Using an extended X-ray absorption fine structure (EXAFS) technique, the formation constant of the pentaaquachloroiron(III) complex was determined to be $3.8 \pm 0.4$ mol$^{-1}$ dm$^3$ at 25.0 ± 0.1 °C in a 1.00 mol dm$^{-3}$ HClO$_4$ aqueous solution. The structures of [Fe(OH$_2$)$_6$]$^{3+}$ and [FeCl(OH$_2$)$_5$]$^{2+}$ were determined on the basis of the same EXAFS data. The Fe–O bond length (2.05 Å) in the latter is longer than that (2.01 Å) in the former due to the electron donation and charge neutralization by the coordinating chloride ion with the Fe–Cl bond length of 2.26 Å.