

The Nature of Water in Hydrazine Salt Hydrates

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Infrared spectra, differential thermal analysis, and conductivity studies have been carried out to determine the nature of water of constitution in hydrazine salt hydrates. The possibility of water being present as the oxonium ion, H_3O^+ , has been investigated.

It is of interest to determine the nature of water of constitution in crystalline hydrates and to distinguish between a true hydrate and a pseudohydrate.¹ X-Ray crystallography can be a useful tool for such investigations. This technique is, however, restricted to salts where single crystals can be obtained. I.r., Raman, and ¹H n.m.r. spectra have been used to distinguish between a true hydrate and a pseudohydrate. The absence of i.r. absorptions in the range 1 700—1 600 cm^{-1} due to the water bending frequency $\delta(\text{H}_2\text{O})$ is usually taken as proof of the absence of normal water of hydration. A combination of X-ray crystallography and i.r., Raman, and n.m.r. spectroscopy has been used to show that oxonium ions are present in hydrofluoric acid monohydrate ($\text{H}_3\text{O}^+\text{F}^-$),²⁻⁶ hydrochloric acid monohydrate ($\text{H}_3\text{O}^+\text{Cl}^-$),^{6,7} perchloric acid monohydrate ($\text{H}_3\text{O}^+\text{ClO}_4^-$),⁸⁻¹³ nitric acid monohydrate ($\text{H}_3\text{O}^+\text{NO}_3^-$),^{10,11,14} and sulphuric acid dihydrate (H_3O^+)₂ SO_4^{2-} .^{11,15}

A survey of the literature¹⁶ on hydrazine salts reveals that only a few hydrazine salts form hydrates, e.g. $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$, $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, $\text{N}_2\text{H}_6\text{Br}_2 \cdot 2\text{H}_2\text{O}$, $\text{N}_2\text{H}_6\text{I}_2 \cdot 2\text{H}_2\text{O}$, $(\text{N}_2\text{H}_5)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, $(\text{N}_2\text{H}_5)_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and hydrazinium(1+) picrate hemihydrate, $\text{N}_2\text{H}_5\text{C}_6\text{H}_2\text{O}(\text{NO}_2)_3 \cdot 0.5\text{H}_2\text{O}$. Very little work has been carried out to throw light on the nature of water present in hydrazine salt hydrates. The X-ray crystal structure of $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ has been studied by Liminga¹⁷ and interestingly he has indicated that the water is H-bonded to N_2H_5^+ ions. Surprisingly the i.r. spectra of hydrazine salt hydrates have not been reported except for the work by Jacobs and Russell-Jones¹⁸ who reported the water bending frequency $\delta(\text{H}_2\text{O})$ at 1 600 cm^{-1} . However, they did not deal with the aspect of the nature of water present in $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$, the objective of the present investigation.

Experimental

Hydrazinium(1+) perchlorate hemihydrate, $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ was prepared by the reaction¹⁹ of ammonium perchlorate with hydrazine hydrate as well as by the conventional method.²⁰ Anhydrous hydrazinium perchlorate, $\text{N}_2\text{H}_5\text{ClO}_4$, was prepared by the dehydration of $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ kept in an air oven at 100 °C for 5 h. Hydrazinium(2+) perchlorate dihydrate, $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, was prepared by the neutralisation of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (99.5%) with 60% perchloric acid at 0 °C, as described in the literature.²⁰ Hydrazinium(2+) bromide dihydrate, $\text{N}_2\text{H}_6\text{Br}_2 \cdot 2\text{H}_2\text{O}$ was prepared by neutralising $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ with excess of dilute hydrobromic acid (47%) at 0 °C. All these hydrated hydrazine salts were washed with chloroform to free them from adsorbed acid. These salts were characterised by chemical analysis, i.r. spectra, and differential thermal analysis (d.t.a.). The hydrazine content was determined by titration with 0.025 mol dm^{-3} KIO_3 under Andrews' conditions.²¹ The i.r. spectra were recorded using Carl Zeiss UR-10 and Perkin-Elmer spectrophotometers. The samples were prepared as Nujol mulls and KBr pellets. Differential thermal analysis was carried out

using a d.t.a. unit²² constructed in the laboratory and fitted with a Omniscrite two-pen stripchart recorder. All d.t.a. runs were made in air. Platinum cups were used as sample holders; 30-mg samples were used for d.t.a. experiments. Thermogravimetry experiments were carried out in nitrogen atmospheres using a Stanton-Redcroft 750/770 thermobalance. The heating rate employed was 5 °C min^{-1} ; ca. 7 mg of the sample was used for each experiment. Thermogravimetric experiments on the hydrazine perchlorate salts could not be carried out above 100 °C because of the explosive nature of the compounds. The electrical conductivity of $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ was measured using a pellet of the compound by a two-probe method.²³ A GR-1608A impedance bridge fed by a voltage stabiliser and fitted with a GR-1232A tuned amplifier and a null detector was used for this purpose.

Results and Discussion

The observed i.r. absorption frequencies of $\text{N}_2\text{H}_5\text{ClO}_4$, $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$, $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $\text{N}_2\text{H}_6\text{Br}_2 \cdot 2\text{H}_2\text{O}$ have been tabulated and assigned (Table 1).

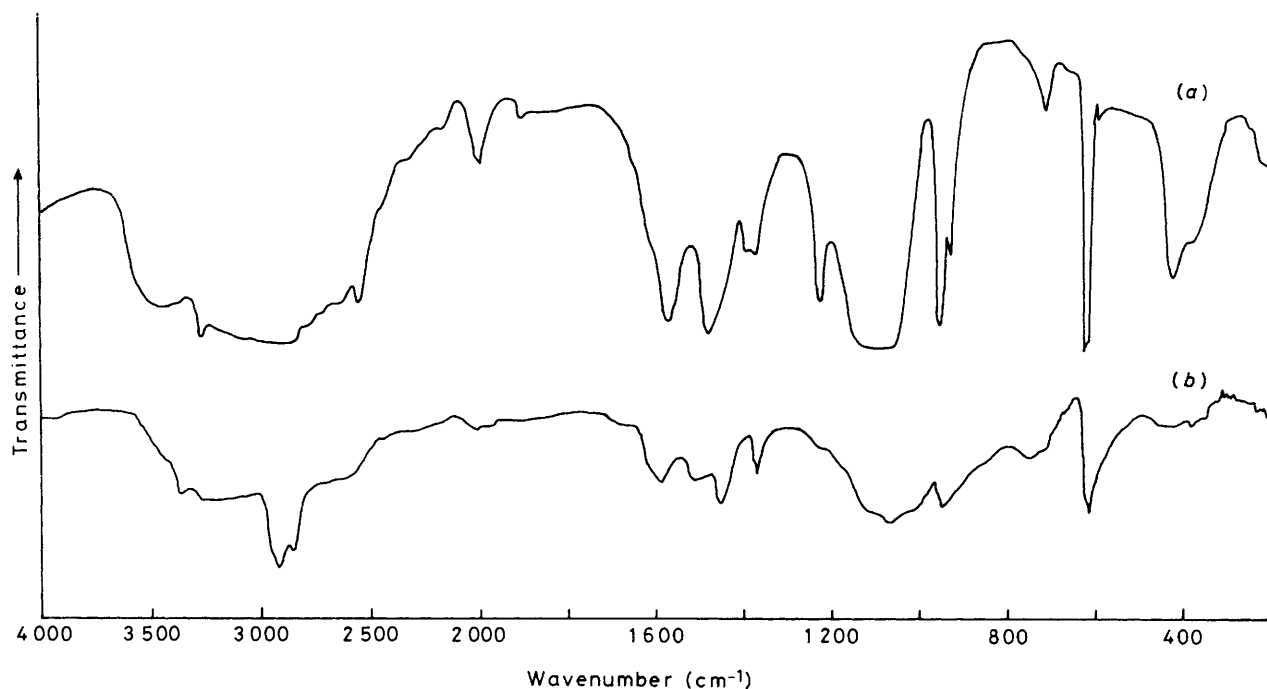
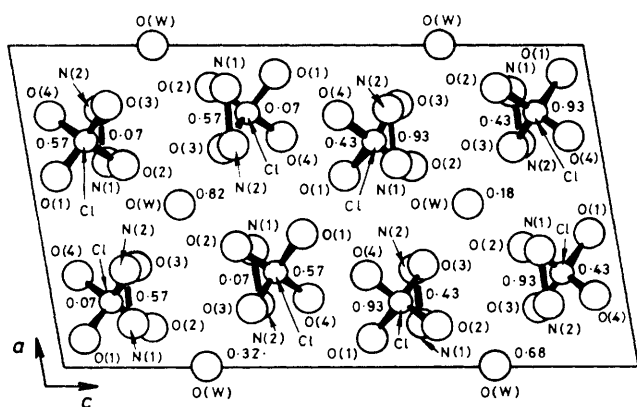
The i.r. spectrum of $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ is shown in Figure 1. Absorption frequencies of N_2H_5^+ are observed at 3 400—3 300, 1 570, and 960 cm^{-1} and those of perchlorate at 1 100 and 620 cm^{-1} . It is interesting to note additional bands at 3 280, 2 560, 2 000, and 1 570 cm^{-1} . The assignment of these absorptions could be made by assuming the presence of oxonium (H_3O^+) ions or H-bonded water since normal H_2O of hydration is not known to exhibit these absorptions.

The X-ray crystal structure (Figure 2) studies of $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ by Liminga¹⁷ show that the water molecules lie on two-fold axes in channels formed between hydrazinium(1+) and perchlorate columns and are linked to N_2H_5^+ ions by hydrogen bonds. The water oxygen atom O(W) and the nearest nitrogen neighbours form a roughly tetrahedral arrangement; the N—O distances are N(2)—H···O(W) 2.837 and O(W)—H···N(1) 2.897 Å. The assumption made was that N(2) and N(1) correspond to the nitrogens NH_3^+ and NH_2 , respectively, of N_2H_5^+ .

It can be seen that the observed N—O distances are slightly less than the sum of van der Waals radii²⁴ of N (1.55 Å) and O (1.50 Å), thus suggesting that the H-bonding in $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ is rather weak.²⁵ For strong H-bonding²⁵ $d(\text{N—O})$ should be ≤ 2.70 Å, therefore the observed i.r. absorptions at 3 280, 2 560, 2 000, and 1 570 cm^{-1} cannot be attributed to strong H-bonding. The presence of weak H-bonding, however, cannot be ruled out and this cannot explain the appearance of the band at 1 570 cm^{-1} . The only alternative, thus appears to be the possibility of the presence of oxonium (H_3O^+) ions. The i.r. absorptions at 2 560, 2 000, and 1 570 cm^{-1} , in particular, are characteristic of H_3O^+ as observed in the case of hydrochloric acid monohydrate, $\text{H}_3\text{O}^+\text{Cl}^-$,⁶ perchloric acid monohydrate, $\text{H}_3\text{O}^+\text{ClO}_4^-$,⁶ nitric acid monohydrate, $\text{H}_3\text{O}^+\text{NO}_3^-$,¹⁰ and sulphuric acid dihydrate, $(\text{H}_3\text{O}^+)_2\text{SO}_4^{2-}$.¹¹ The characteristic i.r. absorption frequencies of oxonium ions of

Table 1. Infrared frequencies (cm^{-1}) of $\text{N}_2\text{H}_5\text{ClO}_4$, $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$, $\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $\text{N}_2\text{H}_6\text{Br}_2 \cdot 2\text{H}_2\text{O}$

Assignment	$\text{N}_2\text{H}_5\text{ClO}_4$	$\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$	$\text{N}_2\text{H}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{N}_2\text{H}_6\text{Br}_2 \cdot 2\text{H}_2\text{O}$
$\nu(\text{O-H})$ of H_2O			3 600br	3 600br
Hydrazine bands $\begin{cases} \nu(\text{N-H}) \\ \nu(\text{N-N}) \end{cases}$	3 380br, m	3 400—3 300br, m	3 400—3 300br, m	3 400—3 300br
	960m	960s	980s	980s
Perchlorate bands $\begin{cases} \nu_3 \\ \nu_4 \end{cases}$	1 100br, m	1 100br, s	1 100s	
	620s	620s	620s	
Oxonium bands $\begin{cases} \nu_1 \\ \nu_3 \\ \nu_2 \\ \nu_4 \end{cases}$		3 280br	3 240s	
		2 560br	2 560m	2 560br
		2 000s	2 060w, 1 940w, 1 810w	2 060s, 1 940s, 1 810s
		1 570br	1 600s	1 600br, w

**Figure 1.** Infrared spectra of (a) $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ and (b) $\text{N}_2\text{H}_5\text{ClO}_4$ as Nujol mulls**Figure 2.** Structure of $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ projected along the b axis: N(1) = nitrogen of NH_2 , N(2) = nitrogen of NH_3^+ . Y Co-ordinates (Å) are given for the Cl atoms and for the centres of the N-N bonds.

$\text{H}_3\text{O}^+\text{Cl}^-$, $\text{H}_3\text{O}^+\text{ClO}_4^-$, $\text{H}_3\text{O}^+\text{NO}_3^-$, and $(\text{H}_3\text{O}^+)_2\text{SO}_4^{2-}$ are listed in Table 2.

It should be noted that the band at 1570 cm^{-1} is due to

Table 2. The characteristic i.r. frequencies (cm^{-1}) of various oxonium compounds

Assignment	H_3OCl	H_3OClO_4	H_3ONO_3	$(\text{H}_3\text{O})_2\text{SO}_4$
	-195°C	-20°C	-180°C	-180°C
ν_1	3 235	3 285		
ν_3	2 590		2 780	2 560
ν_4	1 700	1 577	1 680	1 620
ν_2	1 150, 1 060	1 182	1 135	1 160

both oxonium ion, $\delta(\text{H}_3\text{O}^+)$, and hydrazinium ion, $\delta(\text{NH}_3^+)$. The inference that the oxonium ion is present in $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ is further substantiated by the reduced intensity of the band at 1570 cm^{-1} and the absence of oxonium bands in anhydrous hydrazinium(1+) perchlorate, $\text{N}_2\text{H}_5\text{ClO}_4$ (Figure 1). Although it is possible to dehydrate $\text{N}_2\text{H}_5\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ by keeping the salt in an air oven at 100°C for 5 h, the d.t.a. results (Table 3) show that only partial dehydration takes place at 71°C (endotherm) where the weight loss is 1.72%. Complete dehydration would have resulted in a weight loss of 6.36%. This suggests that not all water is present as

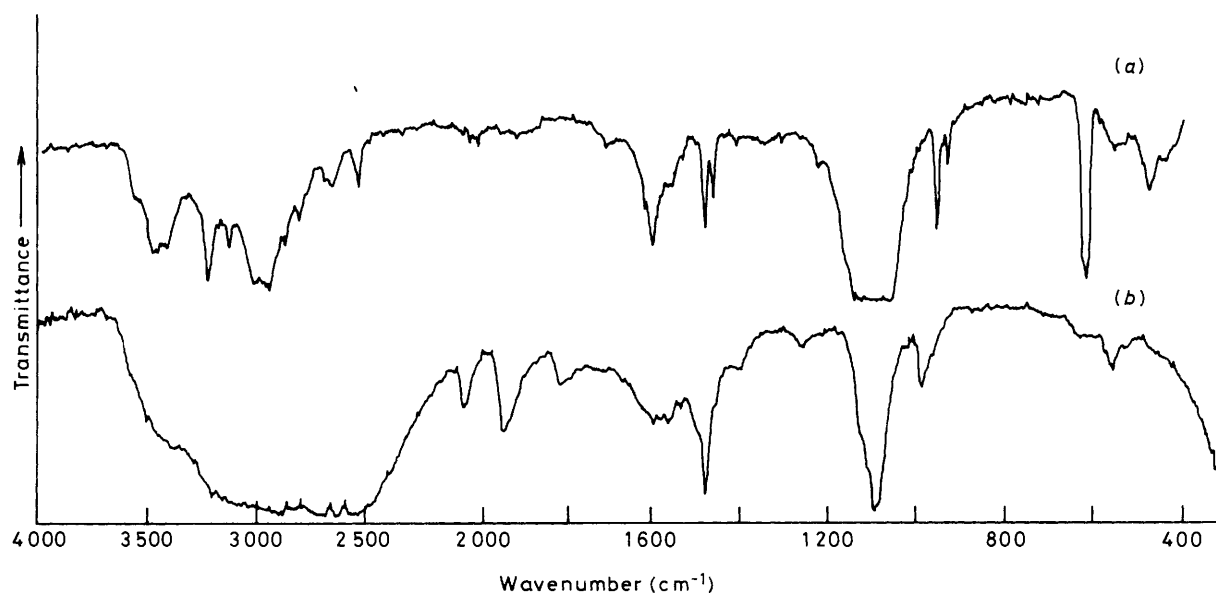


Figure 3. Infrared spectra of (a) $N_2H_6(ClO_4)_2 \cdot 2H_2O$ and (b) $N_2H_6Br_2 \cdot 2H_2O$ as KBr pellets

Table 3. Differential thermal analysis of $N_2H_5ClO_4$, $N_2H_5ClO_4 \cdot 0.5H_2O$, $N_2H_6(ClO_4)_2 \cdot 2H_2O$, and $N_2H_6Br_2 \cdot 2H_2O$

Compound	D.t.a. peak temperature* (°C)	% Weight loss	Reaction
$N_2H_5ClO_4$	149(-) m		Melting
	263(+), 353(+)	explodes	Decomposition
$N_2H_5ClO_4 \cdot 0.5H_2O$	71(-)	1.72	Partial dehydration
	263(+), 353(+)	explodes	Decomposition
$N_2H_6(ClO_4)_2 \cdot 2H_2O$	100(-)	5.33	Partial dehydration
$N_2H_6Br_2 \cdot 2H_2O$	273(+)	explodes	Decomposition
	59(-)	6.54	Partial dehydration
	251(+)	100	Decomposition

* (-) endothermic peak, (+) exothermic peak; m = melting.

H_3O^+ ions, some molecules being present as water of hydration. Since the chemical analysis corresponds to $N_2H_5ClO_4 \cdot 0.5H_2O$, the formula can be written as $(N_2H_5ClO_4)_2 \cdot H_2O \rightleftharpoons N_2H_5^+ H_3O^+ (ClO_4^-)_2 \cdot N_2H_4$.

This new formulation could explain all the observed i.r. and thermal data. The concentration of oxonium ions appears to be small.

Wide-line n.m.r. studies could not be used to establish this phenomenon (as was done in the case of $H_3O^+ ClO_4^-$ ¹³) since the wide-line n.m.r. spectrum of the salt showed a broad absorption at room temperature and it is difficult to distinguish N_2H_4 and H_3O^+ protons. In solution there was rapid exchange and only OH protons could be seen.

Further evidence for the presence of H_3O^+ ions in $N_2H_5ClO_4 \cdot 0.5H_2O$ comes from the conductivity experiments. The conductivity (σ) of $N_2H_5ClO_4 \cdot 0.5H_2O$ was found to be $4.8 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C. This value is comparable with the value of $1 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ reported²⁶ for hydronium alunite, $(H_3O,K)Al_3(SO_4)_2(OH)_6$ at 20°C. The observed conductivity has been attributed to the presence of

oxonium ions. The conductivity value of $H_3O^+ ClO_4^-$ ²⁷ at 25°C is $3 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. Therefore, it appears that some of the water molecules are present as H_3O^+ ions in $N_2H_5ClO_4 \cdot 0.5H_2O$.

In summary, data obtained from the present investigations (i) i.r. studies of $N_2H_5ClO_4 \cdot 0.5H_2O$ at room temperature, (ii) i.r. studies of anhydrous $N_2H_5ClO_4$, (iii) d.t.a. studies coupled with X-ray crystallographic studies on $N_2H_5ClO_4 \cdot 0.5H_2O$, and (iv) conductivity data lead to the conclusion that a small concentration of oxonium ions is present in $N_2H_5ClO_4 \cdot 0.5H_2O$.

The assumption of H_3O^+ ion being present in hydrazine salt hydrates further gains support from the i.r. data of $N_2H_6(ClO_4)_2 \cdot 2H_2O$ and $N_2H_6Br_2 \cdot 2H_2O$ which show i.r. absorptions around 2000 cm^{-1} (Figure 3). This could be due to higher concentrations of H_3O^+ ions being present in these salts: they can be written as $N_2H_6(ClO_4)_2 \cdot 2H_2O \rightleftharpoons (H_3O^+ ClO_4^-)_2 \cdot N_2H_4$ and $N_2H_6Br_2 \cdot 2H_2O \rightleftharpoons (H_3O^+ Br^-)_2 \cdot N_2H_4$ respectively.

Unfortunately, X-ray crystal studies for both of these salts have not been reported. Thermal analyses of the salts (Table 3) show that it is difficult to remove the water of hydration completely without decomposing the compound. Thus for instance the d.t.a. studies of $N_2H_6(ClO_4)_2 \cdot 2H_2O$ show a partial weight loss of 5.33% at 100°C (complete dehydration would have resulted in a weight loss of 15.65%). Therefore, i.r. and d.t.a. studies appear to indicate the presence of some oxonium ions in hydrazinium(2+) perchlorate dihydrate and hydrazinium(2+) bromide dihydrate.

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