

# Influence of temperature, vanadium concentration, and degree of solution acidification on composition of the solid products

## XII. Products of the reactions taking place in acidified solutions of lithium and magnesium metavanadate

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The influence of temperature, vanadium concentration, degree of solution acidification, and reaction time on composition of the solid products arising from the systems  $\text{LiVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  and  $\text{Mg}(\text{VO}_3)_2\text{—HNO}_3\text{—H}_2\text{O}$  was investigated. The compounds  $\text{LiHV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $x = 5.5\text{—}6$ ),  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ , and  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$  ( $x = 16\text{—}17$ ) were prepared under defined conditions.

Изучалось влияние температуры, концентрации ванадия, степени окисления раствора и продолжительности реакции на состав твердых продуктов, образующихся в системах  $\text{LiVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  и  $\text{Mg}(\text{VO}_3)_2\text{—HNO}_3\text{—H}_2\text{O}$ . При определенных условиях были получены соединения  $\text{LiHV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $x = 5,5\text{—}6$ ),  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$  ( $x = 16\text{—}17$ ).

The temperature, degree of solution acidification, concentration of reacting components, and reaction time have a major influence on the composition of the vanadates originating from acidified aqueous solutions [1—9]. The solubility as well as the reactivity of vanadates of a certain cation in a given medium is also a decisive factor. A series of our papers [2—9] deals with the influence of these factors on the composition of polyvanadates of univalent and bivalent cations in the three-component systems  $\text{M}^I\text{VO}_3$  ( $\text{M}^{II}(\text{VO}_3)_2$ )—acid—water ( $\text{M}^I = \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ ;  $\text{M}^{II} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Cd}, \text{Mn}$ ). This paper completes this series by involving the systems  $\text{LiVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  and  $\text{Mg}(\text{VO}_3)_2\text{—HNO}_3\text{—H}_2\text{O}$  with the aim to disclose the possibility of preparing lithium and magnesium hexavanadates under certain chosen conditions and to investigate the properties of these compounds.

### Experimental

The starting chemicals were of anal. grade.  $\text{V}_2\text{O}_5$  was prepared from purified ammonium metavanadate by calcination [10, 11]. The solutions of lithium and magnesium metavanadate were obtained by dissolving  $\text{V}_2\text{O}_5$  in hot aqueous solution of  $\text{LiOH}$  or hot

aqueous suspension of  $\text{MgCO}_3$ . The ratio of amounts of substances was  $n(\text{LiOH}) : n(\text{V}_2\text{O}_5) = 2 : 1$  or  $n(\text{MgCO}_3) : n(\text{V}_2\text{O}_5) = 1 : 1$ . The ratio  $n(\text{Mg}) : n(\text{V})$  in solution was checked analytically and if it was necessary, it was adjusted to the value  $n(\text{Mg}) : n(\text{V}) = 1 : 2$  by adding  $\text{Mg}(\text{NO}_3)_2$ . Two drops of 30 %  $\text{H}_2\text{O}_2$  were added into the solutions of metavanadates in order to oxidize incidental traces of vanadium(IV). After cooling the solutions of metavanadates were filtered and diluted with distilled water to the concentration approx.  $2 \text{ mol dm}^{-3} \text{ LiVO}_3$  and  $0.2 \text{ mol dm}^{-3} \text{ Mg}(\text{VO}_3)_2$ , respectively.

### *Preparation of substances*

Certain amounts were taken from the stock solutions of metavanadates for the synthesis of lithium and magnesium polyvanadates. These amounts were dependent on the required concentration of vanadium in the reaction systems. Distilled water and  $\text{HNO}_3$  were so added into the solutions that the sum of their volumes was always constant. (Nitric acid was added only when the solution of metavanadate had been heated to the required temperature.) The amount of  $\text{HNO}_3$  was given by the degree of acidification  $Z$  of the solution  $\left( Z = \frac{n(\text{HNO}_3)}{n(\text{V})} \right)$ . The volume of the reaction solutions was constant. The syntheses were carried out at the given temperatures and time which was a function of  $Z$ , temperature, and concentration of the reaction solutions (Tables 1 and 2). During the heating of metavanadate solutions as well as during the syntheses, the reaction systems were stirred and the pH values were measured in regular intervals. After their isolation from the solution, the solid lithium polyvanadates were washed with 96 % ethanol while magnesium polyvanadates were washed with cold water. The products were dried in air at laboratory temperature.

### *Identification of substances*

The composition of all investigated starting substances as well as resulting products of the chemical reactions was determined by chemical analysis. The infrared spectrophotometry was used for identifying the solid substances. The powder diffraction patterns were also taken for some solid substances.

Lithium was determined with a flame photometer FLAPHO (Zeiss, Jena) by using an interference filter (671 nm). A silicium diode was used as a sensor [12].

Magnesium was determined with complexon III ( $c(\text{complexon}) = 0.01 \text{ mol dm}^{-3}$ ) by using eriochrom black T in the presence of hydroxylammonium chloride at  $\text{pH} \approx 10$  [13].

Vanadium(V) was determined volumetrically ( $c(\text{FeSO}_4) = 0.1 \text{ mol dm}^{-3}$ ) by using diphenylamine [14].

Vanadium(IV) was determined either manganometrically ( $c(\text{KMnO}_4) = 5 \times 10^{-3} \text{ mol dm}^{-3}$ ) [15] or photometrically in some substances with a Spektromom 202 (MOM, Budapest) according to [16].

The content of H<sub>2</sub>O in solid samples which did not contain vanadium(IV) was calculated according to the formula:  $w(\text{H}_2\text{O}) = 100 - w(\text{V}_2\text{O}_5) - w(\text{Li}_2\text{O}) (w(\text{MgO}))$ .

The infrared spectra were measured in the range  $\tilde{\nu} = 400\text{--}2000\text{ cm}^{-1}$  on 180 Perkin—Elmer or Specord 75 IR (Zeiss, Jena) spectrometers by using the nujol technique. The diffraction patterns were taken on a powder X-ray diffractograph equipped with a goniometer PW 1050 (Philips) by using the CuK $\alpha$  radiation. The concentration of H<sub>3</sub>O<sup>+</sup> was measured with a pH-meter TTT-2 Radiometer by using a combined electrode GK 2401 C.

### Results and discussion

The results of investigation of the systems LiVO<sub>3</sub>—HNO<sub>3</sub>—H<sub>2</sub>O (Table 1) and Mg(VO<sub>3</sub>)<sub>2</sub>—HNO<sub>3</sub>—H<sub>2</sub>O (Table 2) show that only one defined substance,

Table 1  
Products obtained from the system LiVO<sub>3</sub>—HNO<sub>3</sub>—H<sub>2</sub>O

$\theta = 20^\circ\text{C}$			$\theta = 40^\circ\text{C}$		
Z	t/days	Product	Z	t/days	Product
$c(\text{V}) = 0.5\text{ mol dm}^{-3}$			$c(\text{V}) = 0.5\text{ mol dm}^{-3}$		
0.6	2	+	0.4	6	—
0.6	6	+	0.5	6	—
0.6	16	+	0.55	6	—
0.6	150*	P <sup>1</sup>	0.6	1	P <sup>1</sup>
0.8	6	P <sup>3</sup>	0.6	2	P <sup>1</sup>
1.0	6	P <sup>2</sup>	0.65	2	P <sup>1</sup>
1.0	10	P <sup>2</sup>	0.8	6	P <sup>1</sup>
1.0	17	P <sup>2</sup>	0.9	6	P <sup>3</sup>
1.1	6	P <sup>2</sup>	1.0	6	P <sup>3</sup>
1.1	8	P <sup>2</sup>	1.0	8	P <sup>2</sup>
1.1	9	P <sup>2</sup>	1.1	6	P <sup>2</sup>
1.1	10	P <sup>2</sup>	1.1	8	P <sup>3</sup>
1.1	11	HH	1.5	6	P <sup>2</sup>
1.1	13	P <sup>1</sup>			
1.2	6	P <sup>2</sup>	$c(\text{V}) = 0.75\text{ mol dm}^{-3}$		
1.2	10	P <sup>2</sup>	0.6	19	—
1.5	6	P <sup>1</sup>	0.6	24	+
1.5	10	P <sup>1</sup>	0.65	19	P <sup>1</sup>
			0.65	192	P <sup>1</sup>
			0.7	19	P <sup>1</sup>
$c(\text{V}) = 0.75\text{ mol dm}^{-3}$					
0.6	1	P <sup>1</sup>			
0.6	24	P <sup>1</sup>			

— Product does not arise; + small yield.

HH — LiHV<sub>6</sub>O<sub>16</sub> · xH<sub>2</sub>O, P<sup>1</sup> — product with  $n(\text{Li}) : n(\text{V}) > 1.05 : 6$ , P<sup>2</sup> — product with  $n(\text{Li}) : n(\text{V}) < 0.95 : 6$ , P<sup>3</sup> — product with  $n(\text{Li}) : n(\text{V}) = 1 : 6$ , contains vanadium(IV).

\* Time in which identifiable amount of product was formed.

*i.e.*  $\text{LiHV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$  ( $x = 5.5\text{--}6$ ) was obtained in the lithium system at  $20^\circ\text{C}$ ,  $c(\text{V}) = 0.5 \text{ mol dm}^{-3}$ ,  $Z = 1.1$  ( $\text{pH} = 1.10$ ), and reaction time of 11 days. For  $\text{LiHV}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$   $w_i(\text{calc.})$ : 1.028 % Li, 44.88 % V, 17.78 %  $\text{H}_2\text{O}$ ;  $w_i(\text{found})$ : 0.98 % Li, 44.65 % V, 17.87 %  $\text{H}_2\text{O}$ .

Table 2

Products obtained from the system  $\text{Mg}(\text{VO}_3)_2\text{--HNO}_3\text{--H}_2\text{O}$ 

$\theta = 80^\circ\text{C}$			$\theta = 60^\circ\text{C}$			$\theta = 40^\circ\text{C}$		
Z	t/h	Product	Z	t/h	Product	Z	t/h	Product
$c(\text{V}) = 0.05 \text{ mol dm}^{-3}$			$c(\text{V}) = 0.05 \text{ mol dm}^{-3}$			$c(\text{V}) = 0.05 \text{ mol dm}^{-3}$		
0.5	24	+	0.5	24	+	0.5	24	—
0.5	72	P <sup>1</sup>	0.5	72	P <sup>1</sup>	0.5	72	—
0.5	120	P <sup>1</sup>	0.6	24	P <sup>1</sup>	0.6	24	—
0.5	168	H	0.6	72	P <sup>1</sup>	0.6	72	P <sup>1</sup>
0.6	24	P <sup>1</sup>	0.7	24	P <sup>1</sup>	0.7	24	+
0.6	72	P <sup>1</sup>	0.7	72	P <sup>1</sup>	0.7	72	P <sup>1</sup>
0.7	24	P <sup>1</sup>	0.8	24	P <sup>1</sup>	0.8	24	+
0.7	72	P <sup>1</sup>	0.8	72	P <sup>1</sup>	0.8	72	P <sup>1</sup>
0.8	24	P <sup>1</sup>	1.0	24	P <sup>1</sup>	1.0	24	+
0.8	72	P <sup>1</sup>	1.0	72	P <sup>1</sup>	1.0	72	P <sup>1</sup>
1.0	24	HH	2.0	24	P <sup>2</sup>	2.0	24	+
1.0	72	HH	2.0	72	P <sup>2</sup>	2.0	72	P <sup>1</sup>
2.0	24	HH	$c(\text{V}) = 0.02 \text{ mol dm}^{-3}$					
2.0	72	HH	0.5	24	—			
$c(\text{V}) = 0.02 \text{ mol dm}^{-3}$			0.5	72	+			
0.5	25	+	0.6	24	+			
0.5	72	P <sup>1</sup>	0.6	72	P <sup>1</sup>			
0.6	24	P <sup>1</sup>	0.7	24	+			
0.6	72	P <sup>1</sup>	0.7	72	P <sup>1</sup>			
0.7	24	P <sup>1</sup>	0.8	24	HH			
0.7	72	P <sup>1</sup>	0.8	72	P <sup>1</sup>			
0.8	24	HH	1.0	24	HH			
0.8	72	HH	1.0	72	P <sup>1</sup>			
1.0	24	HH	2.0	24	P <sup>2</sup>			
1.0	72	HH	2.0	72	P <sup>1</sup>			
2.0	24	HH						
2.0	72	HH						

— Product does not arise; + small yield.

H —  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ , HH —  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$ , P<sup>1</sup> — product with  $n(\text{Mg}) : n(\text{V}) > 0.52 : 6$ , P<sup>2</sup> — product with  $n(\text{Mg}) : n(\text{V}) < 0.48 : 6$ .

In the magnesium systems we obtained  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$  at  $80^\circ\text{C}$ ,  $c(\text{V}) = 0.05 \text{ mol dm}^{-3}$ ,  $Z = 0.5$  ( $\text{pH} = 5.2$ ), and reaction time of 7 days. For  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$   $w_i(\text{calc.})$ : 3.24 % Mg, 40.86 % V, 21.65 %  $\text{H}_2\text{O}$ ;  $w_i(\text{found})$ : 3.09 % Mg, 41.18 % V, 21.36 %  $\text{H}_2\text{O}$ . Moreover, we prepared  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$  ( $x = 16-17$ ) in a relatively wide interval of  $Z$  ( $\text{pH} \approx 2.2$ ) with both investigated  $c(\text{V})$  at  $80^\circ\text{C}$  and in a narrow interval of  $Z$  with  $c(\text{V}) = 0.02 \text{ mol dm}^{-3}$  at  $60^\circ\text{C}$  (Table 2). For  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot 17\text{H}_2\text{O}$   $w_i(\text{calc.})$ : 1.67 % Mg, 41.96 % V, 22.24 %  $\text{H}_2\text{O}$ ;  $w_i(\text{found})$ : 1.66 % Mg, 41.73 % V, 22.73 %  $\text{H}_2\text{O}$ .

Mixtures always arose from both systems under deviating conditions. As for lithium, most of the mixtures contained vanadium(IV), too. Its content varied within the range 0.18—2.64 %. A relationship between the content of lithium and the content of vanadium(IV) in products was not observed. The following trends manifested themselves in the system  $\text{LiVO}_3\text{—HNO}_3\text{—H}_2\text{O}$ : The content of lithium in reaction products decreases with increasing  $Z$  for  $c(\text{V}) = 0.5 \text{ mol dm}^{-3}$  and a constant reaction time. An increase in  $c(\text{V})$  raises the content of lithium in products. An increase in temperature at  $c(\text{V}) = 0.5 \text{ mol dm}^{-3}$  favours origination of the products in which the content of vanadium(IV) increases. A prolongation of reaction time brings about a decrease in content of vanadium(IV) in products and after a definite time an augmentation of admixtures.

According to infrared spectra the substances obtained from the lithium system contain  $\text{LiHV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$ , compounds of the composition  $\text{Li}_{2+x}\text{V}_{6-x}^{\text{V}}\text{V}_x^{\text{IV}}\text{O}_{16} \cdot x\text{H}_2\text{O}$  and probably  $\alpha$ -bronzes on the base of  $\text{V}_2\text{O}_5$  as well. The ratio of individual components in these mixtures depends on reaction conditions. The presence of the vanadium-oxygen bronze  $\text{Li}_{1+x}\text{V}_3\text{O}_8$  the structure of which is known [17] was not evidenced in the mixtures. Similarly, the presence of  $\text{LiVO}_3$  in the products was not proved on the basis of X-ray diffraction. The authors of paper [18] who investigated the composition of the products prepared at 25 and  $80^\circ\text{C}$  by acidifying the solutions of  $\text{LiVO}_3$  of varying concentration and different degree of acidification usually obtained substances which they laid down as hydrogen dodecavanadates of varying composition  $\text{Li}_x\text{H}_{2-x}\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$ . Under certain conditions they also obtained  $\text{Li}_2\text{V}_{12}\text{O}_{31} \cdot n\text{H}_2\text{O}$  ( $n = 9.4$ ). On the basis of the published data we cannot unambiguously decide whether those substances are identical with the substances arising from the system  $\text{LiVO}_3\text{—HNO}_3\text{—H}_2\text{O}$  investigated by us.

Lithium hexavanadate was not obtained from the investigated system though hexavanadates of other alkali metals are known. Sodium forms the hydrated hexavanadate  $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$  [3] while potassium, rubidium, and caesium may be present in the waterless compound  $\text{M}^{\text{I}}\text{V}_3\text{O}_8$  [19] with laminated structure of

the vanadate anion [20]. Though the structure of hydrated hexavanadate is not known up to now, we assume that the cause of inability of lithium to form hexavanadates consists in small volume of  $\text{Li}^+$  and considerable reduction ability of the lithium atom. On the other hand, these two factors are responsible for great disposition of lithium to form vanadium-oxygen bronzes.

Magnesium hexavanadate and magnesium hydrogenhexavanadate were prepared in the system  $\text{Mg}(\text{VO}_3)_2\text{—HNO}_3\text{—H}_2\text{O}$ .  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$  arises only under specific conditions (Table 2). Other products are usually mixtures of  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$  ( $x = 16\text{—}17$ ) and  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ . The content of  $\text{Mg}(\text{HV}_6\text{O}_{16})_2$  in these mixtures increases with increasing degree of acidification  $Z$ , temperature and decreasing value of  $c(\text{V})$ . *Ivakin et al.* [21] described the compounds  $\text{MgV}_6\text{O}_{16} \cdot 8.5\text{H}_2\text{O}$  and  $\text{MgV}_{12}\text{O}_{31} \cdot 12\text{H}_2\text{O}$ . However, they do not

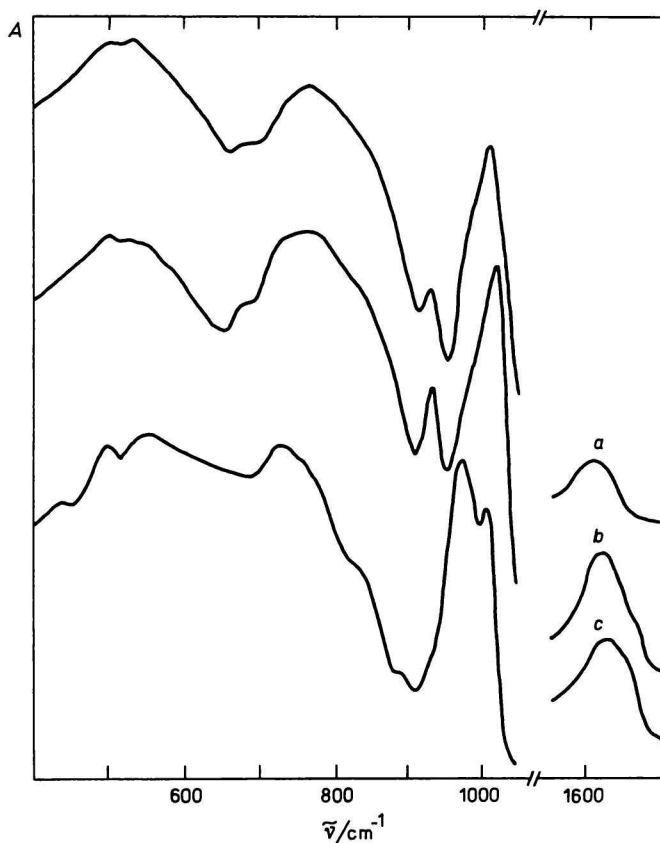


Fig. 1. Infrared spectra: a)  $\text{LiHV}_6\text{O}_{16} \cdot x\text{H}_2\text{O}$ ; b)  $\text{Mg}(\text{HV}_6\text{O}_{16})_2 \cdot x\text{H}_2\text{O}$ ; c)  $\text{MgV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ .

give the precise conditions of preparation of these substances. They obtained the substances at laboratory temperature. We may assume on the basis of published infrared spectra and DTA record that the matter is other hydrates of magnesium hexavanadate or hydrogenhexavanadate and substances containing small amounts of admixtures, respectively.

For simplification, we do not describe other unsuccessful experiments to prepare lithium and magnesium hexavanadate in which different values of temperature,  $Z$ ,  $c(V)$ , and reaction time were applied.

$MgV_6O_{16} \cdot 9H_2O$  is a substance of red-brown colour while  $LiHV_6O_{16} \cdot xH_2O$  and  $Mg(HV_6O_{16})_2 \cdot xH_2O$  are deep-brown. They give the characteristic infrared spectrum (Fig. 1) from which it results that both hydrogenhexavanadates exhibit similar skeleton of anion. The interplanar distances in  $MgV_6O_{16} \cdot 9H_2O$  are given in Table 3.

Table 3

Interplanar distances in  $MgV_6O_{16} \cdot 9H_2O$ 

$d/nm$	$I_r/\%$	$d/nm$	$I_r/\%$
1.059	100	0.234	6
0.615	3	0.230	3
0.554	4	0.224	2
0.526	22	0.216	4
0.405	6	0.201	6
0.349	4	0.197	3
0.341	19	0.179	11
0.310	28	0.177	6
0.298	8	0.172	2
0.290	6	0.170	2
0.269	4	0.164	1
0.245	2	0.161	3
0.234	6		

The powder diffraction patterns of  $LiHV_6O_{16} \cdot xH_2O$  and  $Mg(HV_6O_{16})_2 \cdot xH_2O$  exhibit a small number of diffraction diffractions which indicate a low degree of order of the structure.

The investigation of thermal properties of the prepared substances has revealed that their structure decomposed after dehydration and new phases have come into existence [22, 23].

## References

1. Göczeová, Č., *Chem. Zvesti* 35, 235 (1981).
2. Tkáč, T. and Žúrková, L., *Chem. Zvesti* 33, 749 (1979).
3. Suchá, V. and Žúrková, L., *Chem. Zvesti* 34, 452 (1980).
4. Drábik, M. and Žúrková, L., *Chem. Zvesti* 36, 799 (1982).
5. Žúrková, L. and Ulická, L., *Chem. Zvesti* 36, 809 (1982).
6. Ulická, L. and Suchá, V., *Chem. Zvesti* 38, 85 (1984).
7. Žúrková, L., Suchá, V., and Schraml, J., *Chem. Papers* 39, 629 (1985).
8. Göczeová, Č., *Chem. Papers* 40, 577 (1986).
9. Ulická, L., *Chem. Papers* 41, 195 (1987).
10. Karyakin, Yu. V. and Angelov, Yu. Yu., *Chistye khimicheskie reaktivy*. Gosudarstvennoe Nauchno-tekhn. Izd. Khim. Lit., Moscow, 1955.
11. Brauer, G., *Handbuch der Präparativen Anorganischen Chemie*. F. Enke Verlag, Stuttgart, 1954.
12. Herrmann, R., *Plamenová fotometrie*. (Flame Photometry.) Státní zdravotnické nakladatelství (State Publishing House of Health), Prague, 1968.
13. Sajó, I., *Komplexometria*. Müszaki könyvkiadó, Budapest, 1973.
14. Tomiček, O., *Kvantitativní analýza*. (Quantitative Analysis.) Státní zdravotnické nakladatelství (State Publishing House of Health), Prague, 1958.
15. Collective of authors, *Analytická chémia kvantitatívna*. (Quantitative Analytical Chemistry.) Slovenské pedagogické nakladateľstvo (Slovak Publishing House of Pedagogical Literature), Bratislava, 1966.
16. Agterdenbos, J. and Eggink, A. J. R., *Z. Anorg. Allg. Chem.* 388, 177 (1972).
17. Wadsley, A. D., *Acta Crystallogr.* 10, 261 (1957).
18. Ivakin, A. A. and Chufarova, I. G., *Zh. Neorg. Khim.* 22, 341 (1987).
19. Kelmers, A. D., *Inorg. Nucl. Chem. Lett.* 21, 45 (1961).
20. Evans, H. T., Jr. and Block, S., *Inorg. Chem.* 5, 1808 (1966).
21. Ivakin, A. A., Chufarova, I. G., Petunina, N. I., Perelyaeva, L. A., and Koryakova, O. V., *Zh. Neorg. Khim.* 24, 953 (1979).
22. Žúrková, L. and Korenková, S., *J. Therm. Anal.* 32, 1559 (1987).
23. Göczeová, Č., unpublished results.

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