bi–S(1)	90.6(2)	86.9(1)	Cl(2)–Bi–Cl(5)	178.5(2)	83.2(1)
Bi–Cl(2)	2.536(6)	2.883(3)	Cl(1)–Bi–Cl(2)	90.5(2)	92.2(1)	Cl(3)–Bi–S(1)	89.8(2)	86.7(1)
Bi–Cl(3)	2.730(4)	2.839(3)	Cl(1)–Bi–Cl(3)	178.6(3)	171.9(1)	Cl(3)–Bi–Cl(4)	91.3(2)	89.3(1)
Bi–Cl(4)	2.710(6)	2.575(3)	Cl(1)–Bi–Cl(4)	87.9(2)	95.7(1)	Cl(3)–Bi–Cl(5)	90.4(2)	102.7(1)
Bi–Cl(5)	2.825(6)	2.683(2)	Cl(1)–Bi–Cl(5)	88.3(2)	83.8(1)	Cl(4)–Bi–S(1)	172.8(2)	91.4(1)
Bi–S(1)	2.829(5)	2.935(3)	Cl(2)–Bi–S(1)	94.2(2)	99.4(1)	Cl(4)–Bi–Cl(5)	86.2(2)	87.1(1)
			Cl(2)–Bi–Cl(3)	90.6(2)	83.9(1)	Cl(5)–Bi–S(1)	86.7(2)	170.5(1)
			Cl(2)–Bi–Cl(4)	92.7(2)	166.8(1)			

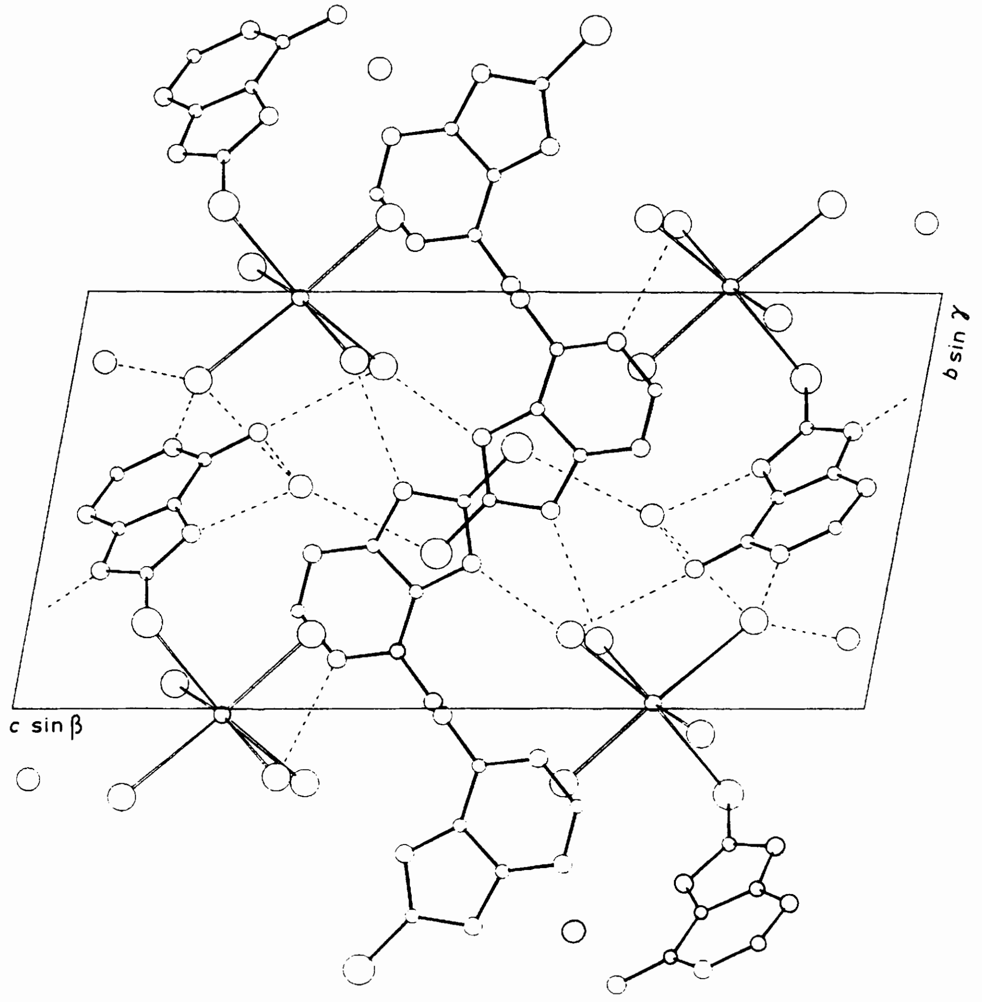
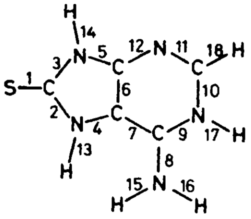


Figure 2. Structure of (3) projected along the *a* axis

system (Table 7), give a helpful criterion to establish when these atoms are protonated, as in (2) and (3) the presence of the very heavy bismuth atom does not allow the hydrogens to be reliably located. This is expressed by the empirical rule of Singh[9] for six-membered nitrogen heterocycles, which states that the angle at the nitrogen will fall in the range 125 ± 3° if the nitrogen is protonated and 116 ± 3° when hydrogen is not present; a similar trend is observed also in five-membered rings.[8] The rule is verified in the structure of (1) in which the protonated nitrogens N(1), N(7), and N(9) show the values 123.7(2), 109.7(2), and 110.0(2)° for their angles and N(3) (not protonated) 112.5(2)°. Also, the nitrogen atoms in the rings of the three molecules in (2) seem to be protonated, excepting N(31), N(32), and N(33): the smaller values for N(72) and N(73) show differences which are not significant. In (3) the two organic cations show a molecular geometry similar to those described above: all the nitrogens appear protonated excepting N(31) and N(32). The organic molecules in these compounds are not exactly planar as found in most cases, only molecule B of (2) is close to planar, whereas all the imidazole rings and the thiourea groups are planar. The angles formed between the mean planes of the imidazole and pyrimidine rings in each molecule are as follows: in (1), 1.43(7)°; in (2), 1.9(7) (molecule A), 1.4(7) (B), 3.1(7)° (C); in

Table 6. Structural parameters of the ligand molecules



(*a*) Bond distances (Å)

Compound	Molecule	1	2, 3	4, 5	6	7	8	9
(1)		1.659(2)	1.344(3), 1.377(4)	1.376(3), 1.366(3)	1.375(5)	1.394(3)	1.313(4)	1.371(4)
(2)	A	1.61(2)	1.37(3), 1.43(2)	1.37(3) 1.40(2)	1.37(3)	1.36(3)	1.31(3)	1.38(3)
	B	1.74(2)	1.34(3), 1.36(2)	1.35(2), 1.36(2)	1.35(3)	1.45(2)	1.35(3)	1.25(3)
	C	1.65(2)	1.44(2), 1.39(3)	1.41(2), 1.39(3)	1.40(3)	1.39(2)	1.38(3)	1.23(3)
(3)	A	1.70(1)	1.34(1), 1.39(1)	1.38(1), 1.38(1)	1.37(1)	1.41(1)	1.31(1)	1.38(1)
	B	1.66(1)	1.36(1), 1.37(1)	1.38(1), 1.36(1)	1.38(1)	1.37(1)	1.36(1)	1.35(1)

(*a*) Bond distances (Å)

Compound	Molecule	10	11	12	13, 14	15, 16	17	18
(1)		1.358(4)	1.305(3)	1.345(3)	0.91(4), 0.91(3)	0.86(4), 1.06(3)	1.02(2)	0.98(3)
(2)	A	1.32(3)	1.42(3)	1.31(2)				
	B	1.43(3)	1.29(3)	1.37(3)				
	C	1.37(3)	1.36(2)	1.27(3)				
(3)	A	1.36(1)	1.32(1)	1.34(1)				
	B	1.35(1)	1.30(1)	1.35(1)				

(*b*) Angles (°)

Compound	Molecule	1/2, 1/3	2,3	2/4, 3/5	4/6, 5/6	4/7, 5/12	6/7
(1)		126.7(2), 127.0(2)	106.2(2)	109.7(2), 110.0(2)	107.6(2) 106.3(2)	132.6(3) 127.1(2)	119.6(3)
(2)	A	131(1), 125(1)	103(1)	111(1), 109(1)	108(2) 106(1)	129(2) 125(1)	120(2)
	B	123(1), 125(1)	111(2)	104(1), 109(2)	110(1) 104(2)	133(2) 130(2)	116(2)
	C	122(1), 130(1)	107(1)	105(1), 111(2)	105(1) 109(1)	134(2) 129(2)	115(2)
(3)	A	127(1), 124(1)	108(1)	108(1), 108(1)	108(1) 106(1)	132(1) 125(1)	119(1)
	B	127(1), 126(1)	106(1)	109(1), 109(1)	107(1) 107(1)	135(1) 126(1)	117(1)

(*b*) Angles (°)

Compound	Molecule	7/9	7/8	8/9	9/10	10/11	11/12
(1)		112.6(3)	126.1(3)	121.2(2)	123.7(2)	124.8(3)	112.5(2)
(2)	A	111(2)	130(2)	118(2)	125(2)	122(2)	110(2)
	B	118(2)	121(2)	119(2)	121(2)	124(2)	113(2)
	C	118(2)	119(2)	121(2)	124(2)	120(2)	115(2)
(3)	A	112(1)	126(1)	121(1)	123(1)	125(1)	111(1)
	B	115(1)	125(1)	119(1)	122(1)	125(1)	112(1)

(3), 2.8(3) (molecule A), 3.0(3)° (B); these values agree with those found in similar compounds.[10] No systematic modifications in the co-ordinated and unco-ordinated molecules are apparent. An important feature of these compounds is the possible presence of base stacking; in (1) (Figures 3 and 4) two sets of molecules are stacked with a minimum intermolecular spacing C(8)···C(2^{i}) of 3.411(4) Å (i = $\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$). In (2) the angles formed between the mean

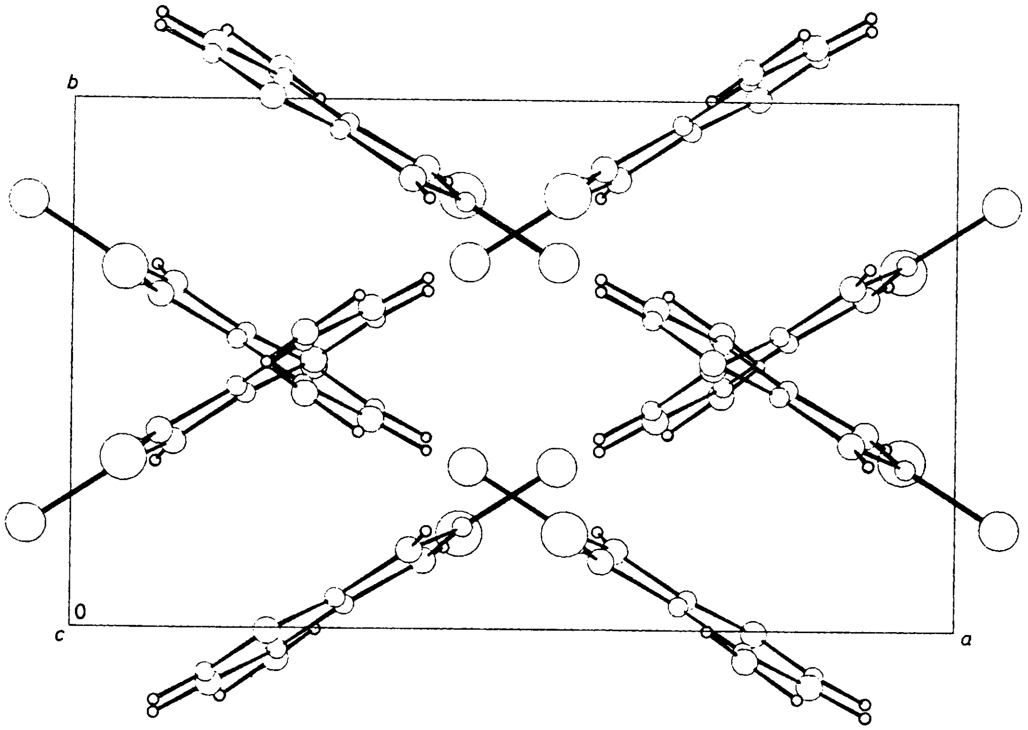


Figure 3. Stacking of the molecules of (1) viewed along the *c* axis

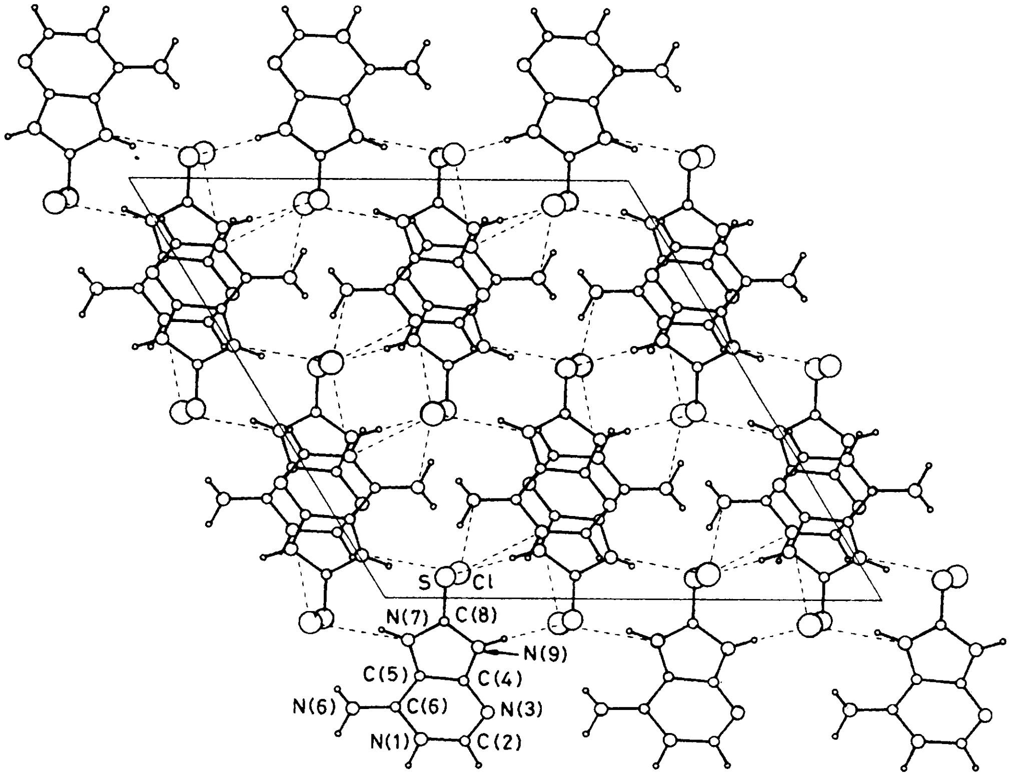


Figure 4. Hydrogen-bond system in the structure of (1)

planes of the three molecules are: A—B 1.5(3), A—C 0.5(3), and B—C 2.0(3)°, so that in this structure the ligands are all roughly parallel; the two unco-ordinated ligands are related by a 'quasi-centrosymmetry' which gives correlations of the type S(2) ≡ S(3), O(1) ≡ O(2), O(3) ≡ O(4), O(5) ≡ Cl(6). These molecules are stacked in ribbons along the *c* axis showing the short distances N(93) $\cdots$ C(82) 3.46(3), N(92) $\cdots$ $N(33^{i})$ 3.45(3), and N(32) $\cdots$ $N(93^{ii})$ 3.43(3) Å (ii = *x*, *y*,

Table 7. Hydrogen-bond distances (Å) and angles (°)

(*a*) In the ligand

N(9)–H	0.92(3)	N(9) ··· S^{i}	3.274(3)	H ··· S^{i}	2.36(3)	N(9)–H ··· S^{i}	174(2)
N(6)–H	1.06(3)	N(6) ··· Cl^{ii}	3.134(3)	H ··· Cl^{ii}	2.13(3)	N(6)–H ··· Cl^{ii}	156(3)
N(7)–H	0.91(4)	N(7) ··· Cl	3.036(3)	H ··· Cl	2.14(4)	N(7)–H ··· Cl	163(3)

(*b*) Possible hydrogen bonds in (2): hydrogens at calculated positions (N–H 1.00 Å)

N(91) ··· Cl(5)	3.03(2)	H ··· Cl(5)	2.08	N(1)–H ··· Cl(5)	157	O(3) ··· S(2)	3.30(2)
N(62) ··· O(4)	2.95(3)	H ··· O(4)	2.00	N(62)–H ··· O(4)	159	O(1) ··· O(4^{viii})	2.89(3)
N(72) ··· O(4)	2.71(3)	H ··· O(4)	1.79	N(72)–H ··· O(4)	151	O(1) ··· O(2)	2.82(3)
N(93) ··· Cl(6)	3.04(2)	H ··· Cl(6)	2.06	N(93)–H ··· Cl(6)	165	O(2) ··· O(3)	2.97(3)
N(71) ··· Cl(6^{iii})	3.04(2)	H ··· Cl(6^{iii})	2.05	N(71)–H ··· Cl(6^{iii})	168	Cl(6) ··· O(1)	3.11(2)
N(11) ··· Cl(4^{iv})	3.20(2)	H ··· Cl(4^{iv})	2.37	N(11)–H ··· Cl(4^{iv})	139	O(2) ··· O(5^{iii})	2.79(3)
N(92) ··· O(5^{v})	2.74(3)	H ··· O(5^{v})	1.74	N(92)–H ··· O(5^{v})	173		
N(12) ··· Cl(1^{vi})	3.26(3)	H ··· Cl(1^{vi})	2.31	N(12)–H ··· Cl(1^{vi})	159		
N(63) ··· Cl(3^{vii})	3.18(2)	H(1) ··· Cl(3^{vii})	2.21	N(13)–H(1) ··· Cl(3^{vii})	162		
N(73) ··· O(3^{vii})	2.64(3)	H ··· O(3^{vii})	1.74	N(73)–H ··· O(3^{vii})	148		
N(63) ··· O(3^{vii})	2.90(3)	H(2) ··· O(3^{vii})	1.98	N(63)–H(2) ··· O(3^{vii})	152		

(*c*) In the complex (3)

N(91) ··· O(2^{ix})	2.69(1)	H ··· O(2^{ix})	1.70	N(91)–H ··· O(2^{ix})	173	Cl(1) ··· O(1)	3.304(7)
N(92) ··· Cl(2^{x})	3.267(7)	H ··· Cl(2^{x})	2.27	N(92)–H ··· O(2^{x})	160	N(1) ··· O(2^{ix})	2.69(1)
N(12) ··· Cl(2^{xi})	3.23(1)	H ··· Cl(2^{xi})	2.32	N(12)–H ··· Cl(2^{xi})	151	Cl(3) ··· O(1^{xii})	3.228(7)
N(11) ··· Cl(3^{xii})	3.06(1)	H ··· Cl(3^{xii})	2.02	N(11)–H ··· Cl(3^{xii})	150	S(2) ··· O(1^{xii})	3.231(7)
N(61) ··· O(1)	3.00(1)	H ··· O(1)	2.00	N(61)–H ··· O(1)	171		
N(71) ··· O(1)	2.70(1)	H ··· O(1)	1.64	N(71)–H ··· O(1)	157		
N(72) ··· Cl(5)	3.172(8)	H ··· Cl(5)	2.18	N(72)–H ··· Cl(5)	160		

Symmetry operations

$\mathrm{i} = \bar{x}, y, \frac{1}{2} - z$
$\mathrm{ii} = \frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$
$\mathrm{iii} = \bar{x}, y - \frac{1}{2}, 1 - z$
$\mathrm{iv} = x - 1, y, 1 + z$
$\mathrm{v} = 1 - x, y - \frac{1}{2}, \bar{z}$
$\mathrm{vi} = 1 - x, \frac{1}{2} + y, \bar{z}$
$\mathrm{vii} = 1 + x, y, z$
$\mathrm{viii} = x, y, 1 + z$
$\mathrm{ix} = 2 - x, \bar{y}, \bar{z}$
$\mathrm{x} = 2 - x, -1 - y, 1 - z$
$\mathrm{xi} = 2 - x, \bar{y}, 1 - z$
$\mathrm{xii} = x - 1, 1 + y, z$
$\mathrm{xiii} = x, y - 1, z$

$z - 1$). In (3) the two independent Hamp^{+} cations are mutually disposed so that their mean planes form an angle of 50.9(1)°; the co-ordinated molecules show some stacking with a minimum distance N(91) ··· N(31^{iii}) of 3.26(1) Å (iii = $1 - x, -1 - y, \bar{z}$).

Molecular Packing.—All these structures are packed by van der Waals contacts and hydrogen bonds (Table 7). In (1) they are of the type N ··· S and N ··· Cl (Figure 4); in (2) the close packing involves the five water molecules, the chloride ion, several nitrogens and the S(2) atoms of the purine, and all the co-ordinated chlorines, excepting Cl(2) (Figure 1). Also in (3) (Figure 2) the hydrogen-bond system includes the two water molecules, Cl(2), Cl(3), Cl(5), and S(2) with several purine nitrogen atoms.

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Received 24*th January* 1984; *Paper* 4/130