

**Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products IX. Products of the reactions taking place in acidified solutions of rubidium and cesium metavanadate and study of the  $^{51}\text{V}$  NMR spectra of aqueous solutions of polyvanadates**

<sup>a</sup>E. ŽÚRKOVÁ, <sup>a</sup>V. SUCHÁ, and <sup>b</sup>J. SCHRAML

<sup>a</sup>*Department of Inorganic Chemistry, Faculty of Natural Sciences, Komenský University, CS-842 15 Bratislava*

<sup>b</sup>*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, CS-165 02 Prague*

Received 16 August 1984

Accepted for publication 15 January 1985

It has been revealed on the basis of the  $^{51}\text{V}$  NMR spectra of aqueous solutions of  $\text{NaVO}_3$  in acid region that the degree of their acidification and temperature influence chemical shifts, i.e. the composition of solutions.

The optimum conditions of preparation of  $\text{M}'_2\text{V}_6\text{O}_{16}$  and  $\text{RbHV}_6\text{O}_{16}$  have been determined for the systems  $\text{M}'\text{VO}_3\text{—HNO}_3\text{—H}_2\text{O}$  ( $\text{M}' = \text{Rb, Cs}$ ).

В результате исследования  $^{51}\text{V}$  ЯМР спектров водных растворов  $\text{NaVO}_3$  в кислой области было найдено, что степень их подкисления и температура влияют на химические сдвиги, то есть, на состав растворов.

В системах  $\text{M}'\text{VO}_3\text{—HNO}_3\text{—H}_2\text{O}$  ( $\text{M}' = \text{Rb, Cs}$ ) были определены оптимальные условия получения  $\text{M}'_2\text{V}_6\text{O}_{16}$  и  $\text{RbHV}_6\text{O}_{16}$ .

Different types of polyvanadates may arise by crystallization from acid aqueous solutions according to temperature. Thus decavanadates were obtained at laboratory temperature [1, 2], pentavanadates at 40 °C [3, 4], and hexavanadates at 80 °C [5]. It is, therefore, obvious that the temperature has influence on the composition of polyvanadates crystallizing from acid aqueous solutions. The first explanation of this influence is based on the idea that the temperature affects the equilibria of different kinds of the polyvanadate ions in solutions, which manifests itself in composition of the solid phases. Other explanation rests upon different solubility of individual types of polyvanadates at the above temperatures. In this case, the influence of temperature shows itself as late as in the course of crystallization.

The first part of this paper deals with the influence of temperature on the composition of acid aqueous solutions of vanadates investigated by the method of  $^{51}\text{V}$  NMR spectroscopy while the second part is concerned with the influence of temperature, concentration of solution, and degree of acidification  $Z$  on the composition of solid rubidium and cesium polyvanadates.

## Experimental

### *NMR spectral measurements*

The  $^{51}\text{V}$  NMR spectra were taken with a spectrometer Varian XL-200 working in the frequency 52 MHz in pulse regime. The ratio magnetic field : frequency was held constant by means of the  $^2\text{H}$  NMR signal of solvent ( $^2\text{H}_2\text{O}$ ). The chemical shifts were measured with respect to the signal of  $\text{VOCl}_3$ .  $\text{VOCl}_3$  was prepared according to [6]. The capillary with this standard was freely placed in 5 mm cells containing the measured samples. The spectra were measured in spectral width of 40 kHz, FID's were accumulated (2000—3000 "scans") during the acquisition time of 0.32 s. Before transformation FID was completed to 32 k words by zeros and weighed exponentially while the lines were expanded by 3.18 Hz. Owing to the line widths and reference method, the chemical shifts are given with approximate precision of  $\pm 0.3$  ppm. The chemical shifts are expressed in the  $\delta$  scale.

The measurements were performed with solutions of  $\text{NaVO}_3$  in  $^2\text{H}_2\text{O}$ , the concentration being  $0.1 \text{ mol dm}^{-3}$  or  $0.2 \text{ mol dm}^{-3}$ .  $\text{HNO}_3$  ( $c = 1 \text{ mol dm}^{-3}$ ) was added in such amount that the value of  $Z$  was 0.4, 0.55, and 0.7;  $Z = n(\text{HNO}_3)/n(\text{NaVO}_3)$ . The measurements were carried out at 23 °C, 40 °C, and 80 °C. The solutions were thermostated at required temperature till the equilibrium was established. The value of pH which did not vary for 24 h served as criterion of equilibrium establishment.

### *Preparation of vanadates*

$\text{RbVO}_3$  and  $\text{CsVO}_3$  which served as starting substances for studying the influence of temperature on the composition of solid rubidium and cesium vanadates crystallizing from acid aqueous solutions were prepared by dissolving  $\text{V}_2\text{O}_5$  in the corresponding carbonate [7]. Their composition was verified by chemical analysis and the X-ray powder method. The concentrations of the starting solutions of  $\text{RbVO}_3$  and  $\text{CsVO}_3$  were  $0.1 \text{ mol dm}^{-3}$ . Under selected conditions, the concentrations were  $0.025 \text{ mol dm}^{-3}$  and  $0.05 \text{ mol dm}^{-3}$  for  $\text{RbVO}_3$  and  $0.01 \text{ mol dm}^{-3}$ ,  $0.05 \text{ mol dm}^{-3}$ , and  $0.075 \text{ mol dm}^{-3}$  for  $\text{CsVO}_3$ .  $\text{HNO}_3$  ( $c = 1 \text{ mol dm}^{-3}$ ) was added into the solution of vanadates in such amount that the degree of acidification  $Z$  was in the interval 0.4—1.0 (with the step of 0.2) and subsequently 2.0 and 3.0; for  $\text{RbVO}_3$  the highest additional degree of acidification was 4.0. The volume of the reaction solution was  $100 \text{ cm}^3$ . It was held constant during the whole process of synthesis. The syntheses were carried out at 20 °C, 40 °C, 60 °C, and 80 °C. The reaction time varied in the interval 5 min—24 h for the Cs compounds and in the interval 15 min—24 h for the Rb compounds.

In most syntheses, the reaction solution was stirred. The pH value of reaction system was checked in course of all syntheses.

The pH values were measured with a pH-meter TTT-2 (Radiometer) equipped with a combined electrode OP 807-1/A.

The prepared polyvanadates were identified by the X-ray phase analysis (diffractograph Philips, PW 1050, goniometer,  $\text{Cu}(K_{\alpha})$  radiation,  $\Theta$  range  $4^{\circ}$ – $30^{\circ}$ ), infrared spectroscopy (IR spectrophotometer PE 180, Nujol suspension,  $\bar{\nu} = 400$ – $2000 \text{ cm}^{-1}$ ), and chemical analysis. Vanadium(V) was determined volumetrically by titrating with  $\text{FeSO}_4$  ( $c = 0.05 \text{ mol dm}^{-3}$ ) and using diphenylamine as an indicator. Rubidium and cesium were determined gravimetrically by precipitating the analyzed solution by  $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$  according to paper [8].

## Results and discussion

### NMR spectral measurements

The resonances with the chemical shifts ( $\delta/\text{ppm}$ )  $-424.3$ ,  $-500.7$ ,  $-515.7$  ( $23^{\circ}\text{C}$ );  $-424.3$ ,  $-499.8$ ,  $-515.0$  ( $40^{\circ}\text{C}$ );  $-421.3$ ,  $-498.8$ ,  $-514.9$  ( $80^{\circ}\text{C}$ ) (Fig. 1, Table 1) were assigned to  $\text{V}_{10}\text{O}_{28}^{6-}$  or its protonated forms in conformity with papers [9–12]. These kinds of resonance were also present as the only ones in all spectra of the solutions with  $Z=0.55$  ( $\text{pH}=4.0$ – $4.2$ ) and  $Z=0.7$  ( $\text{pH}=2.1$ – $2.3$ ) at both concentrations ( $0.1 \text{ mol dm}^{-3}$  and  $0.2 \text{ mol dm}^{-3}$ ) and all investigated temperatures (Table 1). The intensity ratio of the above three lines depended on temperature and degree of acidification  $Z$  and varied about the value

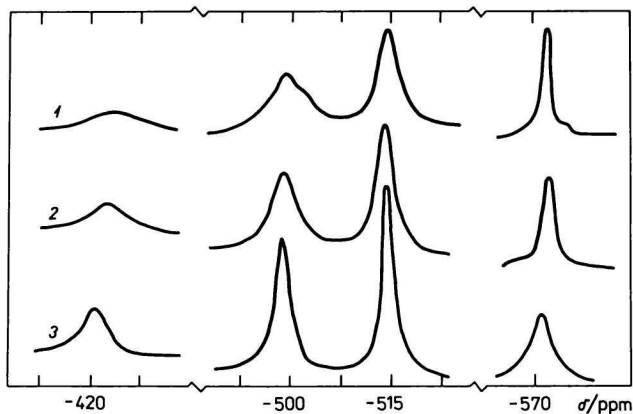


Fig. 1.  $^{51}\text{V}$  NMR spectra of  $\text{NaVO}_3$  solution in  $^2\text{H}_2\text{O}$  ( $c = 0.1 \text{ mol dm}^{-3}$ ;  $Z = 0.4$ ,  $\text{pH} = 6.1$ ) at different temperatures.

1.  $23^{\circ}\text{C}$ ; 2.  $40^{\circ}\text{C}$ ; 3.  $80^{\circ}\text{C}$ .

Table 1

Survey of chemical shifts and half-widths of lines in  $^{51}\text{V}$  NMR spectra

$c/(\text{mol dm}^{-3})$	$Z$	$\theta/^\circ\text{C}$	pH	$\delta/\text{ppm}$ (half-width/Hz) <sup>a</sup>				
				Line 1	Line 2	Line 3	Line 4	Line 5
0.1	0.4	23	6.1	-424.3(400)	-500.7(360)	-515.7(176)	-577.2( 72)	-581.1(?)
		40	6.1	-424.3(260)	-499.8(240)	-515.0(160)	-577.3(100)	
		80	6.1	-421.3(195)	-498.8(126)	-514.9( 92)	-572.8(159)	
	0.55	23	4.2	-425.8(480)	-506.0(300)	-522.8(227)		
		40	4.1	-424.2(330)	-504.6(222)	-520.8(164)		
		80	2.1	-422.9(270)	-504.6(137)	-522.7(108)		
	0.7	23	2.3	-427.2(520)	-509.3(314)	-527.6(240)		
		40	2.3	-424.4(360)	-506.8(237)	-524.8(217)		
		80	2.1	-422.9(270)	-504.6(137)	-522.7(108)		
0.2	0.4	23	6.1	-424.3(480)	-500.4(374)	-515.7(220)	-577.1( 60)	
		40	6.1	-423.8(340)	-499.4(230)	-514.9(160)	-577.0(100)	
	0.55	23	4.0	-425.8(520)	-504.5(356)	-520.9(260)		
		40	4.1	-424.8(380)	-503.5(226)	-520.1(164)		
		80	4.2	-422.7(199)	-501.6(134)	-518.5( 99)		

a) Chemical shift in  $\delta$  scale: diamagnetic shift negative with respect to external  $\text{VOCl}_3$ , precision  $\pm 0.3$  ppm; precision of half-width  $\pm 6$  Hz for lines with smaller half-width than 400 Hz, for other lines 20–30 Hz.

1:2:2. This intensity ratio was also found by other authors [10–12] and is consistent with the structure  $V_{10}O_{28}^{6-}$  in solid decavanadates [1, 13]. The decavanadate ion consists of ten  $VO_6$  octahedrons. Two groups of these octahedrons containing four octahedrons each have one by one terminal oxygen and two octahedrons are inside the anion (Fig. 2a). In Fig. 2, the atoms of vanadium present

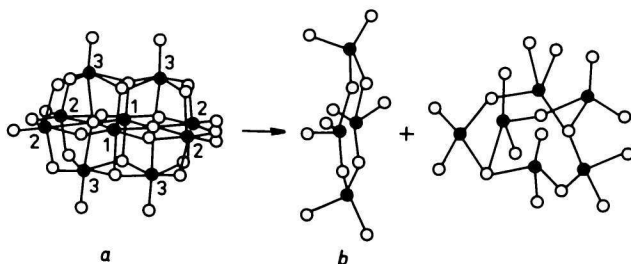


Fig. 2. Depiction of the decomposition of the decavanadate ion (a) into the metavanadate (b) and hexavanadate (c) ion.

in the centres of octahedrons of the first two groups are denoted by numbers 2 and 3 whereas the atoms of vanadium belonging to inside octahedrons are denoted by number 1.

It is obvious from Fig. 1 and Table 1 that the chemical shifts and half-widths of the three lines corresponding to the decavanadate anions are sensitive to temperature and the value of  $Z$ . An increase in temperature as well as in pH (decrease in the value of  $Z$ ) manifests itself in the same manner in the values of chemical shifts. However, the influence of these two factors on the half-widths of lines is not absolutely equal. An increase in temperature brings about contraction of all three lines. An increase in  $Z$  brings about contraction of lines 1 and 3 while line 2 is always most contracted at  $Z = 0.55$ .

A concentration increase of solutions manifests itself by increase in intensity of lines and does not practically affect the values of chemical shift.

The influence of temperature and pH on the NMR spectra of vanadate solutions was also studied by other authors [9, 11]. All of them so interpret the influence of protonation on the spectra of vanadate that a protonation of the oxygen atoms in the decavanadate ion sets in with decreasing pH of the solutions, owing to which the symmetry of electron density in proximity to the nuclei of vanadium atoms decreases and thus the rate of quadrupole relaxation (increase in the width of lines) as well as the screening of the nuclei of vanadium atoms increases. We may deduce from our results that the protonation of the decavanadate ion proceeds successively. First of all, the protons are likely to be bonded to the oxygen atoms belonging to atom V1 and V3 ( $Z = 0.55$ ). Further addition of acid brings about that the protons are bonded to some of the oxygen atoms belonging to octahedrons V2

( $Z=0.7$ ), too. Thus we may draw conclusion that the bridge atoms of oxygen should be bonded.

Because of a similar influence of temperature and protonation on chemical shifts, we may assume that the equilibrium of protonated and nonprotonated forms of the decavanadate ions shifts to the nonprotonated form with increasing temperature. The influence of temperature on the width of lines is, however, more complicated because the influence of temperature on other exchange processes and correlation times of reorientation of the tensor of the gradient of electric field may also be effective in this case.

We assign the resonance line with the chemical shift  $\delta = -577.2$  ppm at 23 °C and 40 °C ( $Z=0.4$ ) to the metavanadate ions  $V_nO_{3n}^-$  ( $n=3$  or 4) in accordance with the authors of papers [9, 11, 12, 14]. The metavanadate ion, as generally known, consists of three or four tetrahedrons  $VO_4$  joined through oxygen atoms in a six- or eight-membered cycle (Fig. 2*b*). Another line of small intensity with the chemical shift  $\delta = -581.1$  ppm which is missing at 40 °C appears in the spectra at 23 °C. As the equilibrium of the  $V_{10}O_{28}^{6-}$  and  $V_nO_{3n}^-$  ions in solution is established very slowly (which may be due to a change in coordination number of vanadium or formation of a poorly stable intermediate and maybe both these phenomenons), we may assume that the resonance  $\delta = -581.1$  ppm indicates this intermediate because the equilibrium might not be established at 23 °C, but it was established at 40 °C. *Habayeb* and *Hileman* [11] found in the spectrum of aqueous solution of sodium polyvanadate ( $c = 0.5$  mol dm<sup>-3</sup>, 25 °C, pH = 8.8) a line with the chemical shift  $\delta = -582$  ppm which they ascribed to  $V_6O_{17}^-$ . They have assumed that the hexavanadate ion consists of six tetrahedrons  $VO_4$  which are joined through the oxygen atoms (Fig. 2*c*). *O'Donnell* and *Pope* [12] assign the line with the chemical shift  $\delta = -582$  ppm present in the <sup>51</sup>V NMR spectrum of aqueous solution of sodium polyvanadate ( $c = 0.3$  mol dm<sup>-3</sup>, 30 °C, pH = 6.6) to a linear metavanadate ion arising as intermediate by splitting the cycle in the course of transformation of the metavanadate into decavanadate ion. In other paper [14], the resonance  $\delta = -589.4$  ppm is attributed to the cyclic hexavanadate ion of the composition  $V_6O_{18}^{6-}$ .

A relatively wide resonance line with  $\delta = -572.8$  ppm appears in the spectrum of  $NaVO_3$  solution heated to 80 °C. According to the value of chemical shift, it could be assigned to the metavanadate ions  $V_nO_{3n}^-$ . However, the considerable extension of this line in comparison with the width at 40 °C and 23 °C cannot be logically explained by impairment of the symmetry of the V—O polyhedrons due to formation of the protonated metavanadate ions.

It has been alleged in paper [15] that the addition of the oxygen atoms of water molecules to  $V_{10}O_{28}^{6-}$  gives rise to an instable intermediate according to the equation



We assume that the complete decomposition of the decavanadate ion according to Fig. 2 may take place at an increased temperature.

The hexavanadate ion may consist of the polyhedrons  $\text{VO}_6$ ,  $\text{VO}_5$ , and  $\text{VO}_4$  and have according to the type of polyhedrons and their juncture different composition, e.g.  $\text{V}_6\text{O}_{19}^{8-}$ ,  $\text{V}_6\text{O}_{18}^{6-}$  or  $\text{V}_6\text{O}_{17}^{4-}$ . It results from these facts that the deca-, meta-, and hexavanadate ions may be in equilibrium in the investigated solution of  $\text{NaVO}_3$  ( $Z=0.4$ ) at  $80^\circ\text{C}$ . The expansion of the resonance line with  $\delta = -572.8$  ppm due to increasing temperature may be so explained that it is a consequence of the equilibrium of the meta- and hexavanadate ions which are built of the V—O polyhedrons of equal kind. The hexavanadate anion structure proposed by *Habayeb and Hileman* [11] (Fig. 2c) complies best with this our idea.

The NMR spectra point out that the composition of aqueous solutions of vanadates is also influenced by temperature at certain values of  $Z$ . Our conclusion may be explained by the fact ascertained experimentally that deca- or metavanadates preferentially crystallize from aqueous solutions of vanadates at laboratory temperature and  $Z=0.4$  while hexa- and metavanadates crystallize at  $80^\circ\text{C}$  according to solubility of individual polyvanadates of a certain element [1, 16, 17].

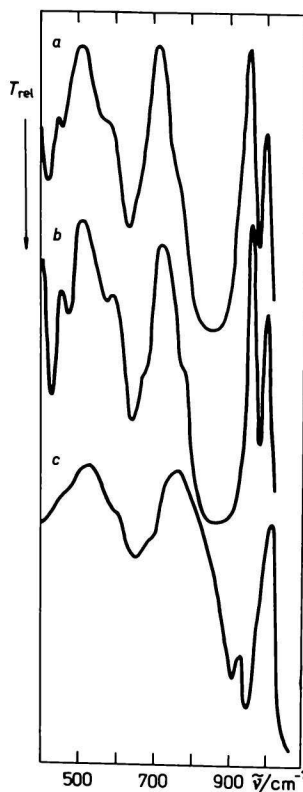


Fig. 3. Infrared spectra of hexavanadates.

- a)  $\text{Rb}_2\text{V}_6\text{O}_{16}$ ; b)  $\text{Cs}_2\text{V}_6\text{O}_{16}$ ;  
c)  $\text{RbHV}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ .

Table 2

## Conditions of hexavanadate formation

Substance	$c/(\text{mol dm}^{-3})$	$\theta/^\circ\text{C}$	$t/\text{h}$	$Z$
$\text{Rb}_2\text{V}_6\text{O}_{16}$	0.1	60	20	0.4–1.0
	0.1	80	20	0.4–0.8
$\text{RbHV}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}^*$	0.1	80	0.25	2.9–3.0
$\text{Cs}_2\text{V}_6\text{O}_{16}$	0.01	20	24	2.0
	0.075	20	168	2.0
	0.1; 0.075	20	3	3.0
	0.1	20	1.5	3.0
	0.075	40	1.5	0.8–2.0
	0.1	40	1.5	1.0
	0.1	40	24	2.0
	0.05	60	1.5	2.0–3.0
	0.075	60	24	3.0
	0.075	60	1.5	0.4–3.0
	0.1	60	1.5	0.4–3.0
	0.05	80	24	3.0
	0.1; 0.075	80	1.5	2.0–3.0
	0.1	80	24	2.0–3.0
	0.1	80	1.5	0.4–0.6

\*Reaction solution was not stirred.

## Preparation of vanadates

We performed 57 syntheses in the system  $\text{RbVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  and 83 syntheses in the system  $\text{CsVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  under the conditions given in Experimental.

We obtained two substances of defined composition, i.e.  $\text{Rb}_2\text{V}_6\text{O}_{16}$  and  $\text{RbHV}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  in the rubidium system and only  $\text{Cs}_2\text{V}_6\text{O}_{16}$  in the cesium system under the conditions given in Table 2. For  $\text{Rb}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$   $w_i(\text{calc.})/\%$ : 12.17 (Rb), 43.53 (V);  $w_i(\text{found})/\%$ : 11.82–12.02 (Rb), 43.22–43.50 (V). For  $\text{Cs}_2\text{V}_6\text{O}_{16}$   $w_i(\text{calc.})/\%$ : 32.12 (Cs), 36.94 (V);  $w_i(\text{found})/\%$ : 30.61–32.30 (Cs), 36.36–36.85 (V).

The prepared substances were also identified by the X-ray powder method and infrared spectra. The infrared spectra of orange hexavanadates and brown hydrogen hexavanadates are characteristic of these groups of substances because the position of absorption bands is only slightly influenced by the present cation. Two intensive absorption bands appear in the region  $\nu(\text{V}=\text{O})$  ( $\tilde{\nu} = 900\text{—}1020\text{ cm}^{-1}$ ) in the presence of anhydrous hexavanadates while only one is to be observed in the presence of hydrogen salts. The absorption band  $\delta(\text{V—OH})$  approximately at  $920\text{ cm}^{-1}$  is characteristic of hydrogen hexavanadates (Fig. 3).



Mixtures of hexa- and hydrogen hexavanadates were usually formed under other conditions. Metavanadates also appeared as admixtures in the products obtained at lower degrees of acidification  $Z$ . In the brown coloured mixtures, we cannot exclude the presence of substances of the composition  $M_2^+V_6O_{16} \cdot xH_2O$  though they have not yet been described. It is obvious from Table 2 that the scope of conditions of the  $Cs_2V_6O_{16}$  preparation is much greater than it is for  $Rb_2V_6O_{16}$ , which is caused by poor solubility of  $Cs_2V_6O_{16}$ . For this reason, we were not able to obtain cesium hydrogen hexavanadate in pure state. Even if the hydrogen salt primarily arose, it was transformed into the less soluble hexavanadate in both systems. Therefore the reaction solutions were not stirred in the course of syntheses of hydrogen hexavanadates and the formed products were isolated in a possibly shortest time interval. Solutions of higher concentration, temperature, and higher value of  $Z$  are more convenient for the preparation of hydrogen hexavanadates. (The optimum value of  $Z$  at a given concentration of solution depends on temperature and shifts towards higher values with increasing temperature.)

### References

1. Evans, H. T., *Inorg. Chem.* 5, 967 (1966).
2. Žůrková, L., Suchá, V., and Dillinger, M., *Collect. Czechoslov. Chem. Commun.* 36, 3788 (1971).
3. Bystrom, A. M. and Evans, H. T., Jr., *Acta Chem. Scand.* 13, 377 (1959).
4. Gáplovská, K. and Žůrková, L., *Acta Fac. Rerum Natur. Univ. Comeniana (Chimia)* 30, 45 (1982).
5. Kelmers, A. D., *J. Inorg. Nucl. Chem.* 21, 45 (1961).
6. Brauer, G., *Handbuch der präparativen anorganischen Chemie*. Enke Verlag, Stuttgart, 1954.
7. Jahr, F. and Preuss, F., *Chem. Ber.* 99, 1602 (1966).
8. Raff, P. and Brotz, W., *Fresenius' Z. Anal. Chem.* 133, 241 (1951).
9. Howarth, O. W. and Richards, R. E., *J. Chem. Soc. A* 1965, 864.
10. Kazanskii, L. P. and Spitsyn, V. I., *Dokl. Akad. Nauk SSSR* 223, 381 (1975).
11. Habayeb, M. A. and Hileman, O. E., *Can. J. Chem.* 58, 2255 (1980).
12. O'Donnell, E. and Pope, M. T., *J. Chem. Soc., Dalton Trans.* 1976, 2290.
13. Swallov, A. G., Ahmed, F. R., and Barnes, W. H., *Acta Crystallogr.* 21, 397 (1966).
14. Heath, E. and Howarth, O. W., *J. Chem. Soc., Dalton Trans.* 1981, 1105.
15. Murman, K. and Giese, K. C., *Inorg. Chem.* 17, 1160 (1978).
16. Suchá, V. and Žůrková, L., *Chem. Zvesti* 34, 452 (1980).
17. Göczeová, Č., *Chem. Zvesti* 35, 235 (1981).

Translated by R. Domanský