

NOTIZEN

Fe(II) in Water: a Proposal for Dimerization

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The ^{57}Fe Mössbauer quadrupole splittings of $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ (known to contain $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$) and fast frozen aqueous solutions of Fe(II) are different. We propose an explanation in terms of the dimerization of Fe(II) in aqueous solution *via* an H_3O_2^- , H_5O_2^+ double bridge.

Several different forms of hydrated hydroxonium ions have now been characterized in crystalline salts [1–4], as has also the monohydrated form of the hydroxide ion [5]. Both H_5O_2^+ and H_3O_2^- often contain a short symmetric hydrogen bond. The bond energy is quite large, 132 kJ/mol for H_5O_2^+ [6] and calculated as 163 kJ/mol for H_3O_2^- [7]. As pointed out by Minyaev [8], these energies are fully comparable to the values of the energies of formation of weak covalent chemical bonds. More recently, the ion H_3O_2^- has been found as a bridge between various metal cations *e.g.* W(IV), Mo(IV), Cr(III), Co(III) and Rh(III) [9–11] in several crystal structures. It was proposed that H_3O_2^- -bridged polymer ions might be a general phenomenon in aqueous solutions of many metal ions [9]. Three-phase vapour tensiometry was successfully used to demonstrate the presence of bis- H_3O_2^- -bridges in an aqueous solution of $\text{Cr}(\text{bipy})_2$ [12]. Very recently we have been able to show *via* Mössbauer spectroscopy that $[\text{Fe}(\text{H}_3\text{O}_2)\text{Fe}]_{\text{aq}}^{5+}$ is a major hydrolysis product of ferric ion in water [13]. Here we address the question of whether ^{57}Fe Mössbauer spectroscopy provides any evidence for H_3O_2^- bridge formation for Fe(II) in aqueous solution.

The Mössbauer parameter which could be sensitive to H_3O_2^- bridges is the quadrupole splitting which depends on the electric field gradient (EFG) at the nucleus. For the case of Fe(III) which has a spherically symmetric electron charge cloud ($3d^5$, $^6\text{S}_0$)

the EFG is determined by the charge distribution of the surrounding ligands. For Fe(II) there is an extra electron which produces a large valence electron contribution. Ingalls [14] has shown that a tetragonal or trigonal distortion of an octahedral Fe(II) ion leads to the ligand and valence contributions to the EFG having opposite signs. For a given ligand environment the ligand contribution to the quadrupole splitting for Fe(II) is expected to be only about 5% less than the corresponding Fe(III) species. The 20% reduction due to Fe(II) having a larger radius than Fe(III) (78 pm *vs.* 65 pm) is almost counterbalanced by its larger Sternheimer antishielding coefficient (–10.6 *vs.* –9.14 [15]).

As a prototype for a symmetrical $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion in water we consider the ferrous salt $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ in which the ions are surrounded fairly symmetrically by 6 water molecules [16]. This salt has a quadrupole splitting (QS) of 3.7 mm/s at 77 K [17]. Several authors have examined Fe^{2+} in quickly frozen solutions and find a quadrupole splitting of ~ 3.3 mm/s [18–20]. The difference between this value and the value of 3.7 mm/s obtained for $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ is 0.4 mm/s. This is close to the QS observed for the ferric species which we have identified with $[\text{Fe}(\text{H}_3\text{O}_2)\text{Fe}]_{\text{aq}}^{5+}$. We therefore propose that Fe^{2+} in aqueous solution is also coordinated by H_3O_2^- groups.

We now consider the possible geometry for Fe^{2+} bridged by H_3O_2^- bridges. In the Mössbauer spectra essentially all $\text{Fe}^{2+}(\text{aq})$ ions give a quadrupole doublet with $\text{QS} \sim 3.3$ mm/s and thus are associated *via* an H_3O_2^- bridge. However, the first hydrolysis constant, pK_1 , for $\text{Fe}^{2+}(\text{aq})$ is much higher than that for $\text{Fe}^{3+}(\text{aq})$ [21], so a $[\text{Fe}(\text{II})\text{H}_3\text{O}_2\text{Fe}(\text{II})]_{\text{aq}}^{3+}$ dimer (analogous to the $[\text{Fe}(\text{III})\text{H}_3\text{O}_2\text{Fe}(\text{III})]_{\text{aq}}$ already discovered [13]) is not plausible. We need a species which retains the proton released during H_3O_2^- bridge formation. We propose a second bridge of H_5O_2^+ . This species is known to exist in over a dozen compounds [22] and the typical O...O distance is 240–245 pm, quite similar to the 240–255 pm found for bridging H_3O_2^- [11]. It is, of course, unusual to propose a cation (H_5O_2^+) as bridging between two other cations ($\text{Fe}^{2+}_{\text{aq}}$). However, the positive charge of H_5O_2^+ resides on the central proton. At the metal cation coordination by a H_5O_2^+ bridge resembles coordination by H_3O^+ which is isoelectronic with NH_3 . Cations which can form stable amines should also accept bridging by H_5O_2^+ . The formation of a H_3O_2^- , H_5O_2^+ double bridge is energetically fa-

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avourable as the two strong hydrogen bonds amount to ≈ 300 kJ/mol. Also, the negative charge of H_3O_2^- resides on the oxygens close to the positive ferrous ions which leads to an extra electrostatic stabilization energy.

Ruby *et al.* [19] have observed that a quickly frozen glass of FeCl_2 in H_2O with $\text{QS} = 3.35$ mm/s spontaneously crystallizes at 190 K to a phase with $\text{QS} = 3.73$ mm/s assigned to a $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ local structure. We propose that this change in the Mössbauer parameters in fact corresponds to the transformation of H_3O_2^- , H_5O_2^+ double bridges back into H_2O ligands.

Similar double bridges could exist for many metal cations in aqueous solution. The question arises why

Fe^{3+} (aq) does not form such bridges. Ferric amines are unstable and dissociate in water. By contrast Fe(II), Cr(III) and Co(III) amines are stable. It is known that pK_1 for Cr^{3+} (aq) is considerably higher than for Fe^{3+} (aq) despite the fact that Cr^{3+} has a smaller radius. This may reflect the formation of a H_3O_2^- , H_5O_2^+ double bridge in the case of Cr^{3+} . At higher pH the H_5O_2^+ could transform into a second H_3O_2^- bridge giving an aqueous species similar to that observed by Ardon and Bino [10]. A water bridged inner-sphere pathway has been proposed for the $[\text{Co}(\text{OH}_2)_6]^{3+,2+}$ self-exchange reaction [23]. An alternative inner-sphere acid-independent pathway for such reactions could be the H_3O_2^- , H_5O_2^+ double bridge proposed here.

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