

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ as an example.

Co^{3+} has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.

This weakens the O–H bond causing the complex to be acidic in aqueous solution.

Solution A consists of a 0.10 M aqueous solution of $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)](\text{NO}_3)_3$ at 25 °C. Calculate the pH of Solution A. The $\text{p}K_a$ of $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+} = 5.69$.

As $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ is a weak acid, $[\text{H}_3\text{O}^+]$ must be calculated using a reaction table (acid = $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ and base = $[\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+}$)

	acid	H_2O	\rightleftharpoons	H_3O^+	base
initial	0.10	large		0	0
change	-x	negligible		+x	+x
final	$0.10 - x$	large		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10 - x}$$

As $\text{p}K_a = -\log_{10}K_a$, $K_a = 10^{-5.69}$ and is very small, $0.10 - x \sim 0.10$ and hence:

$$x^2 = 0.10 \times 10^{-5.69} \quad \text{or} \quad x = 4.5 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(4.5 \times 10^{-4}) = 3.35$$

$$\text{pH} = 3.35$$

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $[\text{Co}(\text{NH}_3)_5(\text{OH})](\text{NO}_3)_2$ is:

$$\begin{aligned} \text{molar mass} &= (58.93 \text{ (Co)}) + 7 \times 14.01 \text{ (N)} + 7 \times 16.00 \text{ (O)} + 16 \times 1.008 \text{ (H)} \text{ g mol}^{-1} \\ &= 285.128 \text{ g mol}^{-1} \end{aligned}$$

The number of moles present in 28.5 g is therefore:

$$\text{number of moles} = \text{mass} / \text{molar mass} = (28.5 \text{ g}) / (285.128 \text{ g mol}^{-1}) = 0.100 \text{ mol}$$

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If this is present in 1.00 L, then $[\text{base}] = 0.100 \text{ M}$.

As it is a weak base, $[\text{OH}^-]$ must be calculated by considering the equilibrium:

	base	H ₂ O	\rightleftharpoons	acid	OH ⁻
initial	0.100	large		0	0
change	-y	negligible		+y	+y
final	0.100 - y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100 - y)}$$

For an acid and its conjugate base:

$$\text{p}K_a + \text{p}K_b = 14.00$$

$$\text{p}K_b = 14.00 - 5.69 = 8.31$$

As $\text{p}K_b = 8.31$, $K_b = 10^{-8.31}$. K_b is very small so $0.100 - y \sim 0.100$ and hence:

$$y^2 = 0.100 \times 10^{-8.31} \text{ or } y = 2.21 \times 10^{-5} \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65$$

Finally, $\text{pH} + \text{pOH} = 14.00$ so

$$\text{pH} = 14.00 - 4.65 = 9.35$$

$$\text{pH} = 9.35$$

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a $\text{pH} = 7.00$.

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$:

$$7.00 = 5.69 + \log \frac{[\text{base}]}{[\text{acid}]} \text{ so } \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4$$

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As $V_{\text{acid}} + V_{\text{base}} = 1.0 \text{ L}$ and $V_{\text{base}} / V_{\text{acid}} = 20.4$:

$$V_{\text{acid}} = 0.047 \text{ L and } V_{\text{base}} = 0.953 \text{ L}$$