

Note

Hydrogen Trimethylenediaminetetraacetato- chromate(III)-Tetrahydrate의 합성

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(1972. 8. 22 접수)

Synthesis of Hydrogen Trimethylenediaminetetraacetato- chromate(III)-Tetrahydrate

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(Received Aug. 22, 1972)

In the course of studies on the synthesis of alkylenediaminetetraacetatochromate(III) complexes, it was found that the heating method¹ used up to date required rather long periods of time and gave unsatisfactory yield.

In the present work, this fact has been clearly noticed especially when the ligands have longer alkylene chains, and also a faster and better yield procedure for the preparation of the chromium(III) complex with trimethylenediaminetetraacetic acid has been developed.

By using chromium(II) ion, the synthesis of Na(Crtrdta)·3H₂O took a shorter time and produced better yield than the results reported previously.¹

The final product, H(Crtrdta)·4H₂O, was obtained with better yield by substituting hydrogen for sodium in Na(Crtrdta)·3H₂O, which was prepared by using chromium(II) ion.

Experimental

Preparation of chromium(II) solution. This solution was prepared by the usual manner.²

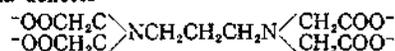
Trimethylenediaminetetraacetic acid (H₄trdta³). H₄trdta was prepared in the same way as had been reported³.

Preparation of Na(Crtrdta) 3H₂O. 1 g of H₄trdta was dissolved into 15 ml of distilled water by adding 0.5 g of NaHCO₃·To the above solution, 10 ml of the solution containing 0.8 g of CrCl₃·6H₂O were added. A 50 ml flask containing the mixed solution was sealed with a serum cap.

After removing the dissolved oxygen from the solution by bubbling nitrogen gas, 1 ml of 0.08 M chromium(II) solution prepared as above was added to the solution with a hypodermic syringe. By shaking the flask vigorously for a few minutes, the color of the solution placed in the flask changed to red.

The resulting red solution was evaporated to

* trdta denotes



10 ml under reduced pressure, and was cooled to 0°C. Red crystals deposited were collected and washed with ethanol and then with ether. The yield was approximately 85 %.

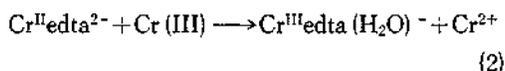
Anal. Calcd. for $\text{Na}(\text{Crtrdta}) \cdot 3\text{H}_2\text{O}$: C, 30.64; H, 4.67; N, 6.50. Found: C, 30.88; H, 4.78; N, 6.49.

Preparation of $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$. The solution of $\text{Na}(\text{Crtrdta}) \cdot 3\text{H}_2\text{O}$ was passed through Dowex 50 W X-8 cation exchange resins in hydrogen form. Ethanol was then added to the solution. After the solution had been cooled to 0°C, the crystals separated were collected and washed with ethanol and then with ether. The compound was recrystallized from water by the addition of ethanol.

Anal. Calcd. for $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$: C, 30.92; H, 5.42; N, 6.56. Found: C, 30.94; H, 5.40; N, 6.49.

Results and Discussion

It was found previously^{4,5} that when a chromium (II) solution was injected into a chromium (III) solution containing ethylenediaminetetraacetic acid (EDTA), the following reaction occurred:



It is known that reaction (1) is much faster than reaction (2). It would be reasonable to consider similar reactions for trimethylenediaminetetraacetic acid (TRDTA):

The fast formation of $\text{Cr}^{\text{II}}\text{trdta}^{2-}$ and the subsequent electron-transfer reaction between $\text{Cr}^{\text{II}}\text{trdta}^{2-}$ and chromium (III) leads to monomeric chromium complex.

Tsuchiya et al⁶ reported that they synthesized $(\text{CrHtrdta}(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}$ where TRDTA functioned as a pentadentate ligand, whereas Weyh

and Hamm¹ reported that TRDTA in chromium (III)—TRDTA complex functioned as hexadentate ligand.

Infrared spectrum of $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$ gave a single and strong carboxylate band at 1630 cm^{-1} , indicating TRDTA in $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$ functions as a hexadentate ligand⁷. (see Fig. 1)

In Fig. 2 the visible absorption spectra of the $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$ were compared with that of $\text{Na}(\text{Credta}(\text{H}_2\text{O}))$.

The tabulated data for the visible absorption spectra and the molar absorptivities of $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$ are shown in Table I.

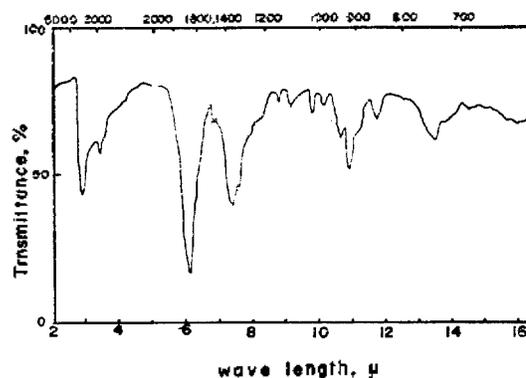


Fig. 1. Infrared spectrum of $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$ in KBr disk.

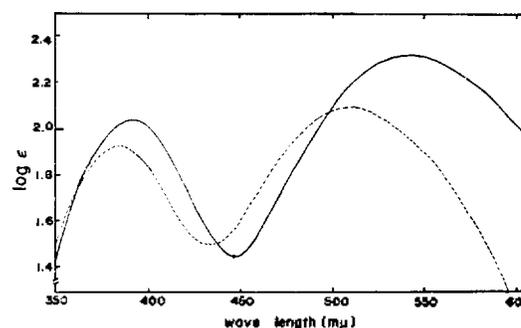


Fig. 2. The visible absorption spectra of the $\text{H}(\text{Crtrdta}) \cdot 4\text{H}_2\text{O}$ (.....) and the $\text{Na}(\text{Credta}(\text{H}_2\text{O}))$ (—) in aqueous solution

Table 1. The visible absorption spectra of $[\text{Credta}(\text{H}_2\text{O})]^-$ and $[\text{Crtrdta}]^-$

$[\text{Credta}(\text{H}_2\text{O})]^-$ *	545nm (ϵ 202)	395nm (ϵ 106)
$[\text{Crtrdta}]^-$	509nm (ϵ 118)	385nm (ϵ 83)

* Reference 1.

The comparatively appreciable difference in the values of the molar absorption of the two complexes, $[\text{Credta}(\text{H}_2\text{O})]^-$ and $[\text{Crtrdta}]^-$, supports the conclusion that the symmetry of the $[\text{Credta}(\text{H}_2\text{O})]^-$ differs from that of $[\text{Crtrdta}]^-$, *i. e.* different polydentate functions of the two ligands in complexes¹.

Acknowledgments

The authors wish to thank professor N. Tanaka and Dr. H. Ogina of Tohoku Unive-

rsity in Japan for their valuable discussions, suggestions and elementary analysis of compounds.

References

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