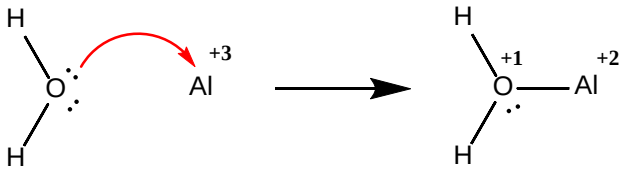
Answers to Exercise 10.4
Aqua Complexes of Metal Cations as Acids

1.

(a)

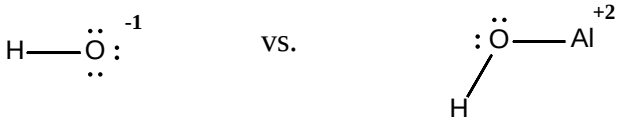


(b) The hydrogen atoms on the Lewis acid-base adduct are more acidic.

The O-H bond in water is polar because oxygen is more electronegative than hydrogen so it pulls more of the electron density in the O-H bond toward itself, leaving a partially positive hydrogen atom.

In the adduct, the strongly positive aluminium cation pulls electron density away from the oxygen atom (as shown by the oxygen atom acquiring a positive formal charge). This makes the oxygen atom pull even more of the electron density in the O-H bond toward itself, leaving an even more partially positive hydrogen atom than in the free water molecule.

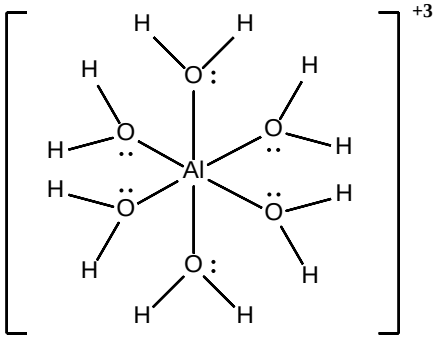
Also, compare the deprotonation products ("conjugate bases") of the two species:



In the conjugate base of water, there is a full -1 charge on the oxygen atom.

In the conjugate base of the adduct, the oxygen atom has a neutral formal charge (preferable to the +1 formal charge before it was deprotonated).

(c)



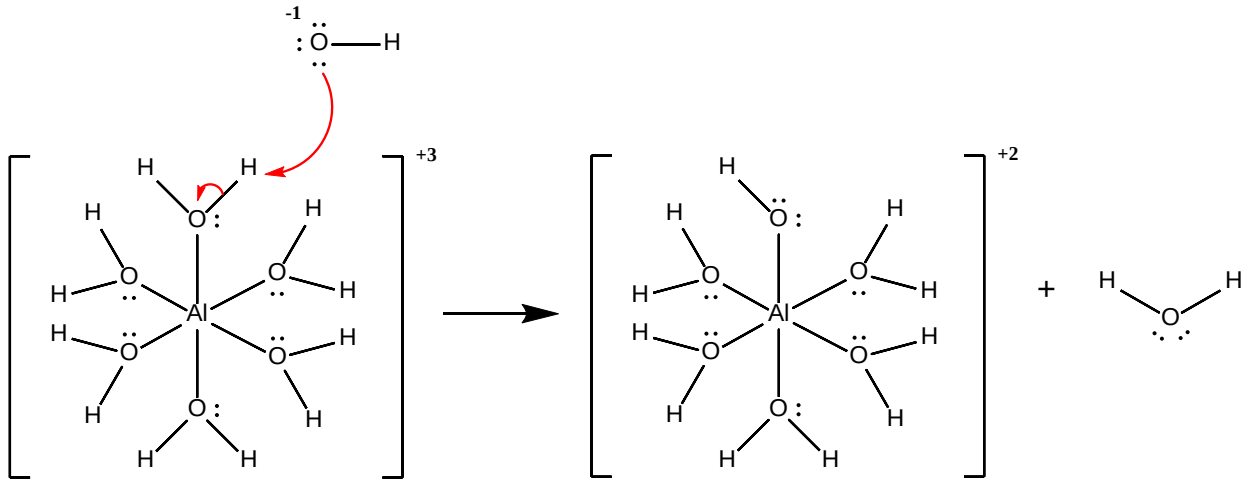
(d) The pK_a of water is 14.

Since the pK_a of $[Al(OH_2)_6]^{3+}$ is 5, its pK_a value is 9 lower than that of water.

Therefore, the acidity of this complex is 10^9 times stronger than that of water.

That's one billion times stronger!

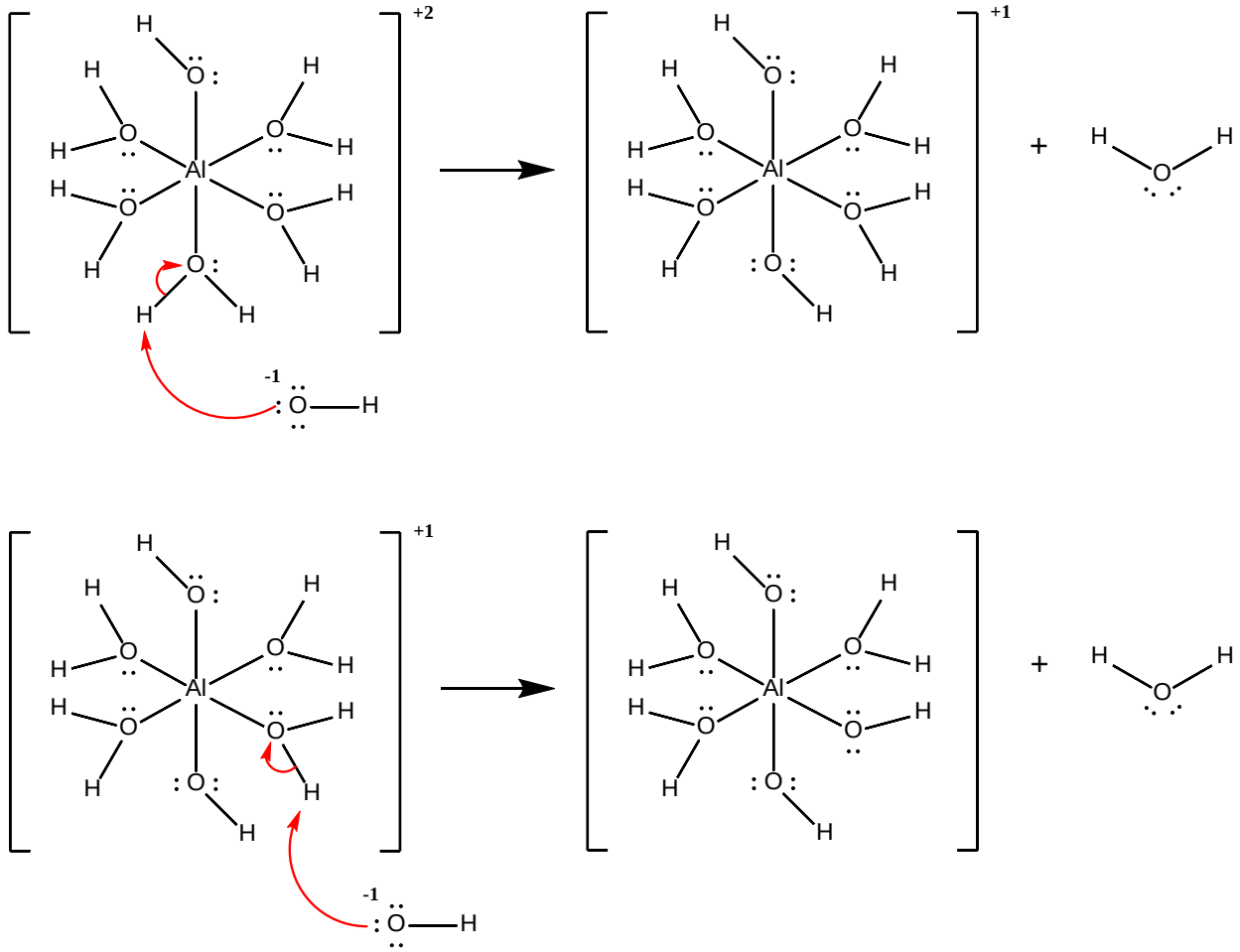
(e)

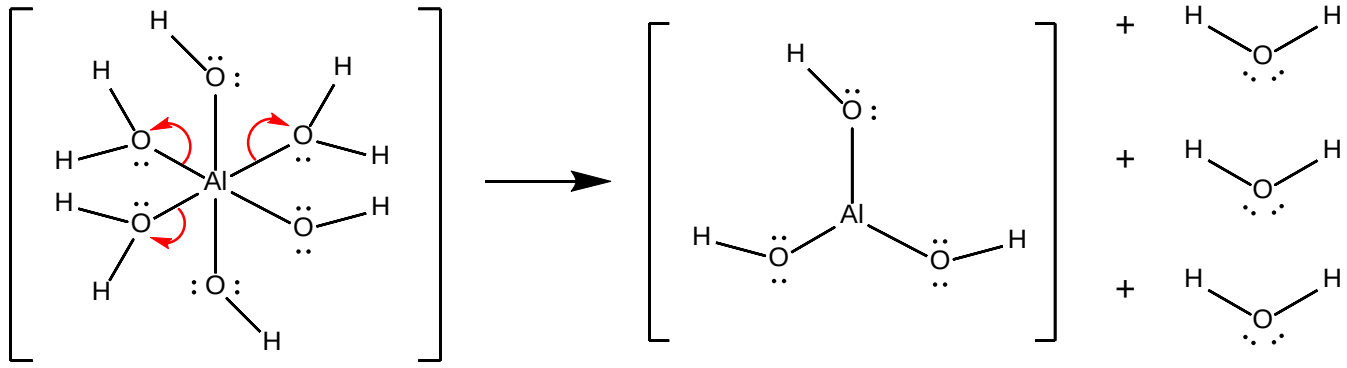


(f) 3

The charge of the complex is reduced by one every time a hydroxide ion removes H^+.

(g)





It is also acceptable to group the water molecules as 3 H_2O.

(h) Al salts will dissolve in aqueous solutions with low pH values since there will not be many hydroxide ions to deprotonate the water-soluble $[Al(OH_2)_6]^{3+}$ complex.

As the pH increases, the concentration of hydroxide increases so there are more hydroxide ions available to deprotonate the aluminium complex, and the insoluble $Al(OH)_3$ is produced.

Recall from the Group 13 topic that when the concentration of hydroxide is high enough (i.e. the pH is high enough), $Al(OH)_3$ will react with another hydroxide to give the water-soluble $[Al(OH)_4]^-$ anion.

Overall, this means that aluminium salts are soluble in low-pH aqueous solutions (<3) and in high-pH aqueous solutions (>11) but not in solutions with midrange pH values (~3-11).