BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2981—2983 (1970)

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

Mitsuhisa NAKATANI, Yoshiaki TAKAHASHI, Akira OUCHI and Kunihiko WATANUKI

Department of Chemistry, College of General Education, University of Tokyo, Komaba, Meguro-ku, Tokyo

(Received April 9, 1970)

In a previous paper[1] we reported the syntheses of the boron trifluoride complexes with ethylenediaminetetraacetic acid (H_4EDTA), cyclohexanediaminetetraacetic acid (H_4CDTA), and nitrilotriacetic acid (H_3NTA), as well as their infrared and ultraviolet spectroscopic properties. According to the results, the boron trifluoride forms 2 : 1 and 1 : 1 adducts with H_4EDTA and H_4CDTA respectively, and a 1 : 1 adduct, NTA·B, with H_3NTA.

Along the lines of extending this work, the boron trifluoride adducts with other aminocarboxylic acids, such as diethylenetriaminepentaacetic acid (H_5DTPA), iminodiacetic acid (H_2IDA), and *N*-hydroxyethylenediaminetriacetic acid (H_3EDTA-OH), were synthesized. New complexes, $H_4DTPA\cdot BF_2\cdot 2H_2O$, $HIDA\cdot BF_2\cdot H_2O$ and $H_3EDTA\text{-}OH\cdot (BF_3)_2$, were obtained from boron trifluoride ethyl etherate ($BF_3\cdot (C_2H_5)_2O$) and aminocarboxylic acids in acetonitrile media.

Experimental

Instruments. The infrared spectra were obtained by the nujol and hexachloro-1,3-butadiene mull procedure using a DS-403G infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. The electronic spectra were obtained with a Hitachi EPS-2 automatic recording spectrophotometer.

Syntheses of Complexes. Table 1 shows the results of elemental analyses, the chemical formulae of the products as calculated from the analytical data, and the yields of the products.

Synthesis of $H_4DTPA\cdot BF_2\cdot 2H_2O$. 0.8 g (0.002 mol) of H_5DTPA and 5 m*l* (0.017 mol BF_3) of a 45% ether solution of $BF_3\cdot (C_2H_5)_2O$ were mixed with 5 m*l* of acetonitrile containing a small amount of water. The mixture was refluxed on a water bath for 30 min and then cooled to room temperature. A small insoluble

---

[1] M. Nakatani, Y. Takahashi, A. Ouchi and K. Watanuki, This Bulletin, **43**, 2072 (1970).

Table 1. Analyses of complexes

Chemical formulae	Yield* (%)		Analyses C	H	N	B	F
$H_4DTPA \cdot BF_2 \cdot 2H_2O$	50	Calcd	35.24	5.49	8.81	2.27	7.96
		Found	35.13	5.70	9.07	1.71	8.21
$HIDA \cdot BF_2 \cdot H_2O$	20	Calcd	24.15	4.05	7.04	5.43	19.10
		Found	24·43	3.83	7.25	5.55	18.51
$H_3EDTA\text{-}OH \cdot (BF_3)_2$	65	Calcd	29.02	4.38	6.77	5.21	27.55
		Found	29.76	3.97	7.30	4.72	27.41

$H_5DTPA = C_{14}H_{23}O_{10}N_3$: Diethylenetriaminepentaacetic Acid
$H_2IDA = C_4H_7O_4N$: Iminodiacetic Acid
$H_3EDTA\text{-}OH = C_{10}H_{18}O_7N_2$: *N*-Hydroxyethylenediaminetriacetic Acid
* Yields were calculated for H_5DTPA, H_2IDA and $H_3EDTA\text{-}OH$.

residue was separated out, to which solution ether was added in order to obtain a white precipitate. This was filtered off and washed with ether. This product was dissolved in 10 : 1 (v/v) acetonitrile-water, and the mixture was heated under reflux for 45 min and then cooled. To the solution was then added an excess of ether, after which the mixture was kept at room temperature for several days in order to obtain a white crystalline product. This was filtered off, washed with acetonitrile and ether, and freed from the solvent under reduced pressure at room temperature.

Synthesis of $HIDA \cdot BF_2 \cdot H_2O$. 1.33 g (0.01 mol) of H_2IDA and 5 m*l* (0.017 mol BF_3) of a 45% ether solution of $BF_3 \cdot (C_2H_5)_2O$ were dissolved in 20 m*l* of acetonitrile containing a small amount of water at room temperature. After the filtration of the insoluble residue, the filtrate was kept overnight at room temperature to give a white crystalline product.

Synthesis of $H_3EDTA\text{-}OH \cdot (BF_3)_2$. 0.6 g (0.002 mol) of $H_3EDTA\text{-}OH$, 3 m*l* (0.01 mol BF_3) of a 45% ether solution of $BF_3 \cdot (C_2H_5)_2O$, and 10 m*l* of acetonitrile containing a small amount of water were mixed and dissolved by heating. After the solution had been refluxed for 2 hr, the precipitate thus obtained was filtered off.

Results and Discussion

Although the ultraviolet absorption spectra of acetonitrile solutions of these complexes are qualitative due to their low solubilities in common organic solvents, their patterns are closely similar to each other. The spectra of all the complexes show a characteristic absorption maximum at $39.3 \pm 0.1 \times 10^3$ cm^{-1} and two shoulders at 40.0 ± 0.1 and $38.2 \pm 0.1 \times 10^3$ cm^{-1}.

The typical pattern of the infrared spectra of these complexes is shown in Table 2. The tentative assignments of their infrared absorption bands are given with reference to the data about free H_5-DTPA, H_2IDA, $H_3EDTA\text{-}OH$, and other BF_3 adducts with nitrogen-containing compounds.[1-6]

Table 2. Infrared spectra of complexes (cm^{-1})

$H_4DTPA \cdot BF_2 \cdot 2H_2O$	$HIDA \cdot BF_2 \cdot H_2O$	$H_3EDTA\text{-}OH \cdot (BF_3)_2$
		1762 s
1725 s	1720 s	1720 sh
1635 s	1560 m	1690 s
1460 1405 1351	1450 1430 1402 1375	1492 1468 1440 1415 1375 1342
1305 w	1320 w	1316 s
1260 s	1290 s	1275 s
1223 w	1255 sh	1241 s
1210 sh	1205 w	1221 w
		1206 w
	1165 sh	
1150 ~ 950 br	1120 s	1200 ~ 1000 br
	1076 s	
	1042 s	
	1025 s	
	970 s	980 963 950
910 w	923 s	913 s
900 m	900 s	
		883 w
857 w	840 s	
845 sh		
801 w		801 m
778 w	766 w	
708 w		

s = strong, m = medium, w = weak, br = broad, sh = shoulder

---

2) K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Amer. Chem. Soc.*, **84**, 2081 (1962).

3) K. Nakamoto, Y. Morimoto and A. E. Martell, *ibid.*, **85**, 309 (1963).

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

5) A. Kreutzberger and F. C. Ferris, *J. Org. Chem.*, **27**, 3469 (1962).

6) W. G. Paterson and M. Onyszchuk, *Can. J. Chem.*, **39**, 986 (1961).

The crystalline H_5DTPA[3] has three strong bands of about the same intensity at 1731, 1700 and 1634 cm^{-1}. The former two correspond to the antisymmetric stretching bands of four>N–CH_2-COOH-type carboxyl groups, while the last one corresponds to that of the >NH^+–CH_2COO^--type group. $H_4DTPA \cdot BF_2 \cdot 2H_2O$ in the solid state shows antisymmetric stretching bands of the carboxyl group at 1725 and 1635 cm^{-1}, but the band at 1700 cm^{-1} of the free ligand disappears. The band at 1725 cm^{-1} probably corresponds to that of four >N–CH_2COOH-type carboxyl groups, as in the case of the free acid, and the band at 1635 cm^{-1} is probably to be identified as the band of the >NBF_2^+–CH_2COO^--type carboxyl group, although the shift is not so great as that of the free ligand. The broad bands in the 1150—950 cm^{-1} region are probably to be identified as those of the B–F stretching mode or of a mixture with another vibration.[5,6]

At pH 2.2, the aqueous solution of H_2IDA shows two bands, at 1721 and 1619 cm^{-1}, which can be identified as the stretching bands of the –NH_2^+–CH_2COOH-type and the –NH_2^+–CH_2COO^--type carboxyl groups respectively.[2] The solid metal complex of H_2IDA has antisymmetric carboxyl bands which are shifted to lower wave numbers.[4]

$HIDA \cdot BF_2 \cdot H_2O$ in the solid state has two antisymmetric stretching bands of carboxyl groups at 1720 and 1560 cm^{-1}. They can probably be identified as of the –$NHBF_2^+$–CH_2COOH carboxyl group and the $-\mathrm{NH}\overbrace{\mathrm{BF_2{-}CH_2COO}}$ carboxyl group respectively. Several bands appear in the 1150—1000 cm^{-1} region; not only the B–F band but also the B–N, C–N, and other band probably appear in this region.[5–7]

Solid H_3EDTA–OH has bands at 1705 (shoulder), 1667, and 1629 cm^{-1}, all of which are identified as antisymmetric stretching bands of the carboxyl group,[3] while in the case of H_3EDTA–$OH \cdot (BF_3)_2$ the corresponding bands occur at 1762, 1720 (shoulder), and 1690 cm^{-1}. The shift to higher wave numbers of the bands of this complex is probably due to the effect of boron trifluoride, which is coordinated with the nitrogen atom in H_3EDTA–OH. As the boron trifluoride is a strong Lewis acid and is expected to take off electrons effectively from the nitrogen atom, the bands shift more. The broad bands appearing in the 1200—1000 cm^{-1} region may include the bands of the B–F band and others.[5,6]

The authors wish to thank Professor Yukichi Yoshino and their other colleagues for their helpful discussions.

---

[7] Y. Tomita and K. Ueno, This Bulletin, **36**, 1069 (1963).