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NMR Spectroscopic Studies of Interactions in Solution during the Synthesis of MoVTeNb Oxide Catalysts

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Aqueous solutions used for the synthesis of MoVTeNb oxide catalysts have been studied with ^{125}Te, ^{95}Mo, ^{51}V, and ^{17}O NMR spectroscopy. Polyoxometalate (POM) anion $V_9TeO_{28}{}^{5-}$ (**I**), which has the decavanadate structure, containing Te^{6+} in one of its two central positions, has been identified for the first time in V^{V}-Te^{VI} solutions. In ternary Mo^{VI}-V^{V}-Te^{VI} solutions, the POMs $TeMo_6O_{24}{}^{6-}$ (**II**) (pH ca. 7.8–2) as well as previously unknown complexes of the proposed compositions $TeV_3Mo_3O_{24}{}^{9-}$ (**III**) (pH ca. 8–5) and $TeMo_3V_5O_{27}{}^{5-}$ (**IV**) (pH ca. 6–1) were observed. In the structure of **IV**, half of the decavanadate anion is combined with half of the octamolybdate anion, in which the central Mo atom is replaced with Te^{6+}. There is an equilibrium, **IV** ⇄ **I** + **II**, in the ternary solutions. Despite its stability in solution, polyanion **IV** could not be isolated in the solid state. During concentration under ambient conditions, less soluble polyanion **II** begins to crystallize first, and the equilibrium in solution gradually shifts to **I**. Upon dissolving the precipitate, complex **IV** forms again. The distribution diagrams have been derived from the NMR spectra for a solution of the cationic composition $Mo_1V_{0.3}Te_{0.23}$ with $NH_4{}^+$ as a counterion, acidified with $HClO_4$ in the pH range 7.25–1. In addition to the above-mentioned complexes, $VO_2{}^+$ and $MoO_2{}^{2+}$ oxalates form in the presence of oxalic acid. Upon adding niobium oxalate, Nb_2O_5 gel forms without any Nb-containing species in solution.

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Introduction

The multicomponent MoVTeNb oxide composition is considered to be the best catalyst for propane ammoxidation to acrylonitrile and oxidation to acrylic acid.[1–11] The possibility of the direct multistep conversion of inexpensive, but chemically fairly inert, propane into these valuable products is provided by the combination, on the atomic scale, of the metal elements in their different oxidation states inside a specific crystalline structure. The formation of this structure is achieved through a poorly reproducible "slurry" method consisting of several steps, which are highly sensitive to the preparation conditions. A slurry forms when aqueous solutions of molybdenum, vanadium, tellurium and niobium compounds are mixed together. Further, the slurry is dried and calcined under special conditions. The drying and calcination steps have been carefully studied and have been shown to be of critical importance for obtaining the active catalyst, while the role of the solution stage remains unclear. The influence of this stage was mainly deduced from the properties of the final catalyst.[2,5,8,11] The best catalyst was obtained at a slurry pH between 2 and 3 and an oxalic acid to niobium mol ratio of approximately 3:1. We have found only one paper devoted to studying the solution. In this report, investigations with Raman spectroscopy showed that the parallel formation of different phases in the resulting catalyst is controlled by the chemical equilibrium in the starting ternary MoVTe solution.[10] The Anderson type heteropolyanion $TeMo_6O_{24}{}^{6-}$ and protonated decavanadates were found to exist in solution, and the formation of TeMoV POMs of the Anderson type was suggested. It was also shown that, upon addition of Nb, the structure of the complexes in solution did not change and that they were preserved in the spray-dried product. Actually, $TeMo_6O_{24}{}^{6-}$ is well-known, and the synthesis of its vanadium-substituted derivative $TeMo_5VO_{24}{}^{7-}$ is described in the literature.[12,13] However, Beato et al.[10] do not take into account the literature data on a variety of mixed complexes forming in Mo-V solutions, including $MoV_9O_{28}{}^{5-}$, $Mo_2V_8O_{28}{}^{4-}$, and $Mo_4V_5O_{27}{}^{5-}$, derived from the decavanadate.[14,15] It was also noted that the role of Te and Nb in the catalyst synthesis was as yet little understood.[8,10] We believed that the composition of starting MoVTe(Nb) solutions was not sufficiently well-known and that for better understanding the problem more detailed studies in different pH ranges were needed. With this aim in mind, we have applied multinuclear NMR spectroscopy, as it is the most informative technique for studying speciation of POMs in solutions.[16–18]

Results and Discussion

Binary V^{V}-Te^{VI} Solutions

In acidic aqueous solutions, vanadates and molybdates exist mainly as POM anions and can easily form mixed

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POMs with one another and with many other chemical elements.[16,19] Polyanion $TeMo_6O_{24}^{6-}$ is a typical example of this kind.[12] Since there was no literature data on the V–Te interaction, we have studied binary solutions with different molar ratios of Te/V (Table 1) in a pH range of 7–3, wherein vanadate exists in the form of metavanadate, $(VO_3^-)_n$ (pH > 6), and decavanadate, $V_{10}O_{28}^{6-}$ (pH < 6). These species can be easily identified from ^{51}V NMR spectra (Table 2).[20–25] When $Te(OH)_6$ was added to NH_4VO_3 or $NaVO_3$ solutions, the color changed to light orange and up to eight new peaks appeared in the ^{51}V as well as the ^{125}Te NMR spectra (Figure 1B, a–c; Figure 2B, a). The intensity of the new peaks observed between –491 and –525 ppm in the ^{51}V NMR spectra and at 740, 752, 757, 766, and 834 ppm in the ^{125}Te NMR spectra increased with the Te/V ratio, at the same time their intensity ratio changed from sample to sample, which indicated the formation of several Te-V complexes. The average Te/V molar ratio evaluated from the ^{51}V and ^{125}Te NMR spectra was approximately equal to 1:3. The acidity range of these complexes was that of metavanadate, which suggested that they are likely some Te-containing metavanadate derivatives. The signals of these complexes gradually decayed upon acidification and disappeared at pH 5.

At pH ≈ 6, a modified ^{51}V NMR spectrum of decavanadate appeared (Table 2; Figure 1B, c–f). Decavanadate contains VO_6 polyhedra of three structural types, V_I, V_{II}, and V_{III} (Figure 3, a), and its spectrum consists of three ^{51}V NMR signals with an intensity ratio of $V_{III}/V_{II}/V_I$ = 2:4:4 (Table 2; Figure 1B, g).[14,15] The modified decavanadate spectrum of the Te-V solutions (Table 2; Figure 1B, d–f) consists of four peaks with an intensity ratio of 1:2:2:4. This spectrum is consistent with complex $V_9TeO_{28}^{5-}$ (**I**) that is based on the decavanadate structure with a Te atom instead of one V_{III} atom. As a result, the pairs of V_{II} atoms become nonequivalent, their peak splits into two peaks, and the chemical shifts of all vanadium nuclei change. At pH < 5, the signals shift to lower frequencies because of the protonation of the complex, as it happens in the case of decavanadate and some other polyoxovanadates.[26,27] In the ^{125}Te NMR spectrum, the signal at δ = 837 ppm corresponds to complex **I** (Table 2; Figure 2B, e). The nuclear spin of $^1/_2$ for ^{125}Te suggests long relaxation times and sharp NMR signals. A relatively large signal width observed for **I** is a result of the influence of quadrupolar ^{51}V (spin $^7/_2$), which is known to broaden the NMR peaks of the adjacent nuclei with spin 1/2 substantially because of spin-spin splitting and scalar relaxation of the second kind.[28] The magnitudes of $^2J_{\text{Te-O-V}}$ in **I** are expected to be comparable with $^2J_{\text{V-O-V}}$ in decavanadate (5–10 Hz).[28] The small couplings and short relaxation times could result in the coalescence of the Te-V spin multiplet into a broad peak.

The formation of $V_9TeO_{28}^{5-}$ is further confirmed by its ^{17}O NMR spectrum (Figure 4, a, b; Table 3) resembling the spectrum of decavanadate but containing more peaks since previously identical O atoms become nonequivalent upon

Table 1. Characterization of typical solutions under study.

No.	Initial compound, mass [g]	Metal, conc. [M]	Mo/V/Te/(Nb)	Color	pH
1	PMA,[a] 1.77; NH_4VO_3, 0.35; H_6TeO_6, 0.53	Mo, 1	1:0.3:0.23	red orange	6.2
1a	MoO_3, 0.82; Na_2MoO_4·aq., 1.04; $NaVO_3$·aq., 0.49; H_6TeO_6, 0.53	Mo, 1	1:0.3:0.23	red	5.2
2	solution 1 + $H_2C_2O_4/HClO_4$	Mo, 1		bright red	3
2a	solution 1a + HCl	Mo, 1		bright red	4; 3
3	solution 1 + 2.5 mL of Nb·oxalate	Mo, 1	1:0.3:0.23:(0.12)	bright red	3
4	MoO_3, 0.43; $NaVO_3$·aq., 0.79; H_6TeO_6, 0.23+ HCl	Mo, 1	3:5:1	bright red	5; 3
4a	MoO_3, 0.43; NH_4VO_3, 0.58; H_6TeO_6, 0.23+ HNO_3	Mo, 0.6	3:5:1	bright red	5; 3
5	PMA, 0.53; NH_4VO_3, 0.40; H_6TeO_6, 0.39; 1 mL aq. ammonia	V, 0.24	1:1.13:0.56	orange	9–7
6	Na_2MoO_4·aq., 0.726; $NaVO_3$·aq., 0.474; H_6TeO_6, 0.344	V, 0.43	1:1:0.5	orange	8.2
7	Na_2MoO_4·aq., 0.363; $NaVO_3$·aq., 0.474; H_6TeO_6, 0.344	V, 0.43	0.5:1:0.5	orange	8
8	Na_2MoO_4·aq., 0.145; $NaVO_3$·aq., 0.474; H_6TeO_6, 0.344	V, 0.43	0.2:1:0.5	orange	7.8

[a] $(NH_4)_6Mo_7O_{24}·4H_2O$.

Table 2. The ^{125}Te, ^{51}V, and ^{95}Mo NMR chemical shifts δ [ppm] and peak widths $W_{1/2}$ [Hz] of some polyanions.

Polyanion	pH	$\delta^{125}Te$, $W_{1/2}$	$-\delta$ ^{51}V (integral)	δ ^{95}Mo (integral)	Ref.
$TeMo_6O_{24}^{6-}$	6	819, 15		8	[a]
$TeMo_3V_3O_{24}^{9-}$	8	723, 320	550 (1), 554 (2)	26 (1), 1.2 (2)	[a]
$V_{10}O_{28}^{6-}$	5.4		420 (2), 495 (4), 511 (4)		[14]
$V_9TeO_{28}^{5-}$	5	837, 115	449 (1), 485 (2), 505 (2), 507 (4)		[a]
$V_9MoO_{28}^{5-}$			422 (2), 492 (2), 512 (2), 501 (2), 521 (1)	115	[14]
$TeV_5Mo_3O_{27}^{5-}$	5	808, 120	503 (4), 520 (1)	–4 (1), –16 (2)	[a]
$V_5Mo_4O_{27}^{5-}$			440 (1), 491 (1), 501 (1), 504 (1), 518 (1)	4 peaks from 25 to –15	[15]
VO_2^+ oxalate			533		[20]
MoO_2^{2+} oxalate				–27	[31]

[a] This work.

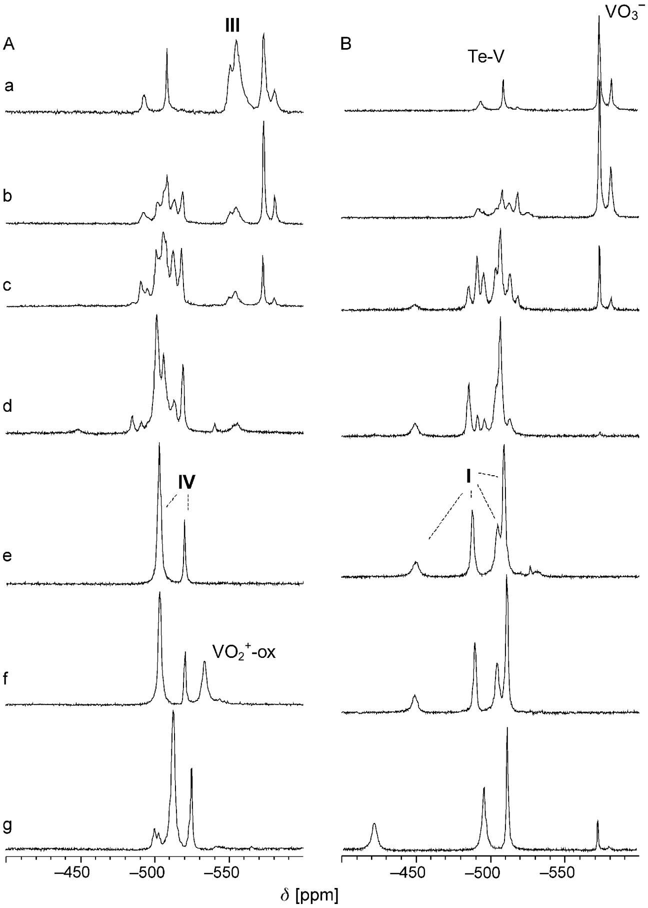

Figure 1. ^{51}V NMR spectra of solutions: A. Mo/V/Te: 1:1.13:0.56, Na^+, pH 7.8 (a); solution 1, pH: 7.25 (b), 6.5 (c), 5.6 (d), 3 (e), 3 (with $H_2C_2O_4$) (f), 1 (g). B. V/Te: 5:1, Na^+, pH 7.5 (a); 9:1, NH_4^+, pH: 7.5 (b), 6.5 (c), 5.5 (d); 5:2, pH: 5 (e), 3 (f); $V_{10}O_{28}^{6-}$ (g).

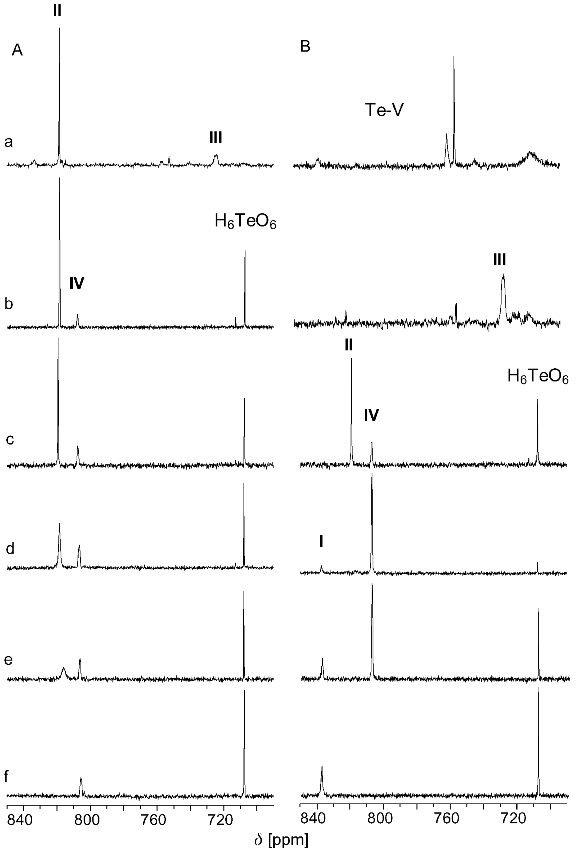

Figure 2. ^{125}Te NMR spectra of solutions: A. Solution 1, pH: 7.25 (a), 4 (b), 3 (c), 2.4 (d), 2.1 (e), 1 (f); solutions d, e, and f contain Mo-Te precipitates. B. Model solutions: V/Te, 5:1, Na^+, pH 7.5 (a); Mo/V/Te, 1:1.13:0.56, Na^+, pH 7.8 (b); solution 3, with Nb_2O_5 gel (c); solution 4, ≈ 3:5:1, pH 4 (d) and ≈ 2.5:5:1, pH 5.2 (e); V/Te, 3:1, Na^+, pH 5 (f).

the insertion of Te. These are three-coordinate O atoms B and bridging O atoms E, half of which are directly connected with tellurium, and, to a lesser extent, terminal O atoms G and bridging O atoms C. The peak-intensity ratio is in agreement with the proposed assignment of the signals. The only peak we do not observe is that of two sixfold bridging O atoms A in the mixed environment $OTeV_5$. Tellurium, when replacing vanadium, shifts the signal of bridging oxygen to lower frequencies more than molybdenum (Figure 4; Table 3). Therefore, the sought signal likely falls in the range of the intense H_2O signal, $\delta \approx 0 \pm 10$ ppm, and cannot be seen.

The central metal ion position V_{III} has appeared to be the most suitable for inserting Te^{6+} into $V_{10}O_{28}^{6-}$, since it provides the regular octahedral oxygen coordination, which is favored by Te^{6+}.[29] Similarly, Te^{6+} replaces the central Mo in $Mo_7O_{24}^{6-}$, which leads to the formation of the stable anion $TeMo_6O_{24}^{6-}$ with a central symmetry. At the same time, mutual replacement of Mo^{6+} and V^{5+} occurs otherwise. For both of them, a distorted octahedron with localized π interaction is preferable, and as a result Mo^{6+}, similar to Te^{6+} in charge and dimensions, can occupy only the V_I position in $V_{10}O_{28}^{6-}$.[14,15]

Mo^{VI}-V^{V}-Te^{VI} Solutions

In Figure 1A, ^{51}V NMR spectra of ternary solutions, sorted by pH and composition, are given. They contain no peaks of known V-Mo complexes.[14,15] The spectrum of solution 1 (Table 1; Figure 1A, c) contains two peaks of residual metavanadate and the peaks from Te-V complexes that were observed in the spectra of the binary V-Te solutions with NH_4^+ as a counterion. A new asymmetric signal, at $\delta = -554$ ppm, of about 10% of the total intensity, represents the only distinction from the spectra of the V-Te solutions, and consequently it can be assigned to a V–Te–Mo complex.

On the other hand, the ^{95}Mo and ^{125}Te NMR spectra show that $TeMo_6O_{24}^{6-}$ (**II**), not revealed by ^{51}V NMR spectroscopy, is a predominant complex in solution 1 and in the other ternary solutions (Figure 2 and Figure 5; Table 2). The ^{125}Te NMR signal of **II** was measured in this study for the first time. Thus, in weakly acidic solution, most of the molybdenum and vanadium individually form their binary complexes with tellurium. It has been suggested that, in the course of the preparation of the MoVTeNbO catalyst, molybdenum in $TeMo_6O_{24}^{6-}$ can be partially replaced with vanadium.[8,10] It could be expected that the resulting complex

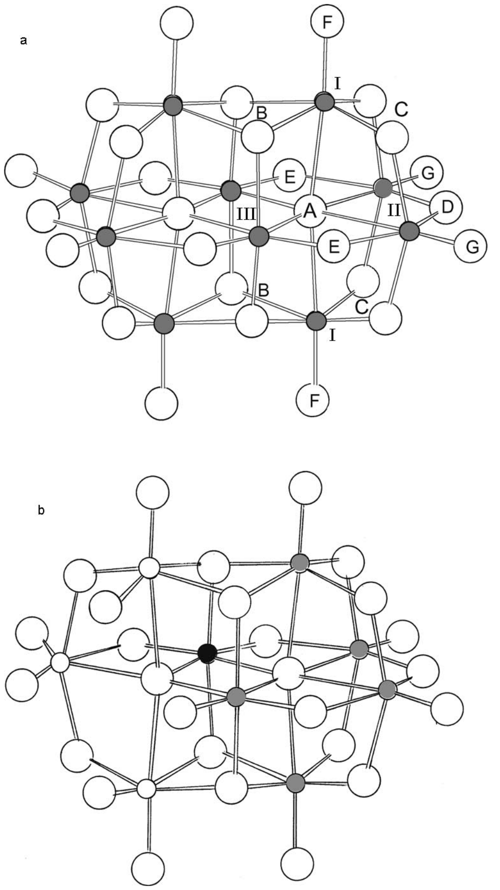

Figure 3. Idealized bond structures of $V_{10}O_{28}^{6-}$ (a) and $TeV_5Mo_3O_{27}^{5-}$ (b). Large open circles represent O atoms, shaded circles represent V atoms, small open circles represent Mo atoms, a filled circle represents the Te atom.

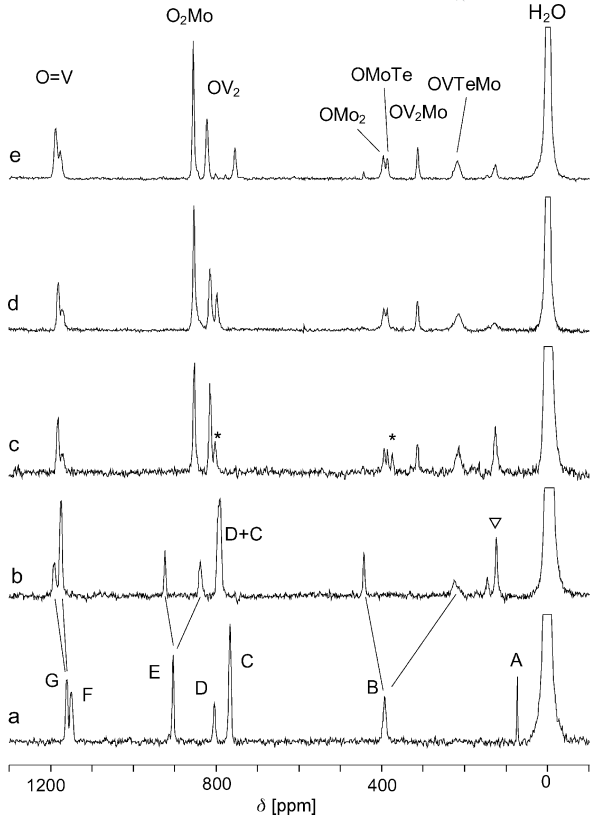

Figure 4. ^{17}O NMR solution spectra of $V_{10}O_{28}^{6-}$ (a), $TeV_9O_{28}^{5-}$ (b), $TeV_5Mo_3O_{27}^{5-}$ at pH 5.2 (c), 4 (d) and 3 (e). The number of scans for each spectrum: 5×10^5; $T = 320$ K. The signals of $TeMo_6O_{24}^{6-}$ and H_6TeO_6 are indicated by * and ▽, respectively.

is detected by the above-mentioned signal at $\delta_V = -554$ ppm. The synthesis of the ammonium salt of $TeMo_5VO_{24}^{7-}$ was described elsewhere.[13] It was prepared from alkaline solutions at the molar ratio Mo/V/Te ≈ 1:1:0.5 and further recrystallized from aqueous acetic acid solution at pH 4.5. We studied similar solutions at a pH range of 7.5–8.5 and found a significant increase in the intensity of the peak at $\delta = -554$ ppm (Figure 1A, a). However, closer examination reveals that this signal consists actually of two unresolved peaks at $\delta = -550$ and –554 ppm with an intensity ratio of approximately 1:2, while $TeMo_5VO_{24}^{7-}$ should give a single ^{51}V NMR peak. The ^{95}Mo NMR spectrum of

Table 3. The ^{17}O NMR chemical shifts [ppm] of some decavanadate-based POMs.

Polyanion	OV	[OMo]	O_2Mo	VOV[Te]			VOMo	MoOMo	OV_3	OV_2Mo	$OVMo_2$	OM_5	OM_6	Ref.
	G, F			E	D	C		[MoOTe]		B		A[a]		
$V_{10}O_{28}^{6-}$	1160 (4)			904 (4)	805 (2)	766 (8)			393 (4)[b]				72 (2)	[14]
	1149 (4)													
$V_9TeO_{28}^{5-}$	1189 (2)			924 (2)	796 (2)	792 (8)			445 (2)	[226 (2)][c]		0 ± 10[d]		[e]
(I) pH 5	1174 (6)			[839 (2)]										
$V_9MoO_{28}^{5-}$	1190 (3)	[880 (1)]		929 (2)	801 (1)	786 (4)	604 (2)		436 (2)	342 (2)			80 (1)	[14]
	1169 (2)			895 (2)	822 (3)								27 (1)	
	1153 (2)													
$V_5TeMo_3O_{27}^{5-}$	1181 (4)		851 (6)	815 (6)				395 (2)		315 (2)	[215 (2)][f]	0 ± 10[d]		[e]
(IV) pH 5	1170 (1)			[850 (1)]				[386 (1)]						
$V_5Mo_4O_{27}^{5-}$	1208 (1)	[867 (1)]	892 (1)	979 (1)	810 (1)	830 (2)	735 (1)	390 (2)		400 (1)	322 (1)	71 (1)	36 (1)	[15b]
	1180 (3)	830 (1)	820 (3)	867 (1)			603 (2)			347 (1)	268 (1)			
		780 (1)												
$TeMo_6O_{24}^{6-}$			807 (12)					383 (6)		180 (6)	$OTeMo_2$			[17]
(II)														

[a] Corresponds to Figure 3. [b] The numbers in round brackets indicate the relative intensity. [c] OV_2Te. [d] Overlaps with H_2O peak. [e] This work. [f] OVMoTe.

the complex also consists of two peaks, but one of them is hidden under the narrower signal of free MoO_4^{2-} present in solutions with a molar ratio V/Mo equal to 1:1 and 2:1 (Figure 6A). At V/Mo = 5:1 and pH = 7.8, all molybdate and approximately one fifth of all vanadate enter into the ternary complex, which shows that the molar V/Mo ratio in the complex is equal to 1:1 (Figure 6B). In the ^{95}Mo NMR spectrum of this solution both peaks of the complex become clearly visible. Their intensity ratio, approximately equal to 2:1, is consistent with three Mo atoms (Table 2). In the ^{125}Te NMR spectrum, the signal at δ = 724 ppm is due to the ternary complex (Figure 2B, b). Its relative intensity, within the error of measurement, supports the formula TeV_3Mo_3. The influence of the adjacent ^{51}V again results in strong broadening of the ^{125}Te NMR signal of **III** (Table 2; Figure 2B, b). The spin-spin coupling with three approximately equivalent ^{51}V nuclei is expected to give a multiplet of 22 components with different intensities in the ^{125}Te NMR spectrum. The parameters of the observed resulting peak with partially resolved components agree with a value of approximately 30 Hz for $^2J_{\text{Te-O-V}}$. The obtained data suggest a formation of $TeMo_3V_3O_{24}^{9-}$ (**III**), a POM of the Anderson type, in which the V atoms as well as the Mo atoms are arranged together. However, to verify the proposed composition of **III**, it would be desirable to measure its ^{17}O NMR spectrum. Unfortunately, this was not possible because of a rather low concentration of **III** ($\approx$ 0.05 mol/L).

A precipitate from a solution of composition $MoV_{0.3}Te_{0.23}$ at pH $\approx$ 8 contained orange and yellow crystals with an average composition approximately corresponding to $TeMo_4V_2$. Their IR spectra corresponded to a POM of the Anderson type. However, we could not reproduce this result in the following experiments; usually the crystalline ammonium salt of $TeMo_6O_{24}^{6-}$ precipitated instead. At pH < 8 the content of complex **III** in solution gradually decreases; it can be observed down to pH $\approx$ 5 by its two ^{51}V NMR peaks, and at pH < 5 it does not form at all.

When solution 1 was acidified with oxalic acid to pH $\approx$ 3 (solution 2), its ^{51}V NMR spectrum contained only three peaks (Figure 1A, f; Table 2). The signal at δ = –533 ppm is related to the oxalate of VO_2^+.[30,31] Independent of the solution composition, signals at –503 and –520 ppm are always observed together with a constant intensity ratio ($\approx$ 4:1), which suggests that they arise from the very same new complex. The ^{95}Mo NMR spectrum of solution 2 consists of four overlapping peaks, two of which arise from $TeMo_6O_{24}^{6-}$ and MoO_2^{2+} oxalate.[30] To increase the concentration of the new complex and to avoid formation of the oxalate complexes, solution 2a was prepared (Table 1). Its ^{51}V NMR spectrum consists only of the two peaks mentioned above (Figure 1A, e), while the ^{125}Te NMR spectrum (Figure 2A, c) contains the signals of $TeMo_6O_{24}^{6-}$, H_6TeO_6, and a new broader signal at δ = 808 ppm correlating in intensity with the two ^{51}V peaks. It is evident that the new complex contains V and Te, since it manifests itself in the spectra on both nuclei. On the other hand, it is impossible to obtain the complex in the absence of Mo in solution. The characteristic bright red color of the solutions is only developed in the presence of all three components, which clearly indicates that yet another V–Mo–Te complex (**IV**) is present. Actually, this was confirmed by the ^{95}Mo NMR spectrum containing three overlapping peaks around δ = 0 ppm (Figure 6, c, d). One of these peaks arises from anion **II**. The other two are new peaks, which are not related to any isopolymolybdate, and which can only arise from the new complex. Their intensity ratio is approximately equal to 1:2, which corresponds to at least three Mo atoms. The new NMR peaks are in the δ range of the MoO_6 octahedra containing two terminal O atoms.[32] With time, the Mo content in solution 2a decreased because of the crystallization of sodium salt $H_xNa_{6-x}TeMo_6O_{24}$. The resulting contents of Mo, V, and Te in solution 2a were found by chemical analysis ($\approx$ 0.36, 0.39, and 0.16 M, respectively). All vanadium is contained in the composition of complex **IV**, while molybdenum is contained in $TeMo_6O_{24}^{6-}$ and in **IV**. From the relative ^{125}Te NMR peak intensities, the contents of Te and Mo were evaluated in the composition of $TeMo_6O_{24}^{6-}$, H_6TeO_6, and **IV**. As a result, the Mo/V/Te mo-

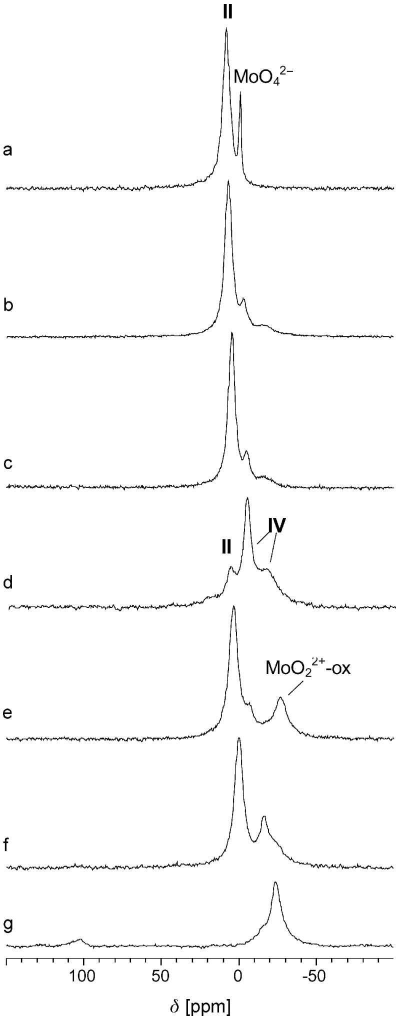

Figure 5. ^{95}Mo NMR spectra of solution 1, pH: 7.25 (a), 4.25 (b), 3 (c), 3 (with $H_2C_2O_4$) (e), 2.1 (f), 1 (g), Mo/V/Te, 1:1.1:0.45, Na^+ (d); solutions f and g contain Mo-Te precipitates.

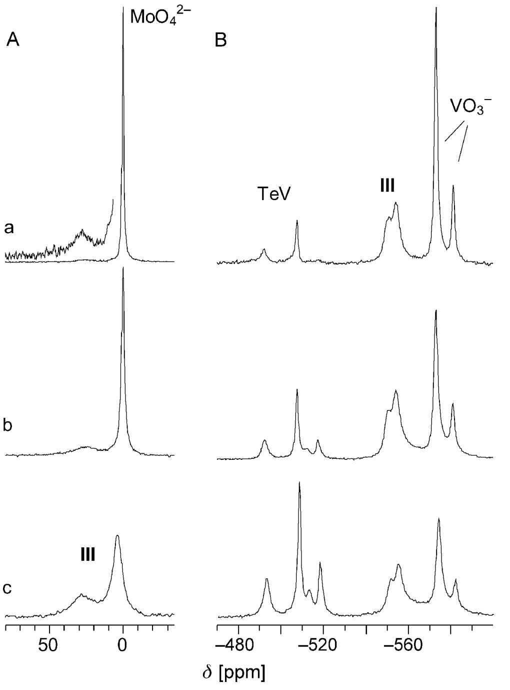

Figure 6. ^{95}Mo (A) and ^{51}V (B) NMR spectra of solutions 6–8 with Mo/V/Te = 1:1:0.5 (a), 0.5:1:0.5 (b) and 0.2:1:0.5 (c).

lar ratio in the ternary complex **IV** was found to be approximately equal to 3.4:5:1. The relative ^{51}V and ^{95}Mo NMR peak intensities from complex **IV**, 4:1 and 2:1, respectively, support the 3:5:1 formula.

The ^{17}O NMR spectrum has allowed the composition and structure of complex **IV** to be further elucidated, since the chemical shifts characterize the structural type of O atoms, and the relative peak intensities reflect the numbers of different O atoms in the structure.[17] This spectrum is surprisingly simple for a mixed V-Mo complex (Figure 4, c; Table 3). It contains two peaks for terminal bonds O=V, one peak for the *cis*-dioxo terminal O atoms of the O=Mo=O groups, and one for the V–O–V bridges. The relative intensities confirm the presence of five V and three Mo atoms in complex **IV**. There are also four weaker signals in the 200–400 ppm range, where Mo–O–Mo bridges and three-coordinate O atoms, connected with Mo or V, can be observed. However, there are no peaks from V–O–Mo bridges in the range 600–650 ppm,[14,15] which indicate a separate arrangement of Mo and V atoms in **IV** and the contact between them only in the sites of high-coordinated O atoms. Comparison of the spectra of $V_{10}O_{28}^{6-}$, $V_9TeO_{28}^{5-}$, and **IV** shows that these complexes are of similar structural type and dimensions. From all the data obtained, we can conclude that polyanion **IV** is evidently based on the decavanadate structure (Figure 3, a, b), in which one of its V_{III} atoms is replaced with Te, the other gains a terminal O atom like the remaining four V atoms, and each of its three Mo atoms has two terminal O atoms. These requirements can be fulfilled in the structure of polyanion $Mo_4V_5O_{27}^{5-}$ discovered in V-Mo solutions by Howarth et al.[15] This POM, derived from decavanadate in the pH range 6–1, coexisted with $V_2Mo_4O_{19}^{4-}$, $V_9MoO_{28}^{5-}$, $V_8Mo_2O_{28}^{4-}$, and some other complexes. The authors have managed to distinguish five ^{51}V NMR signals of equal intensity arising from $Mo_4V_5O_{27}^{5-}$, and with use of two-dimensional ^{51}V-^{51}V correlation spectroscopy they found that all the V atoms are connected with each other and are not separated by Mo atoms. The ^{17}O NMR spectra and potentiometric measurements confirmed the proposed composition and structure of the complex.[15] As compared with decavanadate, this structure lacks one MO_6 octahedron of type M_{II} (Figure 3, b) in the molybdenum part, so that three Mo atoms become each connected to two terminal O atoms, while the fourth Mo and all V atoms including that of type V_{III} each have one terminal O atom. The second V_{III} atom does not have terminal oxygen as in $V_{10}O_{28}^{6-}$, but its signal shifts to –435 ppm. Thus, the halves of the decavanadate and octamolybdate POMs are combined in $Mo_4V_5O_{27}^{5-}$. Howarth et al.[15] called this structure a "chimera".

Ternary Te-Mo-V complex **IV** exists approximately in the same pH range as $Mo_4V_5O_{27}^{5-}$. Tellurium, as heteroatom, easily enters into the central positions of both heptamolybdate and decavanadate, which is difficult for Mo^{6+} and V^{5+} because of their stereochemical properties,[33] and forms complexes more stable than the initial ones. Incorporating itself into the "chimeric" V-Mo POM instead of the unique central V atom and obtaining a necessary symmetrical coordination, tellurium stabilizes only this structure and shifts the equilibrium in its direction. The substitution in the "chimera" occurs at the expense of Mo^{6+} which has the same charge as Te^{6+}. The proposed composition, $TeMo_3V_5O_{27}^{5-}$ (**IV**), is confirmed by the intensity ratio of two ^{51}V NMR signals (4:1) and two ^{95}Mo signals (2:1) and largely by the ^{17}O NMR spectrum (Table 3; Figure 4). The structure that is deduced from the above data is shown in Figure 3 b. As compared with the V-Mo analogue in polyanion **IV**, there are only vanadium atoms with one terminal oxygen atom (5 O atoms) and Mo atoms with two terminal oxygen atoms (6 O atoms) because of the insertion of Te. There are also six V–O–V and two Mo–O–Mo bridges, one V–O–Te and one Mo–O–Te bond, two three-coordinate OV_2Mo atoms and two three-coordinate OVTeMo atoms as well as one five- and one six-coordinate O atom of type **A** in the mixed V–Mo–Te environment. The signals of **A** evidently fall in the range of the H_2O signal as in the case of polyanion **I**. A careful analysis of the observed peak intensities and the application of the known ^{17}O NMR chemical shift scales[17,34] have allowed us to assign the signals and to confirm the suggested composition and structure of the ternary complex. Owing to the substitution of Te^{6+} for Mo^{6+} in $Mo_4V_5O_{27}^{5-}$, the number of the NMR signals decreases from five to two for ^{51}V, from four to two for ^{95}Mo, and from 20 to 10 for ^{17}O (Tables 2 and 3).

The observed spatial isolation of the MoO_6 and VO_6 clusters inside polyanion **IV** evidently facilitates interconversions of the POMs leading to equilibrium (**IV** $\rightleftarrows$ **I** + **II**) in the ternary solutions. During evaporation of the solvent under ambient conditions, the salt of **II** begins to crystallize first because of its lower solubility, and the equilibrium in solution gradually shifts to **I**. Upon further evaporation of the solution, $V_9TeO_{28}{}^{5-}$ or a V-Te POM with a higher Te content also precipitates. On dissolving the precipitate, complex **IV** forms again. It also forms just after mixing solutions of $V_9TeO_{28}{}^{5-}$ and $TeMo_6O_{24}{}^{6-}$. Therefore, we failed in isolating POM **IV**, which is very stable in solution, because of the relatively low solubility of the Te-Mo POM salts. Probably, for isolation of the intact complex some other conditions are necessary, for example evaporation of the solvent at high temperature.

The Influence of Nb^V on the Mo-V-Te Solution

Upon adding strongly acidic (pH ≈ 1) niobium oxalate solution to Mo-V-Te solution 1, the pH drops from 6 to 3 (solution 3, Table 1), and a bright red gel forms after a few minutes. After removing the gel by centrifugation, the solution NMR spectra are the same as after adding oxalic acid alone (solution 2, Table 1) when oxalates of $VO_2{}^+$ and $MoO_2{}^{2+}$ form, together with the above-mentioned complexes. The NMR spectra and the elemental analysis show that there is no Nb-containing species in the filtrate. At the same time, the Nb_2O_5 gel that is separated and washed with water contains a V and Mo admixture captured from solution (in total 10–15%). If the gel is not removed from solution, the ^{51}V as well as ^{125}Te NMR spectra of the almost solid bright red gel remain very similar to those of the pure starting solution (Figure 2A, c; 2B, c). This shows that there are two interpenetrating phases in a common volume: the very porous gel and the ternary solution filling the pores, with no chemical interaction between them. The Nb_2O_5 gel, if dried under special conditions, physically hinders the crystallization of the ammonium salt of Te-Mo POM, which is evidently important for obtaining the good catalyst.[8,10] According to visual evaluation, the gel is most homogeneous at pH ≈ 3, where the isoelectric point of amphotheric Nb_2O_5 is expected.[35] The formation of the gel during the solution stage as well as the other peculiarities of the synthesis show that the "slurry" method of preparing the MoVTeNb oxide catalyst is a kind of "sol–gel" method, which is very effective for synthesizing multicomponent oxides, homogeneous throughout the bulk on a molecular scale.[36–40] It has been noted in the literature that in the gel-based synthesis the ingredients are molecularly mixed and spatially fixed in the gel, reducing diffusion distances during thermolysis and thus lowering the temperature for oxide formation. Additionally, it was reported that the chemical phase separation "can be overcome by controlling the processing conditions during all stages."[36] However, in contrast to the conventional sol–gel syntheses carried out from organometallic precursors in organic solvents,[36–40] the MoVTeNb oxide catalyst is prepared from inorganic starting materials in aqueous solutions containing soluble complexes in addition to the gel. The significant role of niobium is evident. On one hand, it forms a three dimensional polymeric matrix, in which the above complexes are preserved from crystallization after fast drying, and on the other hand, it participates, as a result of its highly dispersed state and its chemical similarity with vanadium and molybdenum, in the formation of the catalytically active mixed-oxide crystalline phases upon further thermal treatment.[3]

The Distribution Diagrams

As a result of this study, the distribution diagrams derived from the ^{125}Te, ^{51}V, and ^{95}Mo NMR spectra have been composed. They show the contents of tellurium, vanadium, and molybdenum in different complexes in solutions with an atomic ratio Mo/V/Te = 1:0.3:0.23, in the absence of oxalic acid, in a pH range of approximately 7.25–1 (Figure 7). At pH < 4.5, there are only $TeMo_6O_{24}{}^{6-}$, $TeV_5Mo_3O_{27}{}^{5-}$, and excess $Te(OH)_6$ in solution. Their relative contents change with the Mo/V/Te ratio in solution. The equilibrium can be shifted almost completely to ternary complex **IV** with an increase in vanadium content (Figure 2B, d).

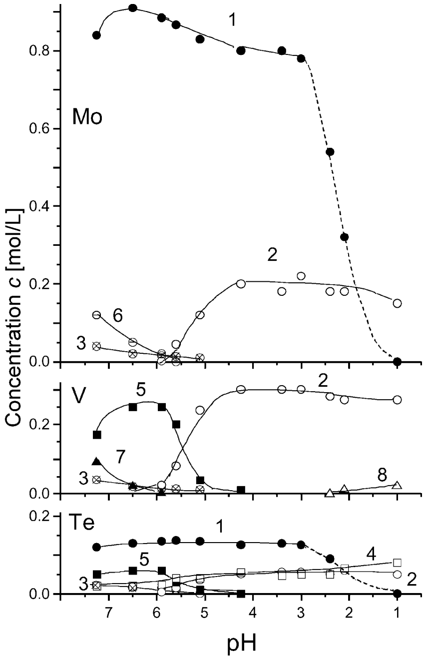

Figure 7.The contents of molybdenum, vanadium, and tellurium in different complexes for composition $Mo_1V_{0.3}Te_{0.23}$ and [Mo] = 1 M, depending on pH: (1) $TeMo_6O_{24}{}^{6-}$, (2) $TeV_5Mo_3O_{27}{}^{5-}$, (3) $TeMo_3V_3O_{24}{}^{9-}$, (4) $Te(OH)_6$, (5) total content of V-Te complexes including $V_9TeO_{28}{}^{5-}$, (6) $MoO_4{}^{2-}$, (7) $VO_3{}^-$, (8) $VO_2{}^+$.

The composition of the ternary solution is practically constant in a pH range of ca. 4.5–3 (Figure 7) except for an increase in the degree of the POM protonation, which causes a shift of the ^{95}Mo and ^{125}Te signals of $TeMo_6O_{24}{}^{6-}$ and the ^{51}V and ^{125}Te signals of $TeV_5Mo_3O_{27}{}^{5-}$to lower frequencies. The presence of protonated POMs at pH 3 can be of significance for their condensation into polymeric oxide networks during thermolysis. On the other hand, a higher protonation of $TeMo_6O_{24}{}^{6-}$ at pH < 3 leads to its destruction and to the gradual precipitation of Mo together with Te in ratio of ca. 1:0.4, according to elemental analysis. Vanadium remains in solution down to pH ≈ 1, mainly in the composition $TeV_5Mo_3O_{27}^{5-}$, but several new weak ^{51}V peaks appear nearby, including that of free VO_2^+ (Figure 1A, g). Simultaneously, in the ^{95}Mo NMR spectrum a new signal at +102 ppm becomes visible, which indicates the appearance of Mo with one terminal O atom (Figure 6, g).[32] This result may indicate further substitution of molybdenum for vanadium in position V_I of **IV** (Figure 3), caused by high solution acidity, which is usual for V-Mo complexes.[14]

Upon addition of Nb oxalate to the POM solution, approximately 25% of the molybdenum and 15% of the vanadium become involved in the oxalate complexes forming at the expense of Nb oxalate. A loss of the oxalate ligands and a decrease in acidity (as compared to the Nb oxalate solution) cause precipitation of hydrated Nb_2O_5.[35] The resulting solution is equal to the one used for catalyst synthesis. It contains $TeMo_6O_{24}^{6-}$, $TeV_5Mo_3O_{27}^{5-}$ as well as the Mo and V oxalates. According to the diagram, the solution composition is almost constant in the pH range 4.5–3. Evidently the formation of homogeneous Nb_2O_5 gel mainly determines the most suitable pH (≈ 3) for the synthesis of the desired crystalline phase and the effective catalyst.[2,5,8,11] The aim of drying the gel is to preserve its homogeneous structure with the embedded POMs and oxalate complexes. The gel mass should (evidently) be sufficient to take up all liquid, so that the undesirable solid phases could not form from the remaining solution.

Te^{VI}, as a strong heteroelement for Mo^{VI} and V^V, shifts the equilibrium in favor of only two, MoTe and VMoTe, stable polyoxocomplexes. They provide a good mixing of the constituent elements already at the solution stage, which is helpful, as was suggested elsewhere,[10] for the formation of required mixed-oxide phases during calcination and for preventing the undesirable MoO_2 and MoO_3 formation. During calcination under an inert atmosphere, Te^{6+} is reduced to Te^{4+}. In this oxidation state it plays quite a different role; it stabilizes the formed crystalline phases and presumably enters into the composition of the catalyst active center.[3]

The Raman and IR spectra show that $TeMo_6O_{24}^{6-}$ is present in the amorphous dry product.[10,11] As for $TeV_5Mo_3O_{27}^{5-}$, evidently it is also preserved during fast gel drying, since the crystallization process leading to its POM decomposition is suppressed. If the decomposition nevertheless takes place, it occurs without phase separation.

Conclusions

The ^{125}Te, ^{51}V, ^{95}Mo, and ^{17}O NMR spectroscopic measurements carried out in this study have provided a considerable amount of data on the composition of Mo-V-Te-(Nb) solutions as reflected in the distribution diagrams. The predominant complex in the pH range 7.5–2 is the well known polyanion $TeMo_6O_{24}^{6-}$. The three other POMs, $V_9TeO_{28}^{5-}$, $V_3Mo_3O_{24}^{9-}$, and $TeV_5Mo_3O_{27}^{5-}$, were observed and identified for the first time. In solutions containing oxalic acid, VO_2^+ and MoO_2^{2+} oxalates are present in addition to the above complexes. Niobium does not incorporate into the soluble complexes and forms Nb_2O_5 gel at pH ≈ 3, which prevents phase separation and causes the formation of a homogeneous amorphous dry product.

Because of difficulties in the isolation of the Te-V-Mo complexes, their in situ identification is of special importance. In this regard, NMR spectroscopy has shown its unique capabilities in the present study.

Experimental Section

For preparing solutions, the following starting materials were used: ammonium paramolybdate (PMA) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$; ammonium and sodium metavanadates (MVA) NH_4VO_3 and $NaVO_3\cdot 2H_2O$; sodium molybdate $Na_2MoO_4\cdot 2H_2O$; molybdenum trioxide MoO_3; telluric acid (TA) H_6TeO_6. The solution acidity was adjusted by adding different acids (HCl, $HClO_4$, HNO_3, $H_2C_2O_4$) and NH_4OH or NaOH. All the compounds were the best available reagent grade and were used without further purification. The characterization of the typical solutions under study is given in Table 1. Thus, for preparing solution 1 with a Mo/V/Te molar ratio corresponding to the optimum catalyst composition $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}$, PMA (1.77 g), MVA (0.351 g), and TA (0.528 g) were dissolved in distilled water (10 mL) at 80 °C with stirring, followed by cooling to ca. 20 °C. The pH of the resulting solution was about 6. For obtaining solution 3, a Nb oxalate solution (2.5 mL, 46.5 mg/mL Nb; $C_2O_4^{2-}/Nb = 3:1$) was added to solution 1. Model V-Te and Mo-V-Te solutions were prepared using Na^+ instead of NH_4^+ salts to increase the concentration of the complex. The synthesis of $Na_6TeMo_6O_{24}\cdot xH_2O$ was carried out according to the method of Filowitz et al.[17] The product composition and its purity were confirmed by elemental analysis and the ^{17}O and ^{95}Mo NMR spectra.[17,18]

NMR spectra were measured with a Bruker Avance-400 spectrometer, at the natural content of ^{125}Te, ^{17}O, and ^{95}Mo (≈ 7, 0.04, and 16%, respectively). The ^{125}Te chemical shifts (δ) given relative to Me_2Te were determined by using telluric acid aqueous solution as a secondary external standard (δ = 707 ppm).[41] The ^{95}Mo and ^{51}V NMR chemical shift values were determined relative to Na_2MoO_4 and $VOCl_3$ (1 M), respectively, and those for the ^{17}O NMR signals relative to internal H_2O. The NMR spectra were measured at room temperature and at 320 K. The portions of V, Mo, and Te in the composition of different complexes were determined by their NMR signal relative intensities found from the integrals. For evaluating intensities of overlapping signals, their decomposition was made with use of a standard NMR program. In most cases, the uncertainty in measuring intensities was about 20%. In the observed ^{17}O NMR spectra, the signals are fairly narrow, which allows their relative intensity to be evaluated with the accuracy of ± 10%. Elemental analyses were conducted by using an atom-emission spectrometer "Optima" (USA) with inductively coupled plasma.

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