Some further Remarks on the Structure of Salt Monohydrates

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The empirical rules governing water molecules in salt hydrates which I attempted to find were derived from the study of the 25 presumably correct structures then published. These 25 structures I took to be representative for all salt hydrate types. As pointed out by Lindqvist the list contains not many salts of trivalent cations. Apart from AlCl₃·6H₂O mentioned by Lindqvist and the isomorphous CrCl₃·6H₂O the list contains only the alum structure in which however a large number of different trivalent cations may be accommodated. An obvious flaw of the list is that it contains no salts of mononuclear acido-aquo-anions, which ought not to have been overlooked. It might — even without knowledge of Lindqvist's structure determination for \((\text{NH}_4)_2\text{FeCl}_6\cdot\text{H}_2\text{O}\) — have been inferred that acido-aquo-anions only with difficulty could be packed in a crystal in such a fashion that a water molecule will have negative neighbours on the opposite side of that touching the central atom of the complex anion. In the case of Lindqvist's salt it is almost a physical impossibility.

Even if the rule that a water molecule in a crystal shall have positive neighbours on one side, negative neighbours * on the opposite side is not without exceptions, the number of exceptions will tend to be small for the following reason: Imagine the full mathematical expression for the lattice energy of a salt in which this rule is not obeyed. The terms in this expression which pertain to the attraction between a water molecule and its immediate neighbours will be small compared with the corresponding terms in the lattice energy expression for a salt hydrate in which a water molecule has positive and negative neighbours on opposite sides. Consequently the total lattice energy can reach a reasonable size only if the lattice energy expression contains other terms which are extraordinarily large, and only in that exceptional case can the salt be stable.

Because the lattice energy expression of such salts contain terms which as pointed out are extraordinarily small one should expect such salts to be very soluble rather than insoluble in water.

Now the question arises: in which compounds can the de-stabilizing effect of these small lattice energy terms be counterbalanced to such an extent that a stable crystal (even if a very soluble one) results? One may perhaps conjecture: in some crystals in which shared electron forces are found, crystal which contain complex ions known as definite chemical entities from solutions.

But not necessarily in all such crystals. CrCl₃·6H₂O and a number of alums contain aquo-lattice-complexes which dissolve as such. Nevertheless all water molecules in these crystals obey the rules formulated by me, which is another reason why I think that exceptions from the rules tend to be rare.

A hydrate like K₆FeCl₆·H₂O contains a water molecule in a state of strain as compared with the state of a water molecule in one of the 25 hydrates from which the rules were derived, and the forthcoming accurate parameter determination will be of more than usual interest.

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