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Synthesis and spectral properties of titanium(IV) polynuclear hydroxo complexes stabilized in solution by the $[PW_{11}O_{39}]^{7-}$ heteropolyanion

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Unsaturated heteropolyanions (HPA) $[PW_{11}O_{39}]^{7-}$ stabilize Ti^{IV} hydroxo complexes in aqueous solutions (Ti : PW_{11} $[PW_{11}O_{39}]^{7-} \le 12$, pH 1—3). Spectral studies (optical, ^{17}O and ^{31}P NMR, and IR spectra) and studies by the differential dissolution method demonstrated that Ti^{IV} hydroxo complexes are stabilized through interactions of polynuclear Ti^{IV} hydroxo cations with heteropolyanions $[PW_{11}TiO_{40}]^{5-}$ formed. Depending on the reaction conditions, hydroxo cations $Ti_{n-1}O_xH_y{}^{m+}$ either add to oxygen atoms of the W—O—Ti bridges of the heteropolyanions to form the complexes $[PW_{11}TiO_{40} \cdot Ti_{n-1}O_xH_y]^{k-}$ (at [HPA] ≈ 0.01 mol L^{-1}) or interact with Ti^{IV} of the heteropolyanions through the terminal O atom to give the polynuclear complexes $[PW_{11}O_{39}Ti—O—Ti_{n-1}O_xH_y]^{q-}$ (at [HPA] ≈ 0.2 mol L^{-1}). When the complexes of the first type were treated with H_2O_2, Ti^{IV} ions added peroxo groups.

Key words: heteropolyanion $[PW_{11}O_{39}]^{7-}$, Ti^{IV} polynuclear hydroxo complexes; peroxo complexes; NMR spectra; absorption spectra; IR spectra.

It is known that heteropolyanions (HPA) of the Keggin's type in which one or more Mo or W atoms are replaced by transition metal ions M can catalyze oxidation reactions.[1—3] The reactivity of the heteropolyanion depends on the number and the arrangement of ions M.[4,5] In this connection, preparation of M-containing heteropolyanions of different compositions and different structures is of interest.

Recently,[6] we have demonstrated that Fe^{III} ions interact with heteropolyanions $[PW_{11}O_{39}]^{7-}$ (hereinafter PW_{11}) to form heteropolycomplexes (HPC) of two types. Heteropolycomplexes of the first type, namely, the metal-substituted heteropolycomplex $[PW_{11}O_{39}Fe(H_2O)]^{4-}$ and the dimeric μ-oxo complex $[(PW_{11}O_{39}Fe)_2O]^{10-}$, contain Fe^{III} ions in the HPA framework. At higher Fe^{III} : HPA ratios and at pH ~4, complexes of another type are formed, namely, soluble Fe^{III} polynuclear hydroxo complexes stabilized by heteropolyanions $[PW_{11}O_{39}Fe_nO_xH_y]^{m-}$ ($n_{aver} \approx 4$). Other highly charged ions, for example, V^{IV} and Ti^{IV}, also give analogous complexes. Thus, the formation of polynuclear V^{IV} hydroxo complexes may account for the high catalytic activities of $[PW_{11}VO_{40}]^{5-}$ and $[PW_{10}V_2O_{40}]^{7-}$ in oxidation of V^{IV} ions by O_2, whereas the heteropolyanions in themselves are not oxidized by oxygen.[4]

To date, heteropolycomplexes in which one or several Ti^{IV} ions are involved in the HPA framework (for example, $[PW_{11}TiO_{40}]^{5-}$,[7] $[PW_{10}Ti_2O_{40}]^{7-}$,[8] and $[Ge_2Ti_6W_{18}O_{77}]^{14-}$) have been prepared and structurally characterized.[9] In this work, we synthesized polynuclear

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Ti^{IV} hydroxo complexes with heteropolyanions (so-called soluble titanium hydroxides) and studied their compositions, structures, and the reaction of HPC obtained with H_2O_2.

Experimental

Aqueous solutions of heteropolycomplexes with a $[Ti^{IV}] : [PW_{11}]$ ratio (n) of (1—12) : 1 and a concentration of 0.01—0.03 or 0.2 mol L^{-1} were prepared from dilute (series I) or concentrated (series II) solutions of $Na_7PW_{11}O_{39}$ and the corresponding amounts of $Ti_2(SO_4)_3$ in H_2SO_4 followed by oxidation of blue solutions obtained by oxygen at ~25 °C. A saturated solution of Na_2CO_3 was added with stirring to colorless solutions of Ti^{IV} heteropolycomplexes to pH 1—3. Solutions of series III ([HPC] = 0.2 mol L^{-1}; pH = 1.7, and n = 1, 2, or 4) were prepared by concentrating the corresponding solutions of series I at ~25 °C ([HPC] = 0.02 mol L^{-1}; and pH 2.0).

The reactions of the heteropolycomplexes with H_2O_2 were studied at concentrations of HPC of 0.01 mol L^{-1} (pH 2.0 and n = 1—6) and 0.2 mol L^{-1} (pH 1.7 and n = 1 or 2) (series I and III, respectively) at the $[H_2O_2] : [HPC]$ ratios varied from 1 : 1 to n : 1.

Solid salts were prepared by precipitating heteropolycomplexes from 0.02 M solutions (series I) at pH 2.0 with a CsCl solution taken in the molar ratio Cs : HPC = 10. Elemental analysis of the salts isolated was carried out for Cs, P, W, and Ti by atomic absorption. Phase analysis of Cs salts of heteropolycomplexes was carried out by the differential dissolution method[10] (H_2SO_4 as the solvent). During dissolution, the concentration of acid was varied from 0.01 to 4 g-equiv. L^{-1} in the temperature range of 15—70 °C. Thermal analysis of Cs salts of heteropolycomplexes was performed on a Q-1500D derivatograph under a stream of He (25 L h^{-1}) in the temperature range of 20—500 °C. The heating rate of samples (200 mg) was 10 K min^{-1}.

The absorption spectra of solutions of heteropolycomplexes were recorded on a Specord M-40 spectrophotometer in the 30000—11000 cm^{-1} region. The IR spectra of solid samples (CsI pellets) were recorded on a Specord M-80 instrument in the 2200—200 cm^{-1} region. The ^{31}P and ^{17}O NMR spectra were recorded on a Bruker MSL-400 spectrometer (161.98 and 54.24 MHz, respectively). The chemical shifts were measured relative to 85% H_3PO_4 and H_2O, respectively.

Results and Discussion

Synthesis and identification of the Ti^{IV} heteropolycomplexes. In the absence of complex formation, water-insoluble titanium(IV) hydroxo compounds precipitated even at pH ≥0.5. At pH 2, Ti^{IV} precipitated completely.[11]

The reaction of $TiCl_4$ with "unsaturated" heteropolyanions generally yield compounds in which Ti^{IV} ions of HPC are stabilized through coordination to W^{VI} ions and completion of the Keggin structure. Thus, the heteropolycomplexes $[PW_{11}TiO_{40}]^{5-}$ (pH 0.7—5)[7] and $[PW_{10}Ti_2O_{40}]^{7-}$ (pH ~8)[8] were obtained, whereas the heteropolyanion $[GeW_9O_{34}]^{10-}$ adds three Ti^{IV} ions to form the dimer[9] $[Ge_2W_{18}Ti_6O_{77}]^{14-}$.

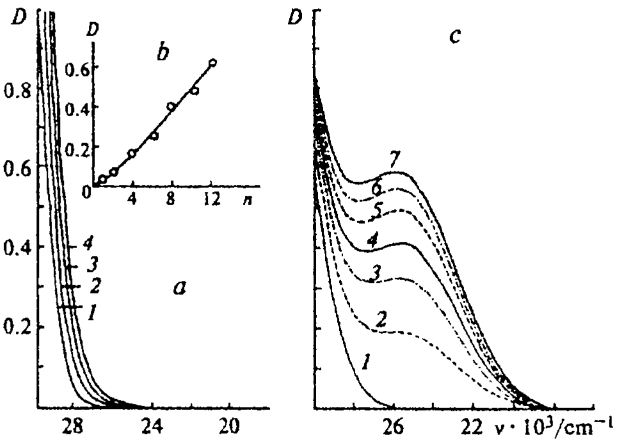

Fig. 1. *a*. Absorption spectra of solutions of Ti^{IV} heteropolycomplexes (series I): $[Ti] : [PW_{11}]$ = 1 (*1*), 2 (*2*), 3 (*3*), and 4 (*4*) ($[PW_{11}]$ = 0.01 mol L^{-1}, pH 2, and l = 0.1 cm). *b*. Dependence of the optical density (ν = 28000 cm^{-1}) of 0.025 M solutions of Ti^{IV} heteropolycomplexes (series I) on the ratio n = $[Ti] : [PW_{11}]$ (pH 2 and l = 0.021 cm). *c*. Absorption spectra of solutions of Ti^{IV} peroxo HPC complexes (series I) at $[H_2O_2]$ = 0 (*1*), 0.005 (*2*), 0.01 (*3*), 0.02 (*4*), 0.04 (*5*), 0.06 (*6*), and 0.09 (*7*) mol L^{-1} ([HPC] = 0.01 mol L^{-1}, n = 6, pH 2, and l = 0.021 cm).

Stable solutions of the heteropolycomplexes with concentrations of 0.01—0.03 mol L^{-1} (series I) containing up to 12 Ti^{IV} ions per initial PW_{11} were obtained by the reaction of $Ti_2(SO_4)_3$ with the heteropolyanion $[PW_{11}O_{39}]^{7-}$ followed by oxidation of Ti^{III} by oxygen and alkalization of the solution from pH ~0.5 to pH 1—3. In the optical spectra, absorption increases as the concentration of Ti^{IV} in the heteropolycomplexes increases (Fig. 1, *a*, *b*). The spectra remained unchanged for two weeks after preparation of solutions. Unlike PW_{11}, in the presence of heteropolyanions $[PW_{12}O_{40}]^{3-}$ at the same [Ti] : [HPA] ratios and at pH ~0.5, Ti^{IV} hydroxo complexes precipitated as $Ti_2(SO_4)_3$ was oxidized.

The data of elemental analysis of samples of Cs salts, which were precipitated from solutions of HPC of series I prepared at pH 2 (Table 1), correspond to the composition of heteropolyanions containing excessive Ti^{IV} ions: $Cs_2H_3[PW_{11}TiO_{40}] \cdot (n-1)TiO_2 \cdot pH_2O$, where n is the number of Ti ions added to a solution per PW_{11} anion, and p is the number of H_2O molecules determined by derivatography.

Cs salts of heteropolycomplexes lost water in the temperature range of 20—150 °C with several (3 or 4) poorly pronounced endo effects, which is typical of crystal hydrates of heteropolycomplexes.[12] No other effects were observed up to 500 °C. The number of H_2O molecules in the heteropolycomplexes increases from 11 to 15 as the number of Ti^{IV} ions increases from 1 to 6 (see Table 1), which can be explained by the presence of hydrated forms of titanium oxides in the compounds obtained.

Table 1. Elemental and phase compositions of Cs salts of HPC precipitated from solutions at pH 2 and at various molar Ti^{IV} : PW_{11} ratios (*n*)

n	Cs : P : W : Ti[a]	Content of the main phase (wt.%)[b]	P : W : Ti in the main phase[b]	Formula
1	2.5 : 1.0 : 11 : 1.2	90.8	0.81 : 11 : 1.2	$Cs_{2.5}H_{2.5}[PW_{11}TiO_{40}] \cdot 11H_2O$
2	1.3 : 1.0 : 11 : 2.2	88.3	1.1 : 11 : 2.2	$Cs_{1.3}H_{3.7}[PW_{11}TiO_{40}] \cdot TiO_2 \cdot 12H_2O$
3	1.5 : 1.0 : 11 : 3.0	91.3	1.0 : 11 : 2.8	$Cs_{1.5}H_{3.5}[PW_{11}TiO_{40}] \cdot 2TiO_2 \cdot 12H_2O$
4	2.6 : 0.96 : 11 : 3.9	95.3	1.0 : 11 : 4.0	$Cs_{2.6}H_{2.4}[PW_{11}TiO_{40}] \cdot 3TiO_2 \cdot 13H_2O$
6	2.5 : 0.96 : 11 : 5.5	86.2	0.88 : 11 : 3.8	$Cs_{2.5}H_{2.5}[PW_{11}TiO_{40}] \cdot 3TiO_2 \cdot 15H_2O$

[a] The data of elemental analysis of the sample.

[b] The data of the differential dissolution method.

Based on the data of differential dissolution, at the molar Ti : PW_{11} ratio of 1—4, the individual compound $PW_{11}Ti_n$ contains a total of 86—95 wt.% of elements (P, W, and Ti) determined. In the case of Ti : PW_{11} = 6, the complex $PW_{11}Ti_4$ was obtained, and remaining titanium was found in a less soluble compound (see Table 1).

At the Ti^{IV} : PW_{11} ratios of 1—6, the regions of vibrations of heteropolyanions in the IR spectra of Cs salts of heteropolycomplexes are identical [$\nu_{as}(P—O_a)$ 1075 cm^{-1}, $\nu_{as}(W{=}O)$ 980 cm^{-1}, $\nu_{as}(W—O_b—W)$ 885 cm^{-1}, and $\nu_{as}(W—O_c—W)$ 800 cm^{-1}] (Fig. 2, spectra *1* and *2*), and correspond to the metal-substituted heteropolyanion[13] $[PW_{11}TiO_{40}]$.$^{5-}$ The difference in the spectra was observed only in the 700—600 cm^{-1} region characteristic of stretching vibrations of W—O—M.[13] In the case of $[PW_{11}TiO_{40}]^{5-}$, a weak band at 700 cm^{-1} was observed. This band "blurred" as the number of Ti ions in HPA increases (see Fig. 2, spectra *1* and *2*). The IR spectrum of the Ti-substituted heteropolycomplex $[PW_{10}Ti_2O_{40}]^{7-}$ obtained according to the known procedure[8] (according to the ^{31}P NMR spectral data, the isomer with the signal at δ −12.0 predominates, and an admixture of the isomer with δ −12.6 is present) differs from the spectra of the Ti^{IV} heteropolycomplexes synthesized by us (see Fig. 2, spectrum *3*) and is characterized by splitting of the band of the central PO_4 tetrahedron (ν 1090, 1068, and 1048 cm^{-1}) due to its severe distortion upon insertion of the second Ti^{IV} ion into the Keggin structure of HPA.

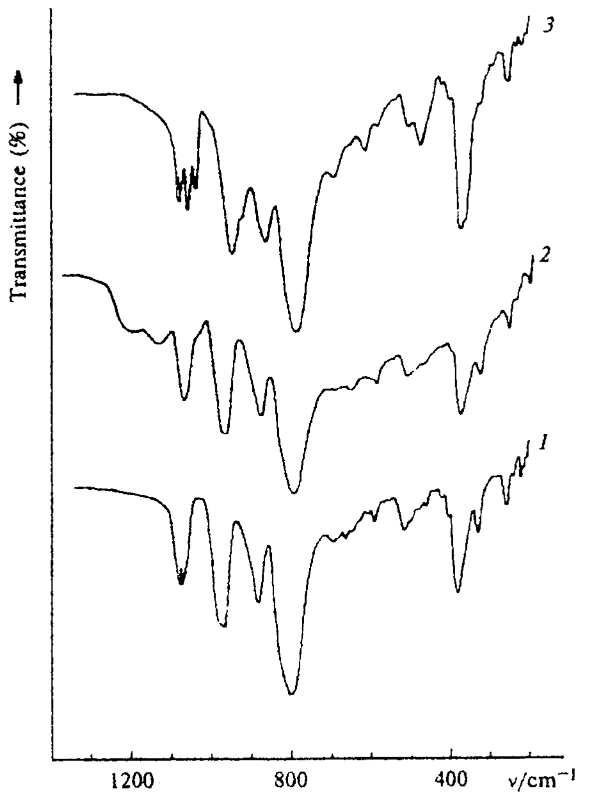

Fig. 2. IR spectra of the salts $Cs_{2.5}H_{2.5}[PW_{11}TiO_{40}] \cdot 11H_2O$ (*1*), $Cs_{2.5}H_{2.5}[PW_{11}TiO_{40}] \cdot 5TiO_2 \cdot 15H_2O$ (*2*), and $Cs_7[PW_{10}Ti_2O_{40}] \cdot 3H_2O$ (*3*).

The data of NMR spectroscopy are given in Tables 2 and 3. The ^{31}P NMR spectra of dilute solutions of the heteropolycomplexes of series I in the pH range of 1—3 at the Ti : PW_{11} ratios of 1—8 (see Table 3) have one narrow signal at δ −13.51±0.07 (Fig. 3). The intensities

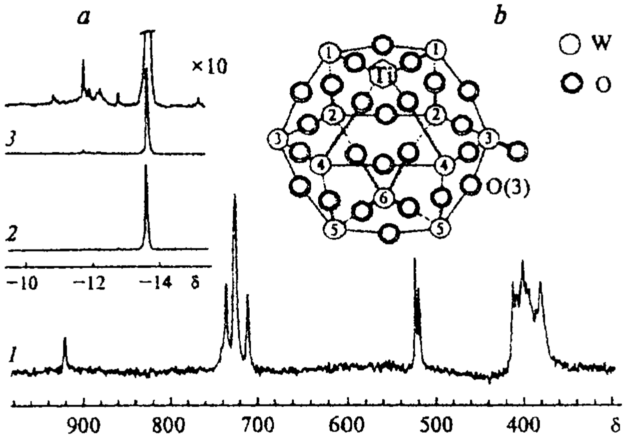

Fig. 3. *a.* NMR spectra of 0.2 *M* aqueous solutions of Ti^{IV} heteropolycomplexes (series I): *1* is the ^{17}O NMR spectrum at the molar Ti : PW_{11} ratio of 1, sample *1*; *2* is the ^{31}P NMR spectrum of sample *1*; *3* is the ^{31}P NMR spectrum at the molar Ti : PW_{11} ratio of 4, sample *3*. *b.* The structure of the metal-oxygen framework of the HPA $[PW_{11}TiO_{40}]^{5-}$ (the terminal O atoms, except for one, are not shown).

Table 2. Data of ^{31}P and ^{17}O NMR spectroscopy for concentrated solutions of heteropolycomplexes obtained at various pH and molar $[Ti^{IV}] : [PW_{11}]$ ratios (*n*) ($[PW_{11}]$ = 0.2 mol L^{-1} and *T* = 295±3 K)

Sample	Series	pH	*n*	$-\delta$ ^{31}P[a] (*I* (%))[b]	δ ^{17}O				
					O=Ti	O=W	Ti—O—W	W—O—W	PO_4
1	III	1.7	1	13.40 [c]	919.2	734.1, 723.2, 709.5	521.9, 517.9	411—380	64
2	III	1.7	2	13.43 [c]	918.9	734.2, 723.8, 709.3	521.3, 517.2	409—380	
3	III	1.7	4	13.47 [c]	918.6	733.2, 722.7, 709.3	520.7, 514.6	411—377	
4 [d]	III	1.4	2	10.65, 11.19, 11.49, 12.55, 13.06[e] (90), 13.40, 13.50		733.1, 724.7, 711.9	531.7	411.7—380.4	62
5	II	1.0	3	10.64, 11.16, 11.55, 11.96, 13.46 (49), 15.00					
6	II	1.0	4	10.64, 10.92, 11.39, 11.54, 12.00, 12.61, 13.45 (42), 15.00, 15.16	908	734.9, 724.2, 710.2	522.4, 517	410—382	
7 [f]	II	2.0	4	11.13, 11.50, 11.55, 11.90, 13.40 (64)					
8	II	2.0	4	10.36, 11.15, 11.50, 11.55, 11.94, 13.46 (46), 15.00					
9	II	2.0	6	10.24, 11.18, 11.49, 11.54, 11.92, 13.45 (39), 15.00					

[a] Chemical shifts were measured relative to the internal standard $[PW_{12}O_{40}]^{3-}$ (δ −15.00). [b] *I* is the relative intensity of the signal of the integrated intensity of all signals of the spectrum at 295±3 K. [c] The singlet (admixtures <5%). [d] H_2O_2 was added in the $[H_2O_2] : [PW_{11}]$ ratio of 1 : 1. [e] The most intense signal is underlined. [f] From $TiCl_4$.

Table 3. Data of ^{31}P NMR spectroscopy for solutions of the heteropolycomplexes of series I obtained at various pH and molar $[Ti^{IV}] : [PW_{11}]$ ratios (*n*)

Sample	$[PW_{11}]$ /mol L^{-1}	pH	*n*	$-\delta$ ^{31}P[a] (*I* (%))
10	0.03	1.0	1	13.50 [b]
11	0.03	1.0	2	13.45 [b]
12	0.03	1.0	3	13.51 [b]
13	0.03	1.0	4	13.50 [b]
14	0.03	1.0	6	13.52 [b]
15	0.027	1.0	8	13.57 [b]
16	0.025	1.0	10	13.50 (79), 10.90, 11.15, 11.22, 11.36 (16), 15.00 (5)
17	0.022	1.0	12	13.53 (78), 11.30 [c] (16), 15.10 (6)
18	0.028	2.0	1	13.55 [b]
19	0.028	2.0	2	13.57 [b]
20	0.028	2.0	3	13.55 [b]
21	0.028	2.0	4	13.56 [b]
22	0.028	2.0	6	13.46 [b]
23	0.027	3.0	1	13.48 [b]
24	0.027	3.0	2	13.47 [b]
25	0.027	3.0	3	13.46 [b]

[a] Chemical shifts were measured relative to the internal standard $[PW_{12}O_{40}]^{3-}$ (δ −15.00). [b] The singlet (admixtures <5%). [c] The center of the group of nonresolved signals.

of other signals (at δ −11 to −13) are very low (see Fig. 3, spectra *2* and *3*). Only at the Ti : PW_{11} ratios of 10—12, do the intensities of these signals substantially increase, and the signal is observed at δ −15, which corresponds to $H_3[PW_{12}O_{40}]$,[14] (see Table 3, samples *16* and *17*). The chemical shift of the major signal in the ^{31}P NMR spectrum is identical to that of the heteropolyanion $[PW_{11}TiO_{40}]^{5-}$ reported previously.[15] When solutions were concentrated tenfold at ~25 °C, the spectral patterns remained unchanged (see Table 2,

Table 4. Intensities of the signals relative to the integrated intensity of the ^{31}P NMR spectrum of solutions of heteropolycomplexes (series II) and the calculated average composition of the complexes corresponding to broadened signals $A + B$

Sample	n	I (%)						Average
		$PW_{11}Ti$ (−13.5)*	$PW_{10}Ti_2$ (−12)*	PW_{12} (−15)*	A (−11.6)*	B (−12.6)*	Other signals	composition ($A + B$)
5	3	47.8	7.8	9.6	15.9	8.0	10.9	$Ti_{9.4}PW_{10.9}$
6	4	42.6	7.4	14.8	18.6	7.5	9.1	$Ti_{12.8}PW_{10.7}$
7	4	62.0	5.2	0.0	15.5	17.2	0.1	$Ti_{10.0}PW_{11.2}$
8	4	44.4	11.1	8.3	13.0	17.0	6.2	$Ti_{11.2}PW_{11.4}$
9	6	37.5	6.2	18.8	17.0	11.0	9.5	$Ti_{19.3}PW_{10.9}$

* The corresponding chemical shifts (δ).

samples *1—3*). A comparison of the overall integrated intensity of the ^{31}P NMR spectrum with the intensity of the signal of the external standard (0.01 *M* NaH_2PO_4 solution) demonstrated that a solution of HPC contained ≥90% of the total amount of phosphorus.

When high concentrations of $[PW_{11}O_{39}]^{7-}$ were used in the synthesis of heteropolycomplexes (series II), the NMR spectra of solutions with the ratios Ti : PW_{11} > 1 have signals whose integrated intensity increased (up to ~50% of the overall intensity) as the concentration of titanium increased (see Tables 2 and 4, samples *5—9*) in addition to the signal at δ −13.5. Judging from the values of the chemical shifts (broadened signals at δ −11 to −13, and two narrow signals at δ −11.95 and −15.4), the first narrow signal can be assigned to one of four isomers of $[PW_{10}Ti_2O_{40}]^{7-}$, which manifest themselves in the ^{31}P NMR spectra (δ −11.43, −10.96, −12.02, and −12.42[8]). The second narrow signal can be assigned to $[PW_{12}O_{40}]^{3-}$. When the Ti^{IV} heteropolycomplexes were prepared from concentrated solutions of reagents, the concentration of H_2SO_4 added together with $Ti_2(SO_4)_3$ was high. This led to a partial rearrangement of HPA during the synthesis to form $H_3[PW_{12}O_{40}]$ and the disubstituted heteropolyanion $[PW_{10}Ti_2O_{40}]^{7-}$. The broadened signals at δ −11 to −13 correspond to other heteropolycomplexes obtained under these conditions.

Reaction of the Ti^{IV} heteropolycomplexes with H_2O_2. The reactions of the Ti-substituted heteropolycomplexes with H_2O_2 yield stable peroxo complexes[15,16] in which the peroxide group is bonded to the Ti^{IV} ion, namely, $[PW_{11}(TiO_2)O_{39}]^{5-}$ and $[PW_{10}(TiO_2)_2O_{38}]^{7-}$. The peroxo complex $[PW_{11}(TiO_2)O_{39}]^{5-}$ is characterized by the absorption maximum at 25500 cm^{-1} (ε is $1.6 \cdot 10^3$ L mol^{-1} cm^{-1}).

The reaction of the Ti^{IV} heteropolycomplexes (Ti^{IV} : PW_{11} > 1) of series I with H_2O_2 yields red complexes. Their absorption spectra are shown in Fig. 1, *c* (for HPC containing six Ti^{IV} ions). At the $[H_2O_2]$: [HPC] ratio of 1 : 1, the positions of the maxima (25600 cm^{-1}) and the values of the optical density (*D*) at ν_{max} for the heteropolycomplexes under study are identical (Fig. 4). An increase in the concentration of H_2O_2 for HPC containing more than one Ti^{IV} ion was accompanied by an increase in the value of *D* (see Fig. 4), which indicate that more than one Ti^{IV} ion of HPC interacts with H_2O_2. The absorption spectra were recorded for transparent solutions within ~10 min after their preparation. At $[H_2O_2]$: [HPC] ≤ 2, solutions of the heteropolycomplexes with various Ti : PW_{11} ratios are stable upon storage, whereas at higher concentrations of H_2O_2, the heteropolycomplexes containing more than one Ti^{IV} ion precipitate with time.

When H_2O_2 was added to a solution of HPC (Ti : PW_{11} = 2) to the $[H_2O_2]$: [HPC] ratio of 1 : 1 or 2 : 1, the ^{31}P NMR spectrum shows the signal corresponding to the complex $[PW_{11}(TiO_2)O_{39}]^{7-}$ (at δ −13.06)[15] instead of the signal at δ −13.5 (the concentration of admixtures was no higher than 10%; see Table 2, sample *4*).

Structures of the Ti^{IV} heteropolycomplexes. The spectral data indicate that one Ti^{IV} ion of the heteropolycomplexes that we obtained is involved in the Keggin framework of the heteropolyanions to form the fragment $[PW_{11}TiO_{40}]^{5-}$, which was identified based on the

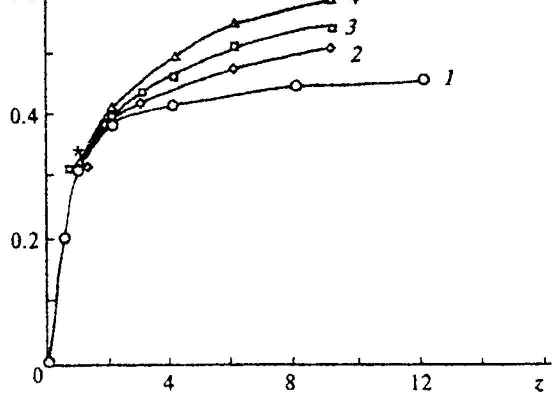

Fig. 4. Dependence of the optical density (ν = 25600 cm^{-1}) of solutions of Ti^{IV} peroxo HPC (series I) on the $[H_2O_2]$: [HPC] ratio (*z*) at n = 2 (*1*), 3 (*2*), 4 (*3*), and 6 (*4*); the asterisk (*) corresponds to n = 1 ([HPC] = 0.01 mol L^{-1} and pH 2).

^{31}P NMR and IR spectra. When Ti^{IV} was bonded in a Ti^{IV} : HPA ratio higher than 1 : 1, the IR spectra of the samples remained virtually unchanged, and they were typical of the metal-substituted heteropolyanion $PW_{11}M$ with the Keggin structure, but this bonding manifests itself in an increase in the intensity of the absorption in the 30 000—26 000 cm^{-1} region. The saturated heteropolyanion $[PW_{12}O_{40}]^{3-}$ cannot stabilize Ti^{IV} ions in solutions, which is typical of $[PW_{11}O_{39}]^{7-}$ possessing a vacancy and structural heterogeneities in its vicinity.

The ^{17}O NMR spectrum of a 0.2 *M* solution of the heteropolyanion $[PW_{11}TiO_{40}]^{5-}$ (see Table 2, sample *1*; Fig. 3) has the signals assigned to the terminal oxygen atoms of O=Ti (δ 919) and O=W (δ 734, 723, and 709), the bridging atoms Ti—O—W (δ 522 and 518), the group of the bridging atoms W—O—W (δ 411—380), and the "internal" atoms of PO_4 (δ 64) in addition to the signals of water and a sulfate ion (δ 164). By analogy with the heteropolyanion $[PMo_{12}O_{40}]^{3-}$ (*cf.* Ref. 17), the broader line corresponding to the Ti—O—W bridges was assigned to the atoms of Ti—O—W(1), whereas the narrower line was assigned to Ti—O—W(4). Undoubtedly, the signal at δ 919 belongs to the oxygen atom of O=Ti by analogy with the signal of O=V of the heteropolyanion $[PW_{11}VO_{40}]^{4-}$ (*cf.* Ref. 18) and taking into account the intensity ratio *I*(O=Ti) : *I*(Ti—O—W) ≈ 1 : 4.

Previously,[19] the scheme of trans-alternation of the bonds upon the replacement of the W atom in the heteropolyanion $[PW_{12}O_{40}]^{3-}$ and strengthening of some bonds has been suggested. Taking into account that an increase in the bond order (the decrease in the shortest O—W distance) leads to the downfield shifts of the signals in the ^{17}O NMR spectrum[20] and the downfield shift of the signals of the "linear" bridges with respect to the "angular" ones, the approximate assignment of the signals of the group of the bridging atoms W—O—W can be made. On this basis, the signals at δ 410.9 and 407 should be assigned to the atoms of W(2)—O—W(1) (O(21)) and O(65). The O(55), O(13), and O(23) atoms of the "linear" bridges and the O(45) and O(26) atoms of the "angular" bridges contribute to the signal at δ 399.4. The O(11), O(22), O(34), and O(35) atoms contribute to the signals at δ 385.3—379.7. This assignment gives a reasonable overall picture for the W—O—W bridges. The signals of the O=W atoms with the intensity ratio of 2 : 7 : 2 made it possible to assign the major peak to the sum of O=W(2) (O(2)), O(3), O(5), and O(6). The signal at δ 709 was assigned to the O(1) atom,[21] and the remaining signal at δ 734 was assigned to O(4).

The ^{17}O NMR spectra of 0.2 *M* solutions of the heteropolycomplexes of series III with $n > 1$ (see Table 2, samples *2* and *3*) have analogous signals. However, the signals of the W—O—Ti bridges are not resolved, and the peak of W(1)—O—Ti is broadened. No new signals were observed in the spectra.

When H_2O_2 was added to the sample with $n = 2$ (see Table 2, sample *4*) in the H_2O_2 : PW_{11} ratio of 1 : 1, the peak of O=Ti in the ^{17}O NMR spectrum disappeared, whereas the signal of the Ti—O—W bridges was substantially shifted and coincided with the high-field signal of the W(1)—O—Ti bridges for the peroxo HPA $[PW_{11}(TiO_2)O_{39}]^{5-}$ (*cf.* Ref. 15). This indicates that the oxygen atom of O=Ti is replaced by the peroxide group. The signal of free H_2O_2 (δ 188) was absent. The peak of coordinated H_2O_2 was not observed. Apparently, this peak is either broadened or masked by the signals of SO_4^{2-} (δ 164) or the internal PO_4 tetrahedron (δ 62). Note that for the complex of H_2O_2 with $[PW_{11}TiO_{40}]^{5-}$ (*cf.* Ref. 15), two signals of the W—O—Ti bridges are well resolved. In solutions with Ti : PW_{11} ≥ 2 (series III), the high-field signal manifests itself as a shoulder, whereas in the ^{17}O NMR spectra of the complexes with H_2O_2, the peaks are not resolved. This means that in the spectrum of sample *4* (see Table 2), the signals of W—O—Ti merge together due to the interaction of HPA with Ti^{IV} hydroxo complexes rather than to complex formation with H_2O_2, which is confirmed by averaging of the Ti—O—W(1) bridges with $n > 1$.

Therefore, the shifts of the signals of the oxygen atoms in the ^{17}O NMR spectra of the samples of series III observed as *n* increases from 1 to 4 and the fact that the position of the signal of the central atom of HPC remains unchanged in the ^{31}P NMR spectrum are indicative of the interaction of "excessive" Ti^{IV} ions with the O atoms of the W—O—Ti bridges of the heteropolyanion, which leads to slight distortions of the Keggin framework of HPA (it was confirmed also by the IR spectra of the complexes). The Ti=O bonds remained unchanged and the complexes, like $[PW_{11}TiO_{40}]^{5-}$, react with H_2O_2 with the replacement of an oxygen atom by a O_2^{2-} group. It follows from the absorption spectra that a portion of other Ti^{IV} ions in the heteropolycomplexes apparently also form peroxide complexes. However, in the presence of a large excess of H_2O_2, the titanium(IV) polynuclear complex was decomposed. The broadening of the signals of the bridging oxygen atoms of W(1)—O—Ti in the presence of "excessive" Ti^{IV} ions may indicate that the complex of $[PW_{11}TiO_{40}]^{5-}$ with titanium ions is labile within the ^{17}O NMR time scale. The O atoms of the W—O—Ti bridges, like the oxygen atoms of the V—O—V and Nb—O—Nb bridges,[22—24] posses higher electron density in the heteropolyanions compared to the atoms of W—O—W and can stabilize electropositive particles (which are, apparently the polynuclear hydroxo complexes $[Ti_{n-1}O_xH_y]^{m+}$ of variable compositions) to form adducts of the type $[PW_{11}TiO_{40} \cdot Ti_{n-1}O_xH_y]^{k-}$.

The synthesis with the use of concentrated solutions of the reagents (series II) yielded Ti^{IV} complexes with the heteropolyanion PW_{11} with an alternative structure, which manifested itself in the ^{31}P NMR spectra (see Table 4). However, the ^{17}O NMR spectra of these solutions differ only slightly from the spectra of the abovementioned complexes with $n > 1$ (see Table 2, sample *6*). In the ^{17}O NMR spectra, signals of the heteropolycomplexes (corresponding to broad peaks in the ^{31}P NMR spectra) may be not observed because of their broadening, low concentrations of the complexes, and their overlapping with the signals of the heteropolyanions $[PW_{11}TiO_{40}]^{5-}$. We believe that in these complexes, titanium(IV) ions add to the heteropolyanion through bonding with Ti^{IV} atoms of the heteropolyanion framework ($PW_{11}O_{39}Ti{-}O{-}Ti_{n-1}O_xH_y$). Hence, the substantial differences in the chemical shifts of the ^{31}P signals of the complexes formed (δ −11 to −13) from that of the $[PW_{11}TiO_{40}]^{5-}$ ion (δ −13.5) are attributable to the replacement of the terminal O atom (Ti=O) in the heteropolyanion by the titanium-oxide fragment, which is in a *trans* orientation with respect to the O atom of the central PO_4 tetrahedron. A substantial broadening of the signals in the ^{31}P NMR spectra of the complexes may be a consequence both of the presence of various $Ti_{n-1}O_xH_y$ fragments and of the further enlargement of the heteropolycomplex as a result of dimerization *via* the $Ti_{n-1}O_xH_y$ fragment (the above-mentioned formula was doubled), like the dimers of the Fe^{III} complexes with PW_{11}.[6]

Assuming that in the complexes tungsten is completely bonded to phosphorus and arbitrarily dividing the broad signals in the region of δ −11 to −13 into two groups, *A* and *B*, depending on the ratio of their integrated intensities (see Table 4), we estimated the average Ti : P : W ratio in these complexes. The stoichiometry of the $PW_{11}Ti$, $PW_{10}Ti_2$, and PW_{12} complexes was taken into account in the calculations. For other compounds, which were present in small amounts (<10%), P : W = 1 : 11 was assumed. The results of the calculations are also given in Table 4. The Ti : P and W : P ratios were estimated from the independent data. The calculations demonstrated that the signals at δ −11.6 (*A*) and −12.3 (*B*) belong to the complexes of series II. We failed to determine the individual stoichiometry of the complexes *A* and *B* from the data in Table 4. The changes in the character of the ^{17}O NMR spectra in the presence of an excess of Ti ($n > 1$) indicate that an alternative mechanism of stabilization of Ti^{IV} in solutions of heteropolyanions PW_{11} is possible. Apparently, in solutions of these compounds, a portion of titanium is stabilized through formation of labile (within the NMR time scale) complexes of $[PW_{11}TiO_{40}]^{5-}$ with $[Ti_{n-1}O_xH_y]^{m+}$, which were not observed in the ^{31}P NMR spectra.

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