Case study 4: XH_3 and derivatives as ligands

The elements of group 15 of the periodic system all form trihydrides.

1 Write down the formula and give names to the hydrides

2 Describe the state of matter of the hydrides and what happens by heating (compare and state if necessary approximate relevant temperatures)

3 Describe what happens to the hydrides when they are exposed to water and to normal air.

4 Describe and compare the acid-base properties of the hydrides and their properties as ligands towards metal ions

A large number of alkyl and aryl analogues to the hydrides are known, and a vide range of monodentate and chelating ligands is possible. A simple derivative is 1,2-ethandiamin (in the following abbreviated as en). Some stability data are given in the table

Stability data expressed as $\log\beta_{mhl}$ for $mM^{n+} + hH^{+} + l(en) \leftrightarrow M_mH_hen_l^{(mn+h)+}$
(1M KNO_3 , 25^0C)

mhl	H^+	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
011	10.20							
021	17.69							
101		5,15	2.77	4.34	5.89	7.51	10.72	5.92
102		9.19	4.87	7.65	10.72	13.86		11.07
103			5.79	9.70	13.82	18.28	21.0	12.93

As is seen from the table the values of $\log\beta_{101}$ for Co^{2+} and Zn^{2+} are approximately the same.

5 Find the consecutive constants for these two metal ions and comment on the variation of the two sets of numbers.

$\log\beta_{101}$ varies in a special way along the series of M^{2+} ions.

6 Comment on this variation.

In the Cr^{2+} case $\log\beta_{103}$ is not given.

7 Discuss what may be expected in this case.

In Cu^{2+} case $\log\beta_{102}$ is not given.

8 Give estimates of the magnitude of $\log\beta_{102}$ using numbers in the table

To a solution (1M KNO_3, 25 ^{0}C) of copper(II) nitrate and 1,2-ethanediamine was added nitric acid, and the resulting concentrations were C_{Cu}^{2+} = 1.00 mM, C_{en} = 3.00 mM, C_{HNO_3} = 2.80 mM. The pH of the solution was measured as 5.71.

9 Use this single experiment and other data from the table to calculate a value for $\log\beta_{102}$

Another bidentate ligand, elucidating the coordination properties of phosphines is 2-(aminoethyl)dimethylphosphine (in the following abbreviated as edmp).

10 Write down the constitution of edmp and characterise qualitatively the compound as a ligand

If rhodium(III) chloride and edmp in ethanol (in the molar ratio 1:5) are heated at the boiling point for a long period of time a pure compound with the empirical formula $Rh(edmp)_3Cl_3(H_2O)_4$ can be obtained (after recrystallisation).

11 Why is a prolonged heating necessary

12 Which complex cation does the compound probably contain.

13 Explain which magnetic property this ion has.

The complex cation may exist in some isomeric forms

14 Describe the isomers and state the type of isomerism.

It is also possible to synthesise a yellow compound with the empirical formula $Rh(edmp)_2Cl_2ClO_4$

15 Give a name to the compound and sketch the geometrical isomers of the complex ion.

The analogous $Co(edmp)_2Cl_2Cl$ is green and the first absorption maximum lies at 602 nm ($\varepsilon_{max.}$ = 138 $cm^{-1}M^{-1}$).
$\lambda_{max.1}$ for cis-$Coen_2Cl_2^+$ and $Coen_3^{3+}$ are 530 and 464 nm, respectively.

16 Calculate an expected value of $\lambda_{max.1}$ for $Co(edmp)_3^{3+}$ and discuss under which assumptions it can be calculated.

17 With the same assumptions and using these spectral data, enter 1,2-ethanbis(dimethylphosphine) in the spectrochemical series.