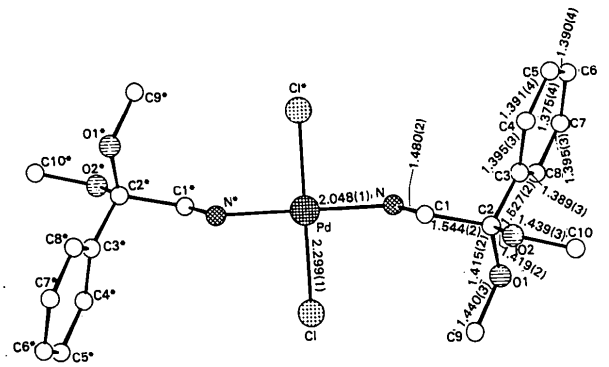

Fig. 1. The molecular structure of (1).

an observation of unit weight. In the final refinement cycle the maximum shift to e.s.d. ratio was 0·6. A correction for the effects of anomalous dispersion for Pd (f' −1·177, f'' 1·007) and Cl (f' 0·132, f'' 0·159) was included in the structure-factor calculations. Atomic scattering curves were taken from *International Tables for X-ray Crystallography* (1974). In the final difference Fourier synthesis, peaks of ±1·5 e Å^{-3} were observed in the vicinity of the Pd atom with much lower values elsewhere.*

Discussion. The results of the X-ray analysis are summarized in Tables 1 and 2, which give the final atomic coordinates and bond angles, and Fig. 1, which shows the molecular structure of (1) and the bond distances. The molecule crystallizes with one molecule in the centrosymmetric space group $P\bar{1}$. The metal atom lies on an exact centre of symmetry and has square-planar coordination geometry with the two amine groups occupying *trans* positions. The Pd—N bond length is comparable with those found in other complexes containing an amine bonded to a Pd atom [2·018 (8) Å, Drew, Riedl & Rodgers (1972); 2·054 (9), 2·055 (9), 1·985 (8) Å, Ferguson & Parvez, (1979)]. Bond distances and angles in the remainder of the molecule are as expected.

There are no intermolecular contacts between non-H atoms less than 3·2 Å.

* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43873 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$\Delta^{1(2)}$-Dehydro-2-methylsparteinium Diperchlorate Monohydrate

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(*Received* 27 *June* 1986; *accepted* 26 *January* 1987)

Abstract. $C_{16}H_{26}N_2^{2+}.2ClO_4^-.H_2O$, $M_r = 463·3$, orthorhombic, $P2_12_12_1$, $a = 13·185$ (1), $b = 17·650$ (2), $c = 9·029$ (1) Å, $V = 2101·2$ (5) Å^3, $Z = 4$, $D_m = 1·46$ (1), $D_x = 1·47$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 31·0 cm^{-1}, $F(000) = 976$, $T = 298$ K, $R = 0·072$ for 1592 unique observed reflections. The quinolizidinium and quinolizidine moieties have quasi-*trans* and *trans* configurations, respectively.

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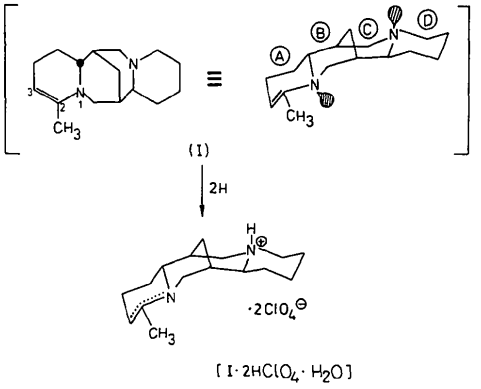
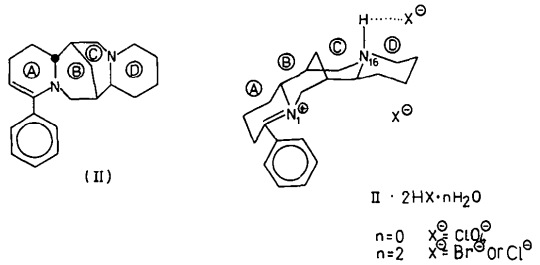
Introduction. This study is a continuation of our previous X-ray and spectroscopic investigations of immonium salts in bis(quinolizidine) systems (Katrusiak, Kałuski, Pietrzak & Skolik, 1983, 1986*a*; Katrusiak, 1983). $\Delta^{1(2)}$-Dehydro-2-methylsparteine diperchlorate monohydrate (herein referred to as $I.2HClO_4.H_2O$) differs from the previously studied immonium salts as its immonium bond is not a common bridge to two piperidinium rings but is located only within the outer ring (*A*), which significantly changes the conformational properties of this part of the sparteine skeleton (Katrusiak & Kałuski, 1982).



During the analysis of the IR spectra of Δ^2-dehydro-2-phenylsparteine (II) and its disalts (hydrobromide – $II.2HBr.2H_2O$, hydrochloride – $II.2HCl.2H_2O$, perchlorate – $II.2HClO_4$)(Boczoń, 1987), we found that the IR spectra of the dihydrobromide and dihydrochloride salts are very similar, whereas that of the diperchlorate salt is essentially different. According to expectations, in the IR spectra of dihalogenide salts there are present very characteristic stretching vibration bands of the immonium group [$-C{=}N(1)^+-$] at 1680 cm^{-1}, resulting from the β protonation of the α,β-enamine system of (II). No such band is observed in the IR spectrum of the diperchlorate salt of (II). To explain these results, strange and difficult to reconcile with our previous studies of immonium salts, it became necessary to determine the precise structure of the cation and so an X-ray analysis of $II.2HClO_4$ has been undertaken (Małuszyńska, Boczoń & Kałuski, 1987).



The X-ray analysis showed that the perchlorate salt of (II) has the same configuration and conformation:

trans A/B chair/chair – *trans C/D* boat/chair

as the free base (II) and its dihydrohalogenide salts, and also possesses the immonium group. Assuming that the IR differences in the localization of immonium bands in perchlorate and hydrochloride salts of (II) are tightly connected with some special interaction between the phenyl-substituted immonium cation and the counter anion, we undertook the synthesis and structural studies of the title compound ($I.2HClO_4.H_2O$) (Boczoń, 1987). The present paper describes the X-ray study of this compound.

Experimental. Colourless orthorhombic bipyramidal crystals of the title compound were obtained by slow diffusion of diethyl ether vapour into its ethanol solution. After several days, during the determination of space group on a Weissenberg camera, cracks in the crystal were noticed, the number of which increased slowly with time. The cracks were not necessarily related to crystallographic directions, although some cracks, apparently along crystallographic planes, were observed as well. The process of breaking up of the crystals was very slow and differed for different samples. The density measurement, by the flotation method, revealed that there are four water molecules per unit cell present in the structure. A fragment, 0·25 × 0·25 × 0·35 mm, was used for data collection – no cracks were noticed in it after the measurement. A Syntex $P2_1$ diffractometer was used with graphite-monochromated Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å. Lattice parameters were determined from measurement of 15 reflections, $14 < 2\theta < 29°$. Two control reflections, monitored after every 50 measurements, showed no systematic variation of intensity. 2θ–θ scan technique with a variable scan speed (ranging from 2·0 to 29·3° min^{-1}) was applied. Up to $2\theta = 125{\cdot}0°$, 1871 independent reflections were measured (h 0/15, k 0/10 and l 0/10), 1592 of which had $I \geq 1{\cdot}96\sigma_I$. The background and integrated intensity for each reflection were obtained by the profile analysis method of Lehmann & Larsen (1974). The intensities were corrected for Lp effects only.

The structure was solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The positions of the H atoms were calculated from the geometry of the dication and recalculated after each cycle of refinement. They were assigned $U_{iso} = 0{\cdot}07$ Å^2 and not refined. Two hydrogens of the water molecule could not be found. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The final cycles gave: $R = 0{\cdot}072$, $wR = 0{\cdot}072$, $S = 1{\cdot}52$, max. $\Delta/\sigma = 0{\cdot}12$; min. and max. peaks on the difference Fourier map, 0·70 and −0·70 e Å^{-3}, respectively, were close to the disordered oxygen atoms of perchlorate

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^3$) *of nonhydrogen atoms*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
O(*W*)	4449 (19)	3110 (10)	494 (20)	390
Cl(1)	3631 (2)	8079 (1)	7844 (3)	70
O(11)	3325 (14)	7389 (5)	8279 (13)	384
O(12)	4455 (8)	7981 (11)	7132 (19)	264
O(13)	2898 (11)	8379 (10)	7052 (16)	247
O(14)	3756 (9)	8544 (5)	9108 (11)	146
Cl(2)	4986 (2)	9752 (1)	2503 (3)	58
O(21)	4315 (7)	9952 (6)	1353 (10)	144
O(22)	5497 (6)	10408 (4)	3031 (9)	111
O(23)	5706 (6)	9260 (5)	1992 (14)	148
O(24)	4382 (6)	9393 (4)	3619 (8)	94
N(1)	6674 (5)	6695 (4)	8873 (8)	46
C(2)	6365 (6)	7311 (5)	9537 (10)	54
C(18)	5686 (7)	7294 (6)	10827 (10)	74
C(3)	6744 (7)	8068 (5)	9086 (12)	70
C(4)	7719 (8)	8033 (6)	8197 (13)	84
C(5)	7601 (8)	7473 (5)	6950 (12)	77
C(6)	7361 (6)	6692 (5)	7554 (10)	55
C(7)	6937 (6)	6153 (5)	6343 (11)	57
C(8)	6837 (6)	5351 (5)	6980 (11)	57
C(9)	6065 (6)	5398 (5)	8272 (10)	51
C(10)	6467 (7)	5925 (4)	9443 (9)	52
C(11)	5019 (6)	5652 (4)	7669 (9)	46
C(12)	4197 (7)	5052 (5)	7875 (11)	66
C(13)	3166 (7)	5335 (7)	7332 (14)	77
C(14)	3224 (8)	5583 (6)	5730 (13)	77
C(15)	4068 (7)	6160 (5)	5496 (11)	68
N(16)	5065 (5)	5868 (4)	6055 (7)	48
C(17)	5892 (6)	6424 (5)	5776 (11)	58

anions. The final atomic parameters are listed in Table 1.* Most of the calculations were performed with *SHELX*76 (Sheldrick, 1976) on a RIAD 32 computer; atomic scattering factors from *International Tables for X-ray Crystallography* (1974) were applied.

The absolute configuration of the dication was assigned according to the previous determination of the absolute configuration for this group of sparteines by spectroscopic methods as C(7) *S* and C(9) *S* (Klyne, Scopes, Thomas, Skolik, Gawroński and Wiewiórowski, 1974).

Two months after the crystallization all the crystals disintegrated into a white, powder-like substance. The IR spectrum of this powder did not demonstrate the presence of water molecules.

Discussion. The highest magnitudes of temperature factors are those of the oxygen atoms of the water molecule and perchlorate anions. The atoms of the dication, especially the most peripheral ones, have high temperature parameters, too. Presumably this is due to a small partial disorder of the structure, often observed in the crystals of perchlorate salts, here consisting of: (i) small disorientations of the perchlorate anions around their centres – *i.e.* chlorine atoms; (ii) small displacements of the water-molecule oxygen atom, which is involved in hydrogen bonds between the two perchlorate anions, and (iii) small disorientation of the dication. This disorder can be blamed for the increased *R* values and relatively high e.s.d.'s of the refined parameters.

Fig. 1 shows the atom numbering, bond lengths and valency angles. The bonds in the perchlorate anions appear to be shorter (Truter, Cruickshank & Jeffrey, 1960) owing to the disordered orientation of the anions.

The length of the immonium bond $>N^+=C<$ is slightly longer, although within three standard deviations, than that observed previously for immonium bonds situated between two piperidinium rings.

Fig. 2 presents a perspective drawing of the dication with the endo- and exocyclic torsion angles as well as torsion angles C(18)–C(2)–N(1)–C(10) and C(18)–C(2)–C(3)–C(4) describing the position of the methyl substitutent. The conformation of the rings can be described as:

ring *A* – intermediate between sofa and half-chair,
ring *B* – chair,
ring *C* – boat,
ring *D* – chair.

The asymmetry parameters (Duax & Norton, 1975) for these rings are:

ring *A*: $\Delta C_s^1 = 12\ (1)$ $\Delta C_2^{1,2} = 13\ (1)$ $\Delta C_2^{2,3} = 55\ (1)°$;
ring *B*: $\Delta C_s^1 = 1\ (1)$ $\Delta C_2^{1,10} = 3\ (1)$ $\Delta C_2^{6,7} = 9\ (1)°$;
ring *C*: $\Delta C_s^8 = 2\ (1)$ $\Delta C_s^{7,17} = 10\ (1)°$;
ring *D*: $\Delta C_s^{11} = 1\ (1)$ $\Delta C_2^{11,16} = 2\ (1)$ $\Delta C_2^{11,12} = 2\ (1)°$.

Ring *B* is only slightly more flattened in the region of atom N(1) than in 2-methylsparteine perchlorate (Katrusiak, Hoser, Kałuski & Boczoń, 1980); despite the sp^2 hybridization of N(1), the C(6)–N(1)–C(10) valency angle is close to the 109° tetrahedral value. Atoms N(1),C(2),C(6) and C(10) form a flat system, as the other two valency angles are larger than 120° and

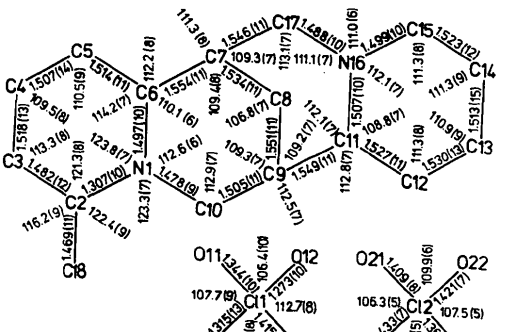


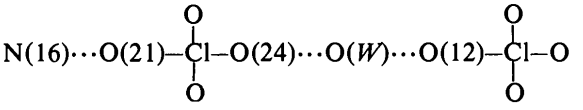
Fig. 1. Bond lengths (Å) and valency angles (°). The quantities in parentheses denote the e.s.d.'s.

* Lists of structure factors, anisotropic thermal parameters and the positions of H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43749 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

compensate for the small value of C(6)–N(1)–C(10). From a number of other bis(quinolizidine) immonium salts studied crystallographically it appears as a rule that the valency angle C–$\overset{\|}{N^+}$–C opposite to the immonium bond (N^+=C) has its value close to 109°, while the two other valency angles C–N^+=C adjacent to the immonium bond are significantly larger than 120°. In $\Delta^{1(6)}$-dehydrosparteinium perchlorate (Katrusiak, Kałuski, Pietrzak & Skolik, 1986*a*), $\Delta^{1(6)}$-dehydrosparteinium diperchlorate (Katrusiak, Kałuski, Pietrzak & Skolik, 1986*b*), $\Delta^{1(6)}$-dehydro-17-oxosparteinium perchlorate (Katrusiak, Kałuski, Pietrzak & Skolik, 1983), $\Delta^{1(6),11(16)}$-didehydrosparteinium diperchlorate (Katrusiak, Kałuski, Pietrzak & Skolik, 1986*c*) and $\Delta^{11(16)}$-dehydrolupaninium perchlorate monohydrate (Katrusiak, Kałuski, Pietrzak & Skolik, 1987) the immonium bond is situated between two adjacent piperidinium rings, differently than in (I); therefore it seems that the observed distortion of the valency angles around N^+ is a characteristic property of the immonium bond, rather than being caused by the strains due to the closing of the rings.

The molecular packing in the unit cell is shown in Fig. 3.

The dication, two perchlorate anions and the water molecule are interconnected by hydrogen bonds:



The geometry of the first of these bonds can be described by the following values: N(16)···O(21) = 2·83 (1), N(16)–H(16) = 1·08, H(16)···O(21) = 1·87 Å and angle N(16)–H(16)···O(21) = 146°. The lengths of the two other hydrogen bonds are: O(*W*)···O(24) = 2·85 (2); O(*W*)···O(12) = 2·79 (2) Å. The O(12)···O(*W*)···O(24) angle equals 116°. These values are similar to those observed in the structure of perchloric acid trihydrate (Almlöf, 1972). Surprisingly, no water of crystallization was noted for the crystals of $\Delta^{1(2)}$-dehydro-2-phenylsparteinium diperchlorate (Małuszyńska, Boczoń & Kałuski, 1987) despite its close resemblance to $I.2HClO_4.H_2O$.

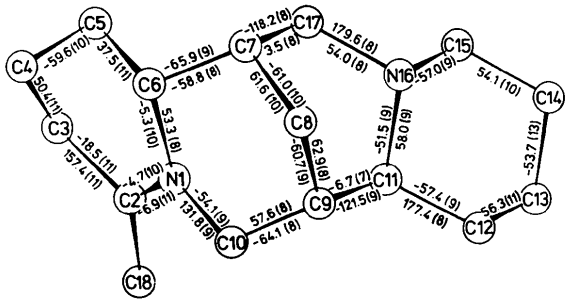


Fig. 2. A perspective view of the dication with torsion angles (°).

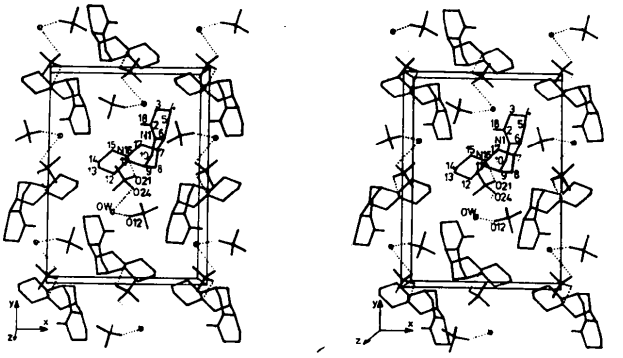


Fig. 3. A stereoscopic view of the unit-cell contents (Motherwell & Clegg, 1978) along **c**.

We thank Professor Maciej Wiewiórowski for suggesting this structure determination. This investigation was supported by the Polish Academy of Sciences, Grant MR-I.9.

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