Fig. 2. The *a* axis projection of the crystal structure. The dashed lines indicate hydrogen bonds.

the distortion of the tetrahedral angles around Zn^{2+} (Fig. 2).

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(+)-Lupanine Perchlorate Monohydrate

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Abstract. $C_{15}H_{25}N_2O^+.ClO_4^-.H_2O$, monoclinic, $M_r = 366.9$, $P2_1$, $Z = 2$, $a = 9.014$ (2), $b = 15.491$ (2), $c = 7.473$ (1) Å, $\beta = 123.32$ (1)°, $\mu(Cu\ K\alpha) = 2.25\ mm^{-1}$, $D_c = 1.40\ Mg\ m^{-3}$; $R = 0.044$, $R_w = 0.049$ for 835 reflections. The C ring of the lupanine skeleton adopts the boat conformation. The lupanine cations are linked together by a hydrogen-bond network utilizing the O atom from the water molecule $[N(16)\cdots O(W)\cdots O(C2): N(16)\cdots O(W) = 2.817$ Å, $O(W)\cdots O(C2) = 2.717$ Å$]$.

Introduction. This work is an extension of the X-ray study on the conformation and structural properties of lupanine derivatives and salts in the solid state. Spectroscopic data (Wiewiórowski, Edwards & Bratek-Wiewiórowska, 1967) confirmed by X-ray analysis (Doucerain, Chiaroni & Riche, 1976) indicated a boat conformation for ring C of the lupanine molecule, both in the solid state and in solution. An interesting exception is 13-hydroxylupanine (Kaluski, Gar-barczyk, Gusiev, Struchkov, Skolik & Wiewiórowski, 1977), where ring C adopts a chair conformation in the solid state, but the boat form in chloroform solution. As far as the stereochemistry of lupanine salts in solution is concerned it was previously suggested, on the basis of

spectroscopic measurements (Wiewiórowski & Lompa-Krzemień, 1969; Skolik, Barciszewski, Rafalski & Wiewiórowski, 1971), that N(16) protonation does not change the boat conformation of ring C in the lupanine skeleton. An X-ray analysis of (+)-lupanine hydrochloride dihydrate (Skrzypczak-Jankun & Kaluski, 1978) has shown that this conformation is also present in the solid state. Spectroscopic studies on other lupanine salts have indicated that in solution the anion does not significantly affect the configuration and conformation of the alkaloid skeleton (Wiewiórowski, Skolik & Perkowska, 1979). In order to find whether this statement also holds for the solid state, an X-ray study of (+)-lupanine perchlorate monohydrate has now been carried out. A further interesting point concerns the influence of the hydrogen-bonding net-work, and other intramolecular forces, on the confor-mation of ring A, containing the lactam group.

The title compound has been obtained and analysed by spectral methods by Skolik (1962). It was recrystal-lized from methanol and ether by vapour diffusion. A crystal $0.3 \times 0.15 \times 0.4$ mm was used on the $P2_1$ Syntex diffractometer; 892 reflections were obtained of which 835 with $I > 1.96\sigma(I)$ were included in the calculations. The cell dimensions were obtained by a

least-squares fit to 15 reflections. The $\theta/2\theta$ scanning technique was used with graphite-monochromated Cu $K\alpha$ radiation ($2\theta < 120°$) and a variable scan speed. Lorentz and polarization corrections were applied, but no absorption corrections were made.

The structure was solved by *MULTAN*. The E map revealed all the nonhydrogen atoms, except for the O atoms of the ClO_4^- group and the water molecule. These were found on the next Fourier map; 19 H atoms out of 27 were found on the difference Fourier map. The positions of six H atoms [attached to C(4), C(12) and C(13)] were calculated using a C–H distance of 1·07 Å and a tetrahedral angle of 109·5°. The positional and isotropic thermal parameters were included in the calculations, but not refined. Full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, was performed with weights (in the last few cycles of refinement), $w = (F_o/5·5)^2$ if $F_o < 5·5$, $w = 1$ if $5·5 < F_o < 12·6$ and $w = (12·6F_o)^2$ if $F_o > 12·6$ to $R = 0·044$ and $R_w = 0·049$ for 835 reflections.* Scattering factors were from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Nova 1200 computer using programs in the Syntex *XTL/E-XTL* structure determination system (Syntex, 1976).

The positional parameters for all atoms are given in Table 1.

Discussion. Fig. 1 shows a schematic view of the lupanine cation with the bond lengths, valency angles (with their e.s.d.'s) and endocyclic torsion angles. The cation consists of two *trans* quinolizidine systems. The bond lengths within the lactam group in ring A are similar to those in ($\pm$)-lupanine (Doucerain *et al.*, 1976) and (+)-lupanine.HCl.2H$_2$O (Skrzypczak-Jankun & Kałuski, 1978). The characteristic distances C(2)=O(C2) [1·245 (9) Å] and N(1)–C(2) [1·357 (11) Å] are equal within 2σ to those found in the above-mentioned structures (1·236, 1·353 Å and 1·222, 1·376 Å respectively). The least-squares plane N(1), C(2), C(6), C(10) is less planar (see Table 2) than that in (+)-lupanine.HCl.2H$_2$O and is comparable with that in (+)-lupanine. The angle between the plane discussed above and the lactam plane defined by N(1), C(2), O(C2), C(3) is the same (about 6°) in the three structures.

The main differences in the conformation of the lupanine skeleton with respect to the two other lupanine derivatives are in ring A (Fig. 1b). The endocyclic torsion angles which differ most are around N(1)–C(6), N(1)–C(2) and C(2)–C(3) bonds, resulting in a different conformation for ring A. The asymmetry parameters (Duax & Norton, 1975) of ring A for these three lupanine structures (Table 3) show that ring A in the structure of the title compound has a dominant twofold axis perpendicular to the N(1)–C(2) bond with $\Delta C_2^{1,2} = 2·3°$, consistent with a half-chair conformation. All the other asymmetry parameters for ring A are large, indicating lack of symmetry. While in ($\pm$)-lupanine (Doucerain *et al.*, 1976) mirror symmetry about the plane through N(1) and C(4) is dominant ($\Delta C_s^1 = 4·5°$), indicating a sofa conformation, in (+)-

Table 1. *Fractional atomic coordinates* ($\times 10^4$, *for H* $\times 10^3$)

B_{iso} for the H atoms is 5 Å^2.

	x	y	z
Cl	7265 (2)	2643 (0)	654 (4)
O(1)	5834 (10)	3222 (6)	9680 (14)
O(2)	8116 (10)	2640 (6)	9484 (16)
O(3)	6687 (14)	1846 (5)	604 (20)
O(4)	8502 (12)	2949 (11)	2651 (19)
O(C2)	6805 (6)	5211 (4)	−1312 (9)
O(W)	6769 (6)	4009 (5)	−3982 (10)
N(1)	9528 (6)	5447 (3)	1651 (7)
N(16)	3051 (6)	3844 (3)	3768 (8)
C(2)	7750 (9)	5339 (4)	655 (11)
C(3)	6931 (8)	5385 (5)	1942 (12)
C(4)	8000 (9)	5869 (6)	4000 (12)
C(5)	9886 (8)	5551 (5)	5201 (11)
C(6)	692 (7)	5713 (4)	3885 (9)
C(7)	2562 (7)	5286 (5)	4916 (11)
C(8)	3290 (8)	5536 (5)	3569 (12)
C(9)	2090 (8)	5126 (5)	1375 (10)
C(10)	269 (8)	5548 (5)	324 (11)
C(11)	1954 (7)	4142 (4)	1485 (9)
C(12)	2535 (9)	3665 (5)	201 (12)
C(13)	2450 (10)	2694 (6)	322 (14)
C(14)	3524 (9)	2417 (4)	2670 (13)
C(15)	2948 (9)	2873 (4)	3972 (12)
C(17)	2525 (8)	4311 (5)	5128 (11)
H(3)	687	476	202
H(3')	428	53	937
H(4)	745	577	495
H(4')	797	654	366
H(5)	930	82	309
H(5')	999	−3	457
H(6)	902	138	617
H(7)	680	58	366
H(8)	673	113	669
H(8')	544	44	539
H(9)	747	24	977
H(10)	965	112	−7
H(10')	64	40	116
H(11)	59	404	109
H(12)	388	385	79
H(12')	169	385	−144
H(13)	111	250	−40
H(13')	300	240	−49
H(14)	353	182	262
H(14')	482	251	332
H(15)	162	263	321
H(15')	371	263	568
H(N16)	423	404	423
H(17)	107	418	424
H(17')	327	399	680

Table 2. *Least-squares planes*

Equations of the planes expressed in orthogonalized space as $AX + BY + CZ = D$

Plane 1: $-0.1520X + 0.9704Y - 0.1879Z = 6.8691$
Plane 2: $-0.0518X + 0.9857Y - 0.1603Z = 7.7419$
Plane 3: $-0.0576X + 0.0657Y - 0.2531Z = 7.4533$

Deviations of atoms from the planes (Å)

Plane	N(1)	C(2)	O(C2)	C(3)	C(4)	C(5)	C(6)	C(10)	χ^2
1	−0.077	0.060	0.104*	0.166*			0.041	0.046	359.8
2	0.000	−0.002	0.000	0.001	0.532*	−0.137*	0.177*		0.1
3	−0.021	0.044	0.165*	−0.022	0.374*	−0.361*	0.017		70.5

The dihedral angle between planes 1 and 2 is 6.0°.
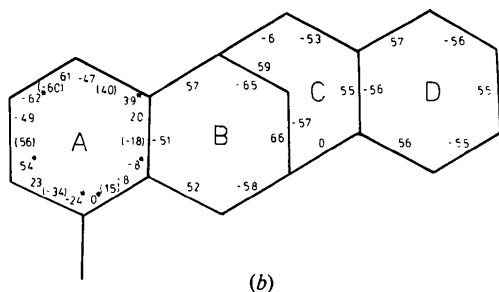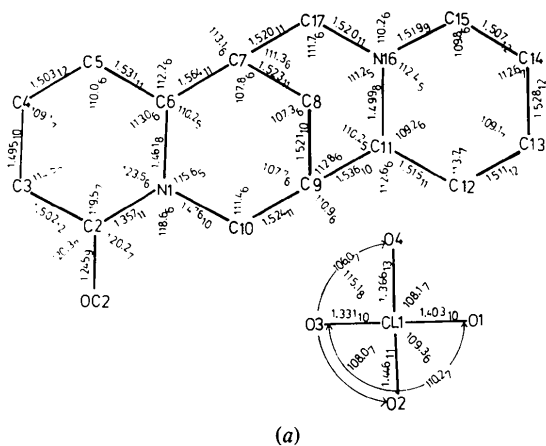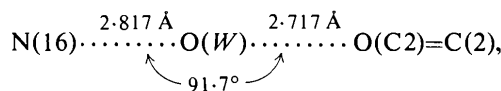
* Atoms not included in plane calculations.

(a)

(b)

Fig. 1. The lupanine cation. (a) Bond lengths (Å) and valency angles (°) with their e.s.d.'s. (b) Endocyclic torsion angles (°). The values in parentheses correspond to those in (±)-lupanine (Doucerain *et al.*, 1976), and values marked by an asterisk to those of (+)-lupanine.HCl.2H₂O (Skrzypczak-Jankun & Kałuski, 1978).

lupanine.HCl.2H₂O (Skrzypczak-Jankun & Kałuski, 1978) ring *A* shows both approximate mirror and twofold symmetries ($\Delta C_s^1 = 10.7°$ and $\Delta C_2^{1,2} = 15.7°$) and its conformation, therefore, lies between a sofa and a half-chair. As in (±)-lupanine and (+)-lupanine.HCl.2H₂O, rings *B* and *D* exist in the chair and ring *C* in the boat conformations. The main deviations

from the ideal chair are in ring *B* ($\Delta C_2 = 14.2°$) due to N—C bonds; the torsion angles and asymmetry parameters of rings *C* and *D* indicate no significant distortion.

The average values of the C—C and N(16)—C bond lengths are 1.521 Å and 1.513 Å, respectively, and are in good agreement with the corresponding values in other lupanine and sparteine derivatives. The perchlorate anion has a relatively high thermal motion, but there are no strong indications of disorder (the mean values of the Cl—O bonds and the O—Cl—O angles are 1.387 Å and 109.4° respectively).

The lupanine cations are linked together by a three-dimensional hydrogen-bond network utilizing the O atom from the water molecule (the water H atoms were not found). This network can be schematically represented by:

$$N(16) \overset{2.817\,\text{Å}}{\cdots\cdots\cdots} O(W) \overset{2.717\,\text{Å}}{\cdots\cdots\cdots} O(C2){=}C(2),$$
$$\underset{91.7°}{\diagdown\qquad\diagup}$$

where O(C2) is at $(1 + x, y, 1 + z)$ [N(16)—H = 0.97 Å, H···O(W) = 1.91 Å, ∠N(16)—H—O(W) = 154°]. The O(W)···O(C2) distance is close to that of the corresponding hydrogen bond in (+)-lupanine.HCl.2H₂O (2.77 Å). There is another short intermolecular contact between O(W) and O(2) from ClO₄⁻ with a distance of 3.037 Å, which falls near the lower

Table 3. *Asymmetry parameters for ring A of (±)-lupanine* (Doucerain *et al.*, 1976) (I), (+)-*lupanine.-HCl.2H₂O* (Skrzypczak-Jankun & Kałuski, 1978) (II) *and the title compound* (III)

	(I)	(II)	(III)
$\Delta C_2^{1,2}$	16.0	15.7	2.3
$\Delta C_2^{2,3}$	41.5	54.1	41.0
$\Delta C_2^{3,4}$	25.5	38.4	38.7
ΔC_s^1	4.5	10.7	17.1
ΔC_s^2	27.1	32.9	20.4
ΔC_s^3	31.6	43.6	37.6
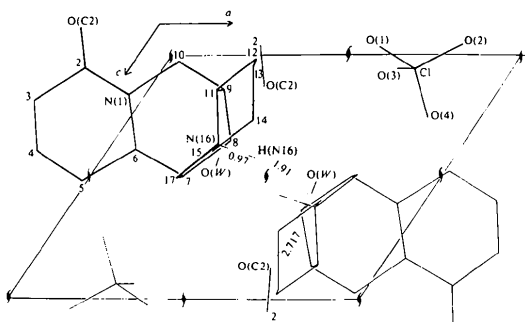
Fig. 2. Projection of the structure along [010].

Fig. 3. ORTEP drawing of the cation with thermal ellipsoids at 50% probability.

limit of the O···O intermolecular-distance range (3·02–3·42 Å, Kitaigorodsky, 1976).

The molecular packing in the unit cell is shown in Fig. 2, and an ORTEP drawing at 50% probability is given in Fig. 3.

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2-Azaadenosine Hemihydrate

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Abstract. $C_9H_{12}N_6O_4 \cdot \frac{1}{2}H_2O$, orthorhombic, $C222_1$, $a = 7\cdot860$ (9), $b = 9\cdot445$ (10), $c = 31\cdot156$ (26) Å, $U = 2312\cdot9$ Å^3, $Z = 8$, $D_c = 1\cdot592$, D_m (flotation in benzene/carbon tetrachloride) $= 1\cdot56$ (1) Mg m^{-3}. The nucleoside adopts the anti conformation with a torsion angle, χ, of $13\cdot8°$. There is approximate 85/15 disorder around the exocyclic bond C(4')–C(5'), the major component exhibiting the gauche–gauche (gg) confor-mation while the minor component is gauche–trans (gt).

Introduction. The nucleoside was generously donated by Dr J. A. Montgomery (Southern Research Institute). Crystals of relatively poor quality were obtained by slow evaporation of an aqueous solution. The crystal used for data collection, like all other crystals examined, was twinned [the twinning plane being (001)] and had approximate dimensions 0·72 ×