ATRANES

XXVII.* 1-HYDROXYVANAD(IV)ATRANE-3,7,10-TRIONIC ACID AND ITS DERIVATIVES

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A method was developed for the preparation of the previously unknown heterocyclic, chelated mixed anhydride of aminotriacetic acid and vanadic acid – 1-hydroxyvanad-
(IV)atrane-3,7,10-trionic acid (\(\text{H}^+\{\text{N}(\text{CH}_2\text{COO})_3\text{V} - \text{O}\}\) – based on the reaction of aminotriacetic acid with \(\text{V}_2\text{O}_5\), \(\text{HVO}_3\), and \(\text{V}_2\text{O}_3\). A number of ammonium salts of 1-hydroxy-
vanad(IV)atrane-3,7,10-trionic acid were obtained.

Previously one of us and Lapsin' [2-5] described 1-oxovanadatranes (I), which were formed by the reaction of tris(2-hydroxyalkyl)amines with vanadium pentoxide via the scheme

\[
\text{V}_2\text{O}_5 + 2\{\text{R}(\text{CH}_2\text{OH})_2\}\text{N} \rightarrow 2\text{V}(\text{OCOCH}_2\text{CH}_2)_2\text{N} + 3\text{H}_2\text{O}
\]

The aim of the present study was the synthesis of the previously unknown, similarly constructed 1-
oxovanadatrane-3,7,10-triones (II) starting from aminotriacetic acid (III):

\[
\text{V}_2\text{O}_5 + 2\{\text{N}(\text{CH}_2\text{COO})_3\}\text{V} \rightarrow 2\text{V}(\text{OCOCH}_2\text{CH}_2)_2\text{N} + 3\text{H}_2\text{O}
\]

\[
\text{HVO}_3 + \text{III} \rightarrow \text{II} + 2\text{H}_2\text{O}
\]

\[
\text{NH}_2\text{VO}_3 + \text{III} \rightarrow \text{II} + 2\text{H}_2\text{O} + \text{NH}_3
\]

Up until now, only complexes of III with \(\text{V}^{3+}\) and \(\text{V}^{4+}\) that simultaneously contain Na or Mg ions [6-9] and have structures of the \([\text{N}(\text{CH}_2\text{COONa})_2(\text{CH}_2\text{COO})_3]\)\(_2\)\(\text{V}\), \([\text{N}(\text{CH}_2\text{COO})_2\text{Mg}(\text{CH}_2\text{COO})_3]\)\(_2\)\(\text{V}\), and \([\text{N}(\text{CH}_2\text{COO})_2-\text{Mg}(\text{CH}_2\text{COO})_3]\)\(_2\)\(\text{V} = \text{O}\) type, obtained by heating aqueous solutions of aminotriacetic acid with \(\text{Na}_2\text{CO}_3\) or \(\text{MgO}\) with the addition of \(\text{V}_2\text{O}_5\) or \(\text{V}_2\text{O}_4\), were known.

We tried to accomplish reactions (2), (3), and (4) by heating a mixture of the reagents in water, after which the water was removed by distillation in a rotary vacuum evaporator.

The reaction of III with \(\text{V}_2\text{O}_5\) and \(\text{HVO}_3\) could also be carried out at room temperature by prolonged mechanical shaking or stirring of an aqueous suspension of the reagents until they dissolved completely. In all cases, however, the reaction product turned out to be a substance of the \(\text{C}_6\text{H}_9\text{NO}_2\text{V}\) composition rather than the expected 1-oxovanadatrane-3,7,10-trione (II); this product can be assigned the 1-hydroxyvanad(IV)atrane-3,7,10-trionic acid dihydrate (IV) structure:

*See [1] for communication XXVI.
Compound IV was obtained as blue crystals that are stable on storing in air and soluble in water, aqueous solutions of ammonia and amines (best above 40°C), dimethylformamide, dimethyl sulfoxide, and mono-, di-, and triethanolamines. Compound IV is insoluble in the usual organic solvents (hydrocarbons, alcohols, ethers, dioxane, acetone, chloroform, etc.).

Aqueous solutions of IV give a strongly acid reaction (pKₐ = 3.9). The potentiometric titration curve of IV (Fig. 1) is complex. Three discontinuities with equivalence points at pH 4.3, 6.2, and 8.7 are observed on it. The first discontinuity corresponds to the formation of a salt, while the second and third are connected with salt formation accompanied by disruption of the atrane structure.

The presence of two molecules of water of crystallization in the IV molecule is confirmed by derivatography (Fig. 2). One of them is split out at 155°, the second is split out at 195-290°.

The molecular weight of IV, determined cryoscopically in water, is 233, while the molecular weight of anhydrous IV (C₆H₇NO₄V) is 256.1.

The structure of IV is confirmed by the results of IR and ESR spectroscopy (Figs. 3 and 4, respectively).

In our opinion, the stretching vibrations of the (V = O)⁻ group are represented in the IR spectrum of IV by the strong absorption band at 995 cm⁻¹ (Table 1). The absence of absorption at 1700-1750 cm⁻¹ indicates that the IV molecule does not contain un-ionized COOH groups [10-12]. All of the CH₂COO groups in IV are equivalent and are bonded to the metal atom, which is confirmed by the presence of only two very strong absorption bands at 1575 cm⁻¹ (hydrated COO⁻) and 1620 cm⁻¹ (COOV).

As in the IR spectra of HVO₃ and V₂O₅, the spectra of IV and its salts contain an absorption band at 560-580 cm⁻¹ that can be ascribed to ν V-O vibrations. It can be assumed that the band at 420 cm⁻¹ is related to either the vibrations of the N→ V bond or to the vibrations of the VO₃ group. The water of crystallization in IV is represented in the IR spectrum by a broad absorption band at 3400-3500 cm⁻¹.

The ESR spectrum* of IV has a hyperfine structure (hfs) (Fig. 4). The hfs components have different widths and are asymmetrical with respect to the center of the spectrum, which indicates axial symmetry of the environment of the paramagnetic particles [13, 14]. The hfs of the ESR spectra has the shape characteristic for tetravalent vanadium with the 3d⁴ configuration and is caused by interaction of the unpaired electron with the nucleus of the vanadium atom (V⁵⁺), the spin (½) of which is 7/2.

The structure of IV is also confirmed by its blue color, which is usually peculiar only to tetravalent vanadyl compounds, and also by the synthesis of IV from III and V₂O₅ (94% yield):

\[
V₂O₅ + 2(HOOCC₂H₅N₂) → 2IV + 2H₂O \tag{5}
\]

Thus, in the reaction of III with V₂O₅, HVO₃, and NH₄VO₃, V⁵⁺ is reduced to V¹⁺ by aminotriacetic acid, apparently via the scheme

\[
3V₂O₅ + N(CH₂COOH)₃ → 3IV + NH₃ + 3CO₂ + 3CH₃O \tag{6}
\]

Similarly, HVO₃ and NH₄VO₃ oxidize III. Thus the formation of IV should be represented by the schemes

\[
3V₂O₅ + 7N(CH₂COOH)₃ → 6IV + 3CO₂ + 3CH₃O + NH₃ + 6H₂O \tag{7}
\]
\[
6HVO₃ + 7N(CH₂COOH)₃ → 6IV + 3CO₂ + 3CH₃O + 7NH₃ + 12H₂O \tag{8}
\]
\[
6NH₄VO₃ + 7N(CH₂COOH)₃ → 6IV + 3CO₂ + 3CH₃O + 7NH₃ + 9H₂O \tag{9}
\]

The formation of CO₂ and CH₃O in reactions (7), (8), and (9) actually does occur.

*The hfs constant (a) for the spectra obtained is 114 Oe, and the spectroscopic splitting factor (g) is 1.9855 ± 0.0003. We thank R. A. Gavar for recording the ESR spectra.