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LETTERS TO THE EDITOR

Supramolecular Compounds of *cis-syn-cis*-Dicyclohexano-18-crown-6 with Complex Fluoroniobic and Fluorotantalic Acids

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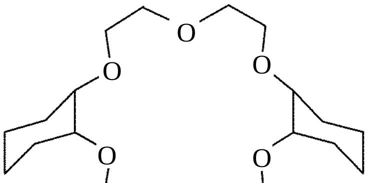
It is known that halides of such metals as Sn, Zr, V, Nb, and Ta in the highest oxidation states under anhydrous conditions either cleave the polyether rings of crown ethers to form linear products or, as with $TaCl_5$, induce recyclization of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) into 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) with ring expansion and formation of the complex $[H_3O^+ \cdot (18\text{-crown-}6)TaCl_6^-]$ in ~10% yield [1]. According to [2], Nb(V) and Ta(V) in hydrofluoric acid form labile mixtures of complex fluoro acids HMF_6 and H_2MF_7 (M = Nb, Ta).

Revealing selective interactions and the cases of stabilization of poorly stable compounds with crown ethers in the form of crystalline inclusion compounds [3, 4] is one of priority fields of supramolecular chemistry. In this context, we examined here the possibility of selective extraction and synthesis of supramolecular complexes of a crown ether with hexa- and heptafluoroniobate and -tantalate species from solutions of Nb and Ta in hydrofluoric acid.

Evaporation of solutions of Nb or Ta and *cis-syn-cis*-dicyclohexano-18-crown-6 (**I**) in hydrofluoric acid results in selective formation of crystalline supramolecular complex **IIa** or **IIb** with hydroxonium hexafluoroniobate or hexafluorotantalate, respectively. Taking into account data of [1] and also the characteristic capability of *cis-syn-cis*-perhydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine **I** to stabilize hydroxonium ions with the “closed” side of the cavity of the macrocyclic ring [5–7], we suggest structure **II** for the complexes synthesized.



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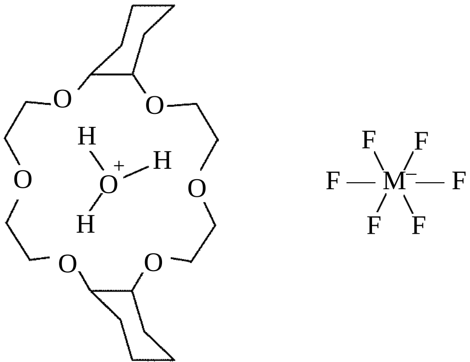

IIa, IIb

II, M = Nb (**a**), Ta (**b**).

The crystalline supramolecular compounds obtained are the first examples of selective extraction of fluoroniobic and fluorotantalic complex acids from acid solutions with a crown ether. The complexes are stable and show promise as containers [3] of these acids.

Crystalline supramolecular complexes IIa and

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IIb. A 1-mmol portion of NbF_5 or TaF_5 was dissolved in 5 ml of 45% HF, 1.01 mmol of *cis-syn-cis*-perhydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin was added, and the mixture was placed in a Teflon desiccator over sulfuric acid. After complete evaporation of the solvents, single crystals of complexes **IIa** and **IIb** were obtained in quantitative yield.

Complex of *cis-syn-cis*-perhydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine with hydroxonium hexafluoroniobate, 1 : 1 (**IIa**): mp 105–107°C. ^{1}H NMR spectrum, δ, ppm: 1.29–1.85 m and 3.64 m (36H, CH, CH_2, CH_2O). Found, %: C 40.18; H 6.65; F 19.12. $C_{20}H_{39}F_6NbO_7$. Calculated, %: C 40.13; H 6.57; F 19.05.

Complex of *cis-syn-cis*-perhydrodibenzo[*b,k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine with hydroxonium hexafluorotantalate, 1 : 1 (**IIb**): mp 103–104°C. ^{1}H NMR spectrum, δ, ppm: 1.28–1.85 m and 3.65 m (36H, CH, CH_2, CH_2O). Found, %: C 35.04; H 5.80; F 16.67. $C_{20}H_{39}F_6O_7Ta$. Calculated, %: C 34.98; H 5.73; F 16.61.

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer (300 MHz, CD_3OD, internal reference TMS).

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