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FACILE ACETYLATION OF THE UNCOORDINATED HYDROXY GROUP OF N-HYDROXYETHYLETHYLENEDIAMINE-N,N',N'-TRIACETATOAQUACHROMIUM(III) COMPLEX

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The uncoordinated hydroxy group of HEDTRA in Cr(hedtra)(H_2O) was readily acetylated by acetic anhydride under a mild condition. The coordinated water of the acetylated complex was reversibly substituted by acetate ions at such a great rate as that of Cr(hedtra)(H_2O).

There have been reported scattered works on the chemical reactivity of the uncoordinated N-hydroxyethyl group of the ligand. The N-hydroxyethyl groups in Co(hen)$_3^{3+}$ § and Co(hdien)$_3^{3+}$ were completely inactive toward a number of reagents which are active to primary alcohols.[1,2] Co$(NO_2)_3$(hdien) and Pt(hen)$_2^{2+}$ reacted with thionyl chloride-dimethylformamide to form the -$NHCH_2CH_2Cl$ group.[3] The hydroxyethyl groups in Cr(hida)$_2^-$ were able to be acetylated, but it required a severe condition.[4] On the other hand, the hydroxy groups in Co$(NO_2)_2$(hen)$_2^+$ and in Co(hida)$_2^-$ were found to be readily acetylated.[5,6] Therefore, there is a large variety of reactivities of the uncoordinated hydroxy groups, and the successful account for those observations has not been given yet. This letter presents another example of a facile acetylation of the uncoordinated hydroxy group, which was found in the course of our continuing study on the chromium(III)-aminopolycarboxylate chemistry; the uncoordinated hydroxy group of pentacoordinated HEDTRA in Cr(hedtra)(H_2O) allowed acetylation under a mild condition to be converted to the >$NCH_2CH_2OCOCH_3$ group.

Finely ground [Cr(hedtra)(H_2O)]·$1.5H_2O$[7] (0.34g) was suspended in 20 ml of acetic anhydride and stirred for 20 hr at room temperature. The resulted reddish-violet solution was filtered, and 100 ml of ice-cold diethyl ether was slowly added with continuous stirring. The reddish-violet powder was filtered, washed with ether and dried in vacuo. The crude product was dissolved in water and concentrated in a rotary evaporator below 30°C. Cooling the concentrated solution, reddish-violet crystals were obtained; yield 0.15g. Anal. Calcd for [Cr(aeedtra)(H_2O)]·$1.5H_2O$: C, 34.79; H, 5.35; N, 6.76; Cr, 12.55%. Found: C, 34.71; H, 5.48; N, 6.73; Cr, 12.52%. The presence of the acetyl group was confirmed by means of the infra-

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§ Abbreviations used in this letter: hen, N-hydroxyethylethylenediamine; hdien, N-hydroxyethyldiethylenetriamine; hida^{2-}, N-hydroxyethyliminodiacetate; hedtra^{3-}, N-hydroxyethylethylenediamine-N,N',N'-triacetate; aeedtra^{3-}, N-acetoxyethylethylenediamine-N,N',N'-triacetate.

red spectra (KBr disks): The [Cr(hedtra)-(H_2O)]·$1.5H_2O$ shows a carboxyl stretching band at 1640 cm^{-1}, while the [Cr(aeedtra)-(H_2O)]·$1.5H_2O$ gives bands at 1740 cm^{-1}, 1690 cm^{-1} and 1650 cm^{-1} (Figure). The visible absorption spectrum of Cr(aeedtra)-(H_2O) is almost identical with that of Cr-(hedtra)(H_2O): $\lambda_{max}(\varepsilon/M^{-1}\ cm^{-1})$ for Cr-(aeedtra)(H_2O), 546 nm (151) and 385 nm (116); for Cr(hedtra)(H_2O), 545 nm (151) and 385 nm (118).

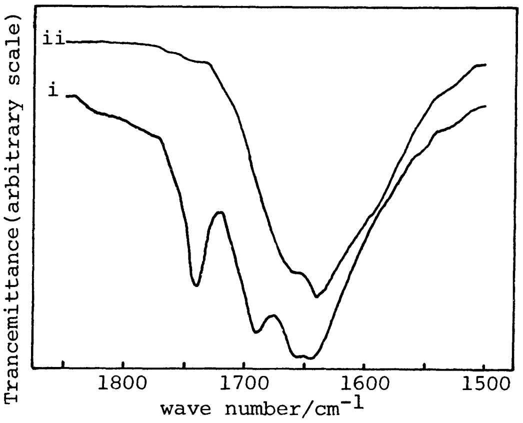

Figure. Infrared Spectra of [Cr(aeedtra)(H_2O)]·$1.5H_2O$(i) and [Cr(hedtra)(H_2O)]·$1.5H_2O$(ii)

The acetylated complex undergoes a reversible ligand substitution reaction with acetate ions. The reaction was followed spectrophotometrically by the stopped-flow method, and the kinetic data were able to be well interpreted by considering Reactions 1 and 2. The rate constants

$$\mathrm{Cr(aeedtra)(H_2O) + OAc^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr(OAc)(aeedtra)^- + H_2O} \qquad (1)$$

$$\mathrm{Cr(aeedtra)(H_2O) + HOAc} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cr(OAc)(aeedtra)^- + H_3O^+} \qquad (2)$$

were determined to be $k_1 = 4.5 \pm 0.7\ M^{-1}\ s^{-1}$, $k_{-1} = 0.38 \pm 0.06\ s^{-1}$, $k_2 = 1.1 \pm 0.3\ M^{-1}\ s^{-1}$, and $k_{-2} = (9 \pm 2) \times 10^3\ M^{-1}\ s^{-1}$, respectively, at I = 1.0 ($NaClO_4$) and at 25.0°C. It has been reported that the pentacoordinated EDTA or HEDTRA in the chromium(III) complex causes the great enhancement of the rate of the ligand substitution at the sixth coordination position.[7,8] The kinetic results obtained in this study reveal that the rate acceleration ability of the coordinated HEDTRA remains almost unchanged upon the acetylation of the N-hydroxyethyl group.[9] Further investigations are in progress.

References and Notes

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9) The rate constants for the reaction of Cr(hedtra)(H_2O) with acetate ions are $k_1 = 7.60 \pm 0.61\ M^{-1}\ s^{-1}$ and $k_{-1} = 0.450 \pm 0.030\ s^{-1}$ (I = 1.0 ($NaClO_4$), 25.0°C).[7]

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