Effect of Outer Sphere Acetate Ion Association on the Methanol Exchange Rate of $Co(MeOH)_5O_2CMe^+$

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Summary The acetate ion in the second co-ordination sphere of $Co(MeOH)_5O_2CMe^+$ appreciably enhances the methanol exchange rate relative to the non-ion-paired complex.

Replacement reaction mechanisms of labile six-coordinate metal complexes usually postulate the existence of an outer sphere association complex (*e.g.* an ion pair) as an intermediate, and further postulate the rate-determining step to be the metal-solvent dissociation rate in the intermediate.[1] Owing to the unavailability of the appropriate data, the intermediate's metal-solvent dissociation rate is almost universally assumed to be equal to the solvent exchange rate of the unassociated metal complex.

Reported here is the first experimental evidence indicating that acetate ion in the second co-ordination sphere alters the methanol exchange rate of $Co(MeOH)_5O_2CMe^+$ ($ROAc^+$). The exchange rate constant per co-ordinated methanol for the *cis* methanols, k_{cis}^{ex}, was determined as a function of acetate concentration by n.m.r. total lineshape analysis of the co-ordinated methanol methyl resonance. Experimental procedures including preparation of anhydrous samples have been described elsewhere.[2] Acetate ion was introduced as anhydrous sodium acetate.

The n.m.r. lineshape is related to k_{cis}^{ex} as follows:[3]

$$k_{cis}^{ex} = \omega_{1/2} - \omega_{1/2}^{0}$$

where $\omega_{1/2}$ and $\omega_{1/2}^{0}$ are the half widths at half height of the resonances in s^{-1} in the presence and absence of exchange, respectively. $\omega_{1/2}^{0}$ was assumed to be equal to the $Co(MeOH)_{2}^{+}$ ($RMeOH^{2+}$) linewidth observed in the same sample. This assumption is supported by the observation that at −90 °C there is negligible exchange broadening of the $ROAc^{+}$ resonance and its linewidth is essentially equal to that of $RMeOH^{2+}$ (Table).

Separate resonances were observed for the co-ordinated and unco-ordinated (bulk) acetate protons and their respective linewidths decreased with increasing temperature indicating acetate exchange was slow on the n.m.r. time scale. The methanol exchange rate was unaffected by addition of acetic acid up to 0·3 M.

TABLE

Co-ordinated methanol methyl n.m.r. linewidth data for $Co(MeOH)_{5}O_{2}CMe^{+}$ and $Co(MeOH)_{6}{}^{2+}$ as a function of acetate concentration

Total acetate concentration/M		0·10	0·20	0·40	0·80
Linewidth[a] of *cis* methanol in $ROAc^{+}$[b]	−90 °C	110	110	170	
	−70 °C	240	279	380	470
Linewidth[a] of $RMeOH^{+}$[b]	−90 °C	100	120	160	
	−70 °C	68	81	91	106
k_{cis}^{ex}/s^{-1}	−70 °C	1100	1200	1800	2300

[a] Linewidths expressed in Hz. [b] R = $Co(MeOH)_{5}$. [c] Total cobalt(II) concentration was 0·133 M.

Linewidth data for the co-ordinated methanol methyl resonance of $RMeOH^{2+}$ and the *cis* methanol of $ROAc^{+}$ at −70 °C are tabulated in the Table, along with corresponding values of k_{cis}^{ex}. Note, k_{cis}^{ex} is a function of the total acetate concentration and its value doubles when total acetate is varied from 0·1 to 0·8 M. Because k_{cis}^{ex} was obtained from n.m.r. measurements on the co-ordinated methanol of the mono-acetate complex and acetate exchange of $ROAc^{+}$ is known to be slow, it follows that dependence of k_{cis}^{ex} on acetate concentration results from variation in acetate concentration outside the primary (first) co-ordination sphere.

In addition, the n.m.r. contact shifts of the co-ordinated methanol methyl resonances of $RMeOH_{2}^{+}$ and $ROAc^{2+}$ vary by about 9 and 20 p.p.m., respectively, over the acetate concentration range used. Specific, localized interactions of the unco-ordinated acetate ion with the co-ordinated methanol would be necessary to cause changes in n.m.r. shifts of the magnitude observed. We conclude that outer sphere association of $ROAc^{2+}$ by acetate ion catalyses methanol exchange by at least a factor of two. Because the outer sphere association constant is unknown, it is impossible to calculate the exact extent of methanol exchange rate enhancement, only set a lower limit. The fact that a similar rate enhancement was not observed for $Co(MeOH)_{6}^{2+}$ as a function of perchlorate concentration[4] indicates that acetate ion is responsible for the rate increase rather than an ionic strength effect.

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