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A NEW SYNTHETIC PROCEDURE OF N-(2-HYDROXYETHYL)ETHYLENEDIAMINETRIACETATOMANGANESE(III) COMPLEX

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When manganese(III) acetate was mixed with Na_3hedtra in an acetic anhydride solution, $Na[Mn(hedtra)(CH_3COO)]\cdot H_2O\cdot 1/2(CH_3CO)_2O$ complex was obtained. This complex was unstable in an aqueous solution, but fairly stable in non-aqueous solvents such as methyl alcohol and dimethyl sulfoxide. This preparative method may be useful to synthesize other manganese(III) complexes.

As most of manganese(III) complexes are unstable in aqueous solutions but stable in some non-aqueous solvents, it may be possible to prepare manganese(III) complexes in non-aqueous solvents. It is reported that Mn(III) acetate is soluble and stable in non-aqueous solvents such as alcohol, pyridine and chloroform.$^{1)}$ Therefore, it seems possible that the reactions of manganese(III) acetate with appropriate ligands in those solvents yield the corresponding manganese(III) complexes. $Mn(hedtra)\cdot 2.5H_2O$(hedtra = N-(2-hydroxyethyl)ethylenediaminetriacetate ion), which was reported by Hamm,$^{2)}$ is soluble in methyl alcohol. In this work, manganese(III) acetate was mixed with Na_3hedtra in an acetic anhydride solution and $Na[Mn(hedtra)(CH_3COO)]\cdot H_2O\cdot 1/2(CH_3CO)_2O$ complex was obtained, which was characterized by elemental analyses, measurements of infrared and visible absorption spectra and conductivity, pH titration and ion-exchange chromatographic techniques.

EXPERIMENTAL

$Mn(NO_3)_2\cdot 6H_2O$(10 g) was added in 40 ml of acetic anhydride and heated slowly on a water bath. After a vigorous exothermic reaction ceased, the solution was cooled in an ice-water bath. Into this solution containing manganese(III) acetate, 11 g of Na_3hedtra was added and stirred with a magnetic stirrer in an ice-water bath for about 50 min. Reddish brown color of the solution was changed to cherry red color. The solution was filtered and 100 ml of ethyl ether was added to the filtrate, then oily product was obtained. The solution was decanted and ethyl ether was removed with air from oily product, which was dissolved in 10 ml of 95 % methyl alcohol and the resulted solution was cooled in an ice-water bath. Reddish orange powder was obtained and washed with 99 % ethyl alcohol and ethyl ether and dried in a silica gel desiccator. Yield was about 5.7 g. This complex was recrystallized with 95 % methyl alcohol containing a small amount of acetic anhydride.

RESULTS AND DISCUSSION

Elemental analysis of the Mn(III)HEDTRA complex obtained was,

Found: C, 34.85; H, 4.86; N, 5.77; Mn(III), 11.5.

Calcd. for $Na[Mn(hedtra)(CH_3COO)]\cdot H_2O\cdot 1/2(CH_3CO)_2O$: C, 34.94; H, 4.82; N, 5.82; Mn, 11.42.

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The Mn(III)HEDTRA complex decomposes to manganese(II) complex in an aqueous solution but fairly stable in 87 wt/wt % methyl alcohol and dimethyl sulfoxide, in which the measurement to determine the formula of the complex was made.

The conductivities of the Mn(III)HEDTRA obtained are given in Table 1, with those of $Na[Co(edta)]\cdot 4H_2O$ and sodium ion, which indicates that the complex obtained is univalent.

Table 1 Limiting Molar Conductivity (in $S\ cm^2\ mol^{-1}$) Determined at 25°C

	Methyl alcohol (87 wt/wt %)	Dimethyl sulfoxide
Mn(III)HEDTRA*	59.1	24.1
$Na[Co(edta)]\cdot 4H_2O$	57.6	23.7
Na^+		13.8³⁾

* Assumed as $Na[Mn(hedtra)(CH_3COO)]\cdot H_2O\cdot 1/2(CH_3CO)_2O$

About 0.4 g of Mn(III)HEDTRA was dissolved in 87 wt/wt % methyl alcohol. After being treated with an anion (Cl^- form) and a cation (H^+ form) exchange resin, the solution was collected in a 100 ml volumetric flask. Red color of Mn(III)HEDTRA complex was observed on the anion exchange resin, which showed that Mn(III)HEDTRA was anionic. The concentrations of Cl^- and H^+ ions in the solution treated with the ion exchange resin were determined by the potentiometric and the pH titration, respectively. It was found that the ratios of Cl^- and of strong acid to Mn(III)HEDTRA were both 1.0. In addition, a small amount of weak acid was found to exist from the titration curve obtained, indicating that there might be some compounds which produced that acid. To determine the amount of those compounds, the following procedures were taken: Excess KOH was added to the solution treated with the ion exchange resin. The solution was kept on standing for four days, and then methyl alcohol was expelled on a water bath. Hydrochloric acid was added to the solution in excess, which was titrated with a KOH solution. The ratio of the weak acid to Mn(III)HEDTRA was found to be 0.9 and pK_a of the weak acid, to be about 4.7. These results indicate that the weak acid might be acetic acid which was produced mainly by hydrolysis of acetic anhydride.

On the infrared absorption spectra obtained with Mn(III)HEDTRA in KBr disk, absorption maxima were observed at 1625, 1645(sh), 1700 and 1735 cm^{-1}, of which the absorptions at 1700 and 1735 cm^{-1} may be due to acetic anhydride.

From the above-mentioned results, the formula of Mn(III)HEDTRA obtained by this preparative method is considered to be $Na[Mn(hedtra)(CH_3Coo)]\cdot H_2O\cdot 1/2(CH_3CO)_2O$.

The visible absorption spectra and the pH titration gave the following results:

$\varepsilon = 387$ (at 470 nm of λ_{max} in 87 wt/wt % methyl alcohol).

$\varepsilon = 363$ (at 490 nm of λ_{max} in dimethyl sulfoxide).

$pK_{a1} = 4.0$, $pK_{a2} = 6.3$ (in 87 wt/wt % methyl alcohol, $\mu = 0.1$ ($NaNO_3$), 25°C).

The complex was not stable in 87 wt/wt % methyl alcohol, when pH was larger than 10, and MnO_2 was precipitated.

References

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