Relatively Slow Water Exchange in a Pentaco-ordinate Macrocyclic Cobalt(II) Complex

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Summary The rate of water exchange in the pentaco-ordinate Co^{II} complex of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane has been determined to be $4{\cdot}2 \times 10^4$ s^{-1} at 25 °C with $\Delta H^* = 36{\cdot}5 \pm 1{\cdot}4$ kJ mol^{-1} and $\Delta S^* = -34 \pm 4$ J mol^{-1} K^{-1}.

METAL complexes of 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (tmc) have unusual characteristics when compared to those of the unsubstituted parent compound.[1,2] Their properties indicate pentaco-ordination of the metal ion, which has been proved by *X*-ray diffraction analysis for $[Ni(tmc)N_3]^+$.[3] Similarly the absorption spectrum of the Co^{II} complex of tmc in aqueous solution, together with equilibrium data are consistent with a similar co-ordination geometry of the metal ion.[2] The macrocyclic Co^{II} complex gives only 1 : 1 adducts with unidentate ligands and is hydrolysed to a monohydroxo-complex with pK_a 8·44 at 25 °C and I 0·5 M.[4] It is therefore reasonable to assume that besides the four nitrogens of the macrocycle, a water molecule is bound to the metal ion at the fifth co-ordination position.

The present n.m.r. study was undertaken to prove the presence of a water molecule in the co-ordination sphere of the Co^{II}. At the same time we determined the rate of solvent exchange. Although many such processes have been studied, the results have mostly concerned octahedral aquo ions,[5] and little is known about complexes with other geometries.

^{17}O Fourier transform n.m.r. line broadening was studied with a 90 MHz Brucker instrument in water enriched to 0·45% with ^{17}O. The reference solution contained all components except the paramagnetic Co^{II} ion. In a series of experiments the pH of the solution was varied from 8·5 to 10·5. Whereas at low pH a significant broadening was observed when the temperature was increased, at pH 10·5 almost no change in line width could be detected even at high temperature. Therefore, we must conclude that the aquo complex (present to the extent of 50% at pH 8·44) exchanges at a much faster rate than the monohydroxo complex. In fact our results show the typical behaviour for a single paramagnetic species and the line width is described well by the Swift–Connick equation for rapid exchange.[6] As with OH^-, the addition of one equivalent of a unidentate ligand such as OCN^- or N_3^- completely represses the broadening, indicating that these ligands replace the labile solvent molecule in the co-ordination sphere of Co^{II}.

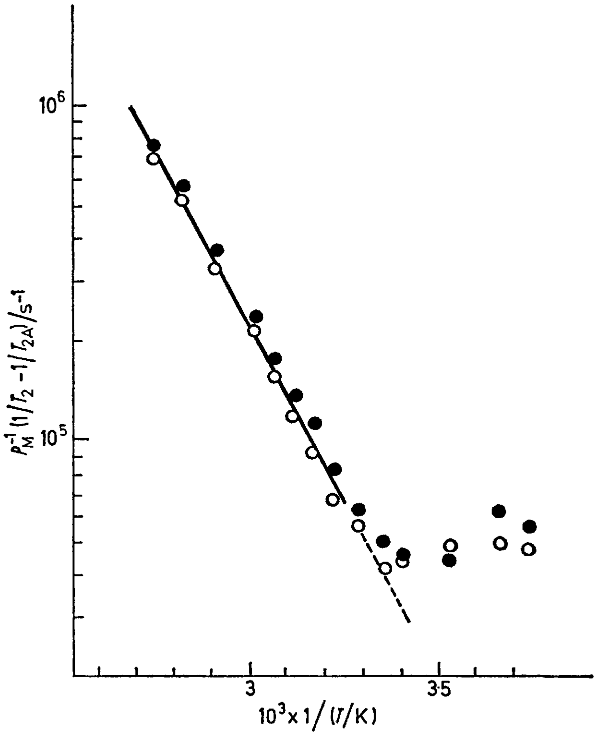

FIGURE. Temperature dependence of the corrected line width of $H_2{}^{17}O$ in the presence of $[Co(tmc)(H_2O)]^{2+}$ at pH 8·55 (○) and pH 9·42 (●) measured by ^{17}O Fourier transform n.m.r. spectroscopy.

The kinetic parameters of water exchange, obtained from the data in the Figure are given in the Table, together with similar results for $[Co(H_2O)_6]^{2+}$[7] and $[Co(NH_3)_2(H_2O)_4]^{2+}$[8] which are presented for comparison.

TABLE. Rate constants and activation parameters for the water exchange in octahedral and pentaco-ordinate Co^{II} complexes at 25 °C measured by ^{17}O-n.m.r. spectroscopy.

	k^a/s^{-1}	$\Delta H^*/$ kJ mol^{-1}	$\Delta S^*/$ J mol^{-1} K^{-1}	Ref.
$[Co(tmc)(H_2O)]^{2+}$	$4·2 \times 10^4$	$36·5 \pm 1·4$	-34 ± 4	This work
$[Co(H_2O)_6]^{2+}$	$2·4 \times 10^6$	43·5	22	7
$[Co(NH_3)_2(H_2O)_4]^{2+}$	$6·5 \times 10^7$	39·3	37	8

[a] Rates are given per water molecule.

The most striking result for the pentaco-ordinate Co^{II} complex is the unexpectedly low rate for the water exchange and the negative value of ΔS^* which is indicative of a greater ordering in the transition state. The activation entropy may imply that the mechanism of water exchange is more associative for $[Co(tmc)(H_2O)]^{2+}$ than for the other two complexes in the Table. On the other hand if the structure of $[Co(tmc)(H_2O)]^{2+}$ is similar to that of $[Ni(tmc)N_3]^+$[3] one would expect that the relatively inflexible macrocyclic ligand could prevent significant expansion or contraction of the co-ordination sphere or a geometric rearrangement in the transition state. These observations are not peculiar to this complex alone, but have been described in other pentaco-ordinate systems in nonaqueous solvents.[9]

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