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The Syntheses and Properties of the Complexes of Boron with Ethylenediaminetetraacetic Acid and Its Analogs*1

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Two compounds of boron with ethylenediaminetetraacetic acid, $H_6EDTA(BF_4)_2$ and $H_4EDTA\text{-}(BF_3)_2$, as well as complexes with cyclohexanediaminetetraacetic acid and nitrilotriacetic acid, have been synthesized. Their properties, including their infrared and ultraviolet spectroscopic data, have been investigated and discussed.

The syntheses and the properties of the ethylenediaminetetraacetato chelates of a large number of metals have been reported in detail.[1] The boron complexes of ethylenediaminetetraacetic acid (H_4EDTA) or other aminopolycarboxylic acids, however, have not yet been reported on. Since Gay-Lussac[2] prepared the addition compound between ammonia and boron trifluoride, $H_3N\text{-}BF_3$, about 160 years ago, a large number of complexes have been prepared by a reaction between boron trifluoride and a variety of nitrogen compounds, such as amines, imines, amides, nitriles, and nitrogen-containing hetero cyclics.[3-5] The lone-pair electrons on the nitrogen atom in these compounds readily form a coordination bond with an acceptor boron trifluoride. The carboxylic acids are less easily coordinated with boron, but some acetic acid have also been reported.[6,7] However, the coordinate compounds of boron with such aminocarboxylic acids as ethylenediaminetetraacetic acid (H_4EDTA), cyclohexanediaminetetraacetic acid (H_4CDTA), and nitrilotriacetic acid (H_3NTA) have not yet been reported on. Therefore, it seemed that it would be interesting to investigate whether or not these acids coordinate with the boron trifluoride.

Experimental

Materials and Instruments. The H_4EDTA, H_4CDTA, and H_3NTA that were used in this experiment were of all of an analytical grade. The 45% ethylether solution of boron trifluoride ethyl etherate ($BF_3\text{-}(C_2H_5)_2O$) and the acetonitrile were of an EP grade. All of them were used without further purification.

The infrared spectra were obtained by a KBr-disc or nujol-mull procedure using a Japan Spectroscopic Co. DS 403 G infrared spectrophotometer. The electronic spectra were obtained with a Hitachi EPS-2 automatic recording spectrophotometer. The pH was measured with a Toa Electronic Co. pH meter, model HM-5A.

Synthesis of the Ethylenediaminetetraacetic Acid Adduct of Boron Trifluoride, $H_4EDTA(BF_3)_2$. Two grams (0.007 mol) of H_4EDTA and 6 m*l* (0.02 mol BF_3) of a 45% ether solution of $BF_3\text{-}(C_2H_5)_2O$ were mixed with 10 m*l* of acetonitrile containing a small amount of water (about 0.3 m*l*). The mixture was warmed on a water bath for a few minutes and then dissolved. A small amount of insoluble residue was filtered off, and the filtrate was refluxed for about 2 hr. A white precipitate was thus obtained. The product was filtered off, washed well with acetonitrile and ethyl ether successively, and dried in a vacuum at room temperature. The yield was about 1.9 g (65% calculated for H_4EDTA).

Found: C, 28.08; H, 4.26; N, 6.57; B, 4.79; F, 25.83%. Calcd for $C_{10}H_{16}N_2O_8B_2F_6$: C, 28.04; H, 3.74; N, 6.54; B, 5.05; F, 26.64%.

Synthesis of Ethylenediaminetetraacetic Acidium Tetrafluoroborate, $H_6EDTA(BF_4)_2$. The acetonitrile solution of H_4EDTA and boron trifluoride ethyl etherate obtained by the former synthesis process was allowed to stand for one day at room temperature without refluxing. The white precipitate thus obtained was filtered off, washed well with acetonitrile and ethyl ether successively, and then dried in a vacuum at room tem-

*1 This paper was presented at the 19th Symposium on Coordination Chemistry, Sendai, September, 1969.

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2) J. Gay-Lussac, *Mémoires de la Société d'Arcueil*, **2**, 211 (1809).

3) H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley & Sons, New York, N. Y. (1949), p. 43.

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perature. The yield was about 80% (calculated for H_4EDTA).

Found: C, 25.99; H, 3.87; N, 6.06; B, 3.94; F, 32.29%. Calcd for $C_{10}H_{18}N_2O_8B_2F_8$: C, 26.57; H, 3.88; N, 5.99; B, 4.62; F, 32.48%.

Synthesis of the Cyclohexanediaminetetraacetic Acid Adduct of Boron Trifluoride, $H_4CDTA(BF_3)$. About 0.5 g (0.0015 mol) of H_4CDTA, about 0.7 m*l* (0.0025 mol BF_3) of a 45% ether solution of BF_3-$(C_2H_5)_2O$, and 1 m*l* of acetonitrile were mixed and dissolved; water was not necessarily added. The solution was refluxed on a water bath for about 1 hr. After the removal of the solvent and the excess of BF_3-$(C_2H_5)_2O$ under reduced pressure, about 10 m*l* of ethyl ether was added to the brown residue. The white precipitate thus obtained was washed well with acetonitrile and ethyl ether before being dried in a vacuum at room temperature. The yield was about 0.13 g (20% calculated for H_4-CDTA).

Found: C, 39.49; H, 5.81; N, 6.21; B, 2.10; F, 14.06%. Calcd for $C_{14}H_{22}N_2O_8BF_3$: C, 40.60; H, 5.36; N, 6.76; B, 2.61; F, 13.76%.

Synthesis of Nitrilotriacetato Boron (NTA·B). The method of synthesizing $H_4EDTA(BF_3)_2$ was used. The yield was about 15% (calculated for H_3NTA).

Found: C, 34.58; H, 3.12; N, 6.99; B, 4.98%. Calcd for $C_6H_6NO_6B$: C, 36.22; H, 3.04; N, 7.04; B, 5.43%.

Results and Discussion

Typical patterns of the infrared spectra of these complexes are shown in Fig. 1, while the alkalimetric titration curve of $H_6EDTA(BF_4)_2$ in an aqueous solution is shown in Fig. 2.

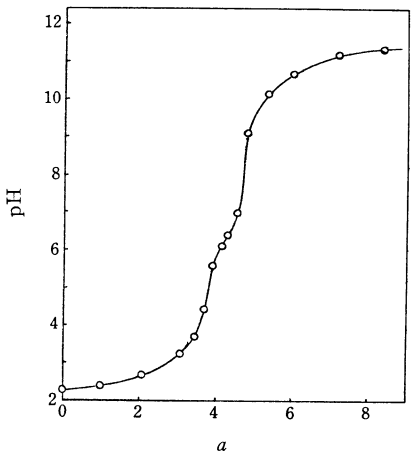

Fig. 2. Alkalimetric titration curve of $H_6EDTA(BF_4)_2$ in aqueous solution.

$a = NaOH/H_6EDTA(BF_4)_2$

Many papers have been published about the infrared spectra of ethylenediaminetetraacetato complexes as well as free acid.[8] According to these papers, the antisymmetric stretching bands of the uncoordinated and unionized carboxyl group of EDTA appears in the 1750—1700 cm^{-1} region, whereas that of the coordinated one appears in the 1650—1590 cm^{-1} region. The band of the free acid appears at 1690 cm^{-1}, and Novak and his co-workers deduced that two protonated nitrogen atoms and two $(-COOHOOC-)^-$ groups seem

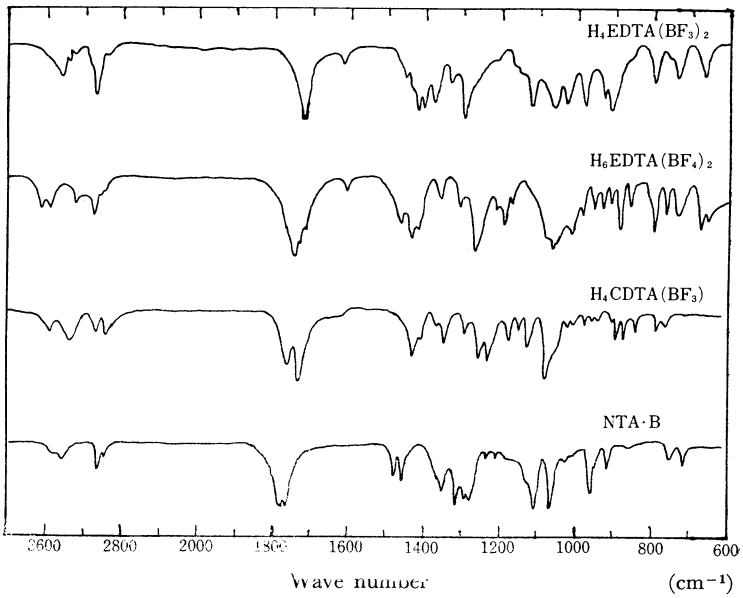

Fig. 1. Infrared spectra of the boron compounds.

8) K. Nakamoto, "Infrared Spectra of Inorganic Coordination Compounds," John Wiley & Sons, New York, N.Y. (1963), p. 205.

to exist in the free acid.[9] The fully protonated salt of ethylenediaminetetraacetic acid, $H_6EDTA \cdot Cl_2$, was also prepared by the reaction between ethylenediaminetetraacetic acid and hydrogen chloride.[10] The infrared spectra of the compound have a strong, characteristic absorption band near 1740 cm^{-1}; this can probably be assigned to the carboxyl groups attached to the protonated nitrogen atoms. There is also a broad band in the 3300—2000 cm^{-1} region; this is probably the OH stretching band of a carboxyl group.[9]

The assignments of the infrared absorption bands of $H_4EDTA(BF_3)_2$ were made with reference to the data about H_4EDTA, its metal complexes, and other B-N compounds. Therefore, the assignments are only tentative. The antisymmetric stretching band of the carboxyl group of this compound appears at 1725 cm^{-1}; this wave number is about 35 cm^{-1} higher than that of the free acid. This is probably due to the effect of coordinated boron trifluoride, which is a strong Lewis acid and which may be expected to have the same effect as a proton bonded to the nitrogen atom, as in the case of $H_6EDTA \cdot Cl_2$. Therefore, no carboxyl group of this complex seem to be coordinated with boron.

The bands near 1100 cm^{-1} are identified as B-F stretching bands following the examples given by Kreutzberger of amine adducts,[11] by Taylor of ammonia and trimethylamine adducts,[12] and by Paterson of hydrazine adducts.[13] The B-N stretching bands may be overlapping in this last case too.

A fresh aqueous solution of the complex does not give positive results in qualitative tests for the tetrafluoroborate ion using potassium chloride[3] or using nitron (1,4-diphenyl-3,5-endoanilinodihydrotriazole).[14] Therefore, the boron atoms of this compound are expected to bond with EDTA, probably with its nitrogen atoms, although no direct proof from the infrared spectra has yet been obtained.

Some peaks of the infrared spectra of $H_6EDTA(BF_4)_2$ have also been assigned by comparing them with those of $H_6EDTA \cdot Cl_2$. The strong bands at 1740—1720 cm^{-1}, the antisymmetric stretching band of the carboxyl group, and the broad band at 3200—2400 cm^{-1}, probably overlapping one of the stretching bands of N^+–H and OH, are visible. Consequently, a proton probably bonds to each nitrogen atoms of ethylenediaminetetraacetic acid, and this makes the stretching band of the carboxyl group shift to the higher-wave-number side, as in the case of $H_6EDTA \cdot Cl_2$. The other broad bands appearing in the 1100—1000 cm^{-1} region seem to be due to the B-F stretching bands of the tetrafluoroborate ion, BF_4^-, because the alkali salts show the same peak, as has been reported by Cote.[15] The broadening of this band was explained by Greenwood in term of the site symmetry and the isotope effect of the ion.[16]

The presence of the BF_4^- ion was also established by qualitative tests using potassium chloride or nitron.[3,14]

The alkalimetric titration curve of this compound, shown in Fig. 2, indicates that one mole of this compound immediately decomposes to two moles of tetrafluoroboric acid and one mole of H_4EDTA. In reality, if the solution is concentrated, a white precipitate of H_4EDTA appears. The former is a strong acid, and its hydrolysis in an aqueous solution, $BF_4^- + H_2O \rightarrow BF_3(OH)^- + HF$, is negligible during the titration, altough it may be gradually decomposed. Therefore, the inflexion point corresponds with the neutralization of two moles of HBF_4 and one mole of H_4EDTA (only to H_2EDTA^{2-}). On the other hand, boron trifluoride is rapidly hydrolysed in an aqueous solution, and the concentrations of BF_4^- and other various ionic species increase faster.[17] The acidity gradually increase during the alkalimetric titration process. In reality, in the alkalimetric titration of $H_4EDTA(BF_3)_2$ it took a long time before the equilibrium was attained after alkali was added.

Debye-Scherrer X-ray powder diffraction patterns of both $H_4EDTA(BF_3)_2$ and $H_6EDTA(BF_4)_2$ were obtained, but they were completely different from each other.

Although the attempt to recrystallize these compounds has not yet been successful, each compound seems to be nearly pure, since two products which were not only analytically but also infrared-spectroscopically characterized were reproducibly obtained in each synthesis of the compounds, even when the mole ratio of the starting materials was changed from 1 : 20 to 1 : 3.

The infrared spectra of $H_4CDTA(BF_3)$ in general resemble those of cyclohexanediaminetetraacetic acid.

The antisymmetric bands of the carboxyl group appear at 1760 and 1730 cm^{-1}, whereas the bands

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17) C. A. Wamser, *J. Amer. Chem. Soc.*, **73**, 409 (1951).

of the free acid appear at 1597 cm^{-1} and in the 1750—1700 cm^{-1} region (three peaks). The stretching band of B-F appears at 1100—1050 cm^{-1}. Probably the B-N band is also overlapping there.

Therefore, the structure of this complex seems to resemble $H_4EDTA(BF_3)_2$.

The infrared spectra of nitrilotriacetic acid and its metal complexes have been investigated in detail.[18,19] On the basis of all these results, the assignments of the spectra of the complex were made as follows. The antisymmetric stretching band of the carboxyl group of this compound appears at 1770 cm^{-1}, about 40 cm^{-1} higher than that of the corresponding band of the free acid (1728 cm^{-1}). This shift is probably due to the effect of the B-O and B-N bonds, which have a strong covalent character. The two strong bands at 1105 and 1070 cm^{-1} seem to be C-N and B-N stretching bands respectively. This complex is very stable towards hydrolysis because the electron shell of boron is filled with the electrons donated by the coordinated nitrogen atom. Others of the same type of compound, boroxazolidines, triethanolamine borate, for example, also show a high resistance to hydration.[20,21] Judging from these results, the ligand seems to work as a tetradentate in this complex.

Alcoholic or aqueous solution of neither $H_4EDTA(BF_3)_2$ nor $H_6EDTA(BF_4)_2$ show any peaks in the ultraviolet region, probably because of the solvolytic decomposition. However, their acetonitrile solutions show a characteristic maxima at 38200 cm^{-1} and two shoulders at about 38200 and 41000 cm^{-1}. As these compounds are only slightly soluble in a solvent, the molar extinction coefficients have not yet been determined. When the solutions were boiled for a while or allowed to stand for a few hours at room temperature, the 39400 cm^{-1} and 41000 cm^{-1}, remained. This is probably due to the solvolysis of the complex. The cyclohexanediaminetetraacetato complex shows almost the same ultraviolet spectra. The nitrilotriacetato complex is insoluble and so its spectra were not examined.

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