

# The structure and selected properties of $\text{Co}_{2.5}\text{VMoO}_8$

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The structure of  $\text{Co}_{2.5}\text{VMoO}_8$  was refined by the Rietveld method. The lattice constants are:  $a = 0.50453$  nm;  $b = 1.03448$  nm;  $c = 1.73925$  nm, space group Pnma. The crystal structure of the compound is isotypic with  $\text{Mg}_{2.5}\text{VMoO}_8$ . The structure is a framework of  $\text{MoO}_4$  and  $\text{VO}_4$  tetrahedra with linking octahedral and trigonal prismatic  $\text{CoO}_6$  groups.  $\text{Co}_{2.5}\text{VMoO}_8$  melts incongruently at  $1080 \pm 5^\circ\text{C}$  depositing solid  $\text{CoMoO}_4$ . © 2003 Kluwer Academic Publishers

## 1. Introduction

Recent reports on the ternary systems of  $\text{MO-V}_2\text{O}_5\text{-MoO}_3$ , where  $\text{M} = \text{Mg, Zn, Mn}$ , proved an existence of vanadomolybdates:  $\text{M}_{2.5}\text{VMoO}_8$  that are potential efficient catalysts of selective hydrocarbon oxidations [1–5]. The structure of these vanadomolybdates reveals one-dimensional columns of linked  $\text{MO}_6$  polyhedra as well as isolated  $\text{VO}_4$  and  $\text{MoO}_4$  tetrahedra.

The  $\text{Mg}_{2.5}\text{VMoO}_8$  and  $\text{Mn}_{2.5}\text{VMoO}_8$  compounds (corresponding actually to the formulae of  $\text{Mg}_{2.54}\text{V}_{1.08}\text{Mo}_{0.92}\text{O}_8$  and  $\text{Mn}_{2.47}\text{V}_{0.94}\text{Mo}_{1.06}\text{O}_8$ , respectively) crystallize in the orthorhombic system, space group  $Pnma$ , their unit cell parameters being close to each other,  $Z = 6$  [2, 6]. They melt incongruently.  $\text{Mg}_{2.5}\text{VMoO}_8$  does not exhibit polymorphism up to  $1100^\circ\text{C}$  when heated in air. The structure of both compounds is formed from  $\text{VO}_4$  and  $\text{MoO}_4$  tetrahedra,  $\text{MO}_6$  octahedra and  $\text{MO}_6$  trigonal prisms ( $\text{M} = \text{Mg, Mn}$ ). The tetrahedra link zigzag sheets and columns formed by the octahedra and trigonal prisms respectively [1].

The  $\text{Zn}_{2.5}\text{VMoO}_8$  compound (corresponding actually to the formula of  $\text{Zn}_{3.77}\text{V}_{1.54}\text{Mo}_{1.46}\text{O}_{12}$ ) crystallizes in the orthorhombic system, space group  $P2_12_12_1$ , its unit cell parameters amounting to  $a = 0.5048(4)$  nm,  $b = 1.0400(2)$  nm,  $c = 1.7560(7)$  nm,  $Z = 4$  [5]. In the  $\text{Zn}_{3.77}\text{V}_{1.54}\text{Mo}_{1.46}\text{O}_{12}$  structure, there are four crystallographically different  $\text{ZnO}_6$  polyhedra [5]. Two sorts of them form the zigzag sheets by sharing edges and corners, face-sharing octahedra of the third sort form one-dimensional chains, and the  $\text{ZnO}_6$  fourth sort-trigonal prisms form columns parallel to the  $a$  axis. The mutual linkage among different polyhedra is identical to that of  $\text{Mg}_{2.54}\text{V}_{1.08}\text{Mo}_{0.92}\text{O}_8$  [6]. The melting temperature of  $\text{Zn}_{2.5}\text{VMoO}_8$  is equal to  $845 \pm 5^\circ\text{C}$  [20].

This work is aimed at the presentation of the structure and certain physicochemical properties of a new  $\text{M}_{2.5}\text{VMoO}_8$  type compound, namely  $\text{Co}_{2.5}\text{VMoO}_8$ .

We have proved that in the pseudobinary system of  $\text{CoMoO}_4\text{-Co}_3\text{V}_2\text{O}_8$ , its phase diagram having been already worked out [7], this new compound can be obtained. The phase equilibria in the  $\text{CoV}_2\text{O}_6\text{-CoMoO}_4\text{-CoO}$  area of the  $\text{CoO-V}_2\text{O}_5\text{-MoO}_3$  system were also investigated [8]. The  $\text{Co}_{2.5}\text{VMoO}_8$  compounds melts incongruently at  $1080 \pm 5^\circ\text{C}$  depositing solid  $\text{CoMoO}_4$  [7]. Its density appeared to be  $4.67$  g/cm<sup>3</sup>. From powder diffraction data an orthorhombic unit cell with:  $a = 1.74161$  nm,  $b = 1.03586$  nm,  $c = 0.50511$  nm has been proposed [9].

## 2. Experimental and data evaluation

The sample of  $\text{Co}_{2.5}\text{VMoO}_8$  was made from  $\text{CoCO}_3$  (p.a., from Aldrich, Germany),  $\text{V}_2\text{O}_5$  (p.a., from Reachim, USSR) and  $\text{MoO}_3$  (p.a., from POCh Gliwice, Poland), which were weighted in stoichiometric amounts, ground together, shaped into pastilles and heated in air in a syllite furnace at  $450\text{--}600^\circ\text{C}$  (72 h),  $650^\circ\text{C}$  (24 h),  $700^\circ\text{C}$  (24 h),  $750^\circ\text{C}$  (24 h),  $800^\circ\text{C}$  (24 h),  $850^\circ\text{C}$  (24 h),  $900^\circ\text{C}$  (24 h),  $950^\circ\text{C}$  (24 h) and at  $1000^\circ\text{C}$  (24 h). After each heating cycle the sample was cooled gradually to ambient temperature, ground again and re-shaped into pastilles. This procedure led to a monophase sample, as evidenced by XRD measurements.

The X-ray diffraction pattern was taken from the diffractometer DRON3 (Bourestnik, Sankt-Petersburg, Russia) with the use of the Bragg-Brentano geometry. The source of radiation was a cobalt tube ( $\lambda_1 = 0.178892$  nm,  $\lambda_2 = 0.179278$  nm) with iron filter. The powder diffraction pattern was scanned in steps of  $0.02^\circ 2\theta$ , and fixed-time counting of 10 s was employed. The diffracted intensities were detected by a single scintillation counter. Experimental details are given in Table II.

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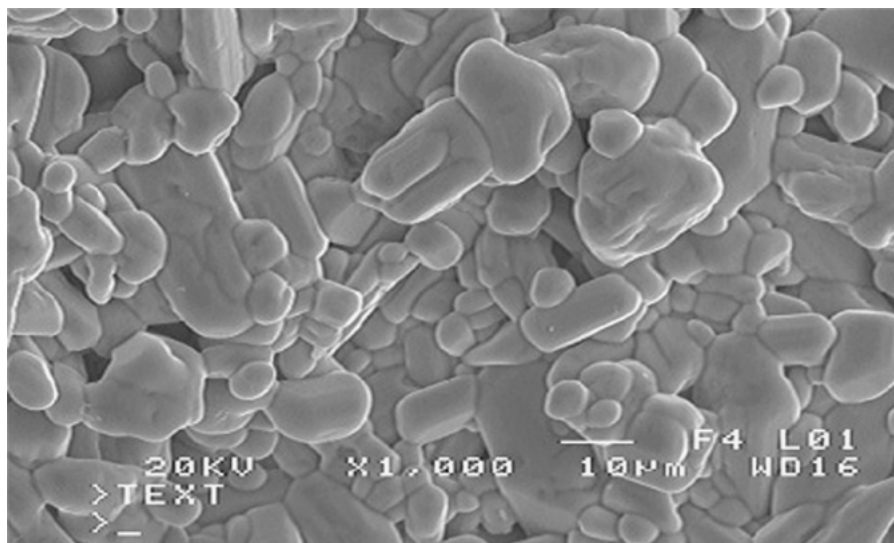


Figure 1 SEM image of  $\text{Co}_{2.5}\text{VMoO}_8$ .

The diffraction pattern was analysed in two steps by using the program FULLPROF [10]: (a) instrumental and peak shape parameters were refined by a pattern matching procedure in which the cell constants and the profile parameters of the Bragg-reflections were treated simultaneously and without prior knowledge on the intensity distribution [11]; (b) coordinates of each atom position in an asymmetric unit as well as overall temperature factor were refined according to the Rietveld method [12].

The benefit of this two-step method is that the refined instrumental and peak shape parameters are not deformed by deficiencies of the structural model. The dependence of the full width at half maximum (FWHM) on the diffraction angle was modeled by the formula of Cagliotti and Paoletti [13]. As a peak shape function the pseudo-Voigt function was taken [14]. The background was determined from the diffractogram and approximated by a linear interpolation between 20 points. No attempt was made to correct for absorption effect. The number of refined parameters in the 1st step was 9, whereas 39 for the refinement of the structural model.

The diffraction pattern corresponded closely to that of  $\text{Mg}_{2.5}\text{VMoO}_8$  [6]. Therefore, the structural parameters of  $\text{Mg}_{2.5}\text{VMoO}_8$  have been applied as a first model for the refinement. Bond lengths and angles were calculated by the program MAPLE4 [14, 15]. The definitions of the reliability factors are as usual [7].

In addition, DTA/TG, IRS and SEM measurements were taken. The DTA/TG measurements were performed by using the SDT 2960 apparatus of TA Instruments. These measurements were carried out in the air atmosphere with the use of platinum crucibles at a heating rate of 10 deg/min. The IR spectra were recorded in the wave-number range of  $1500\text{--}250\text{ cm}^{-1}$  by means of a SPECORD M80 spectrometer, a product of Carl Zeiss, Jena. A technique of mixing the sample with KBr at a weight ratio 1:300 and pressing them together was applied. For the sake of SEM image taking a scanning electron microscope JSM-1600, a product of Joel (Japan), was engaged.

### 3. Results and discussion

Fig. 1 presents a SEM image of the obtained by us  $\text{Co}_{2.5}\text{VMoO}_8$ . Results of the analysis of the biggest grains performed by means of an X-ray microanalyser showed the presence of three metals apart from oxygen, i.e., Co, V, Mo. The determined molar ratio Co:V:Mo was close to the theoretical value and amounted to 2.50:1.00:1.08.

Fig. 2 presents the DTA curve. The melting point of  $\text{Co}_{2.5}\text{VMoO}_8$  is equal to  $1080 \pm 5^\circ\text{C}$ . The compound melts incongruently depositing solid  $\text{CoMoO}_4$ . The kind of the solid product of melting was determined basing on the XRD analysis of the sample heated above the melting temperature, i.e., up to  $1095^\circ\text{C}$ , and then rapidly quenched.

Fig. 3 shows the sample of  $\text{Co}_{2.5}\text{VMoO}_8$  after the above mentioned heating procedure. We have identified the presence of  $\text{CoMoO}_4$  among the melting products by determining the molar ratio Co:Mo at the marked grain and it was near 1:1.

Fig. 4 presents the measured diffractogram in comparison to the calculated and refined diffractogram. The measured reflections have been sharp and thus the sample was well crystallised. The unit cell parameters of

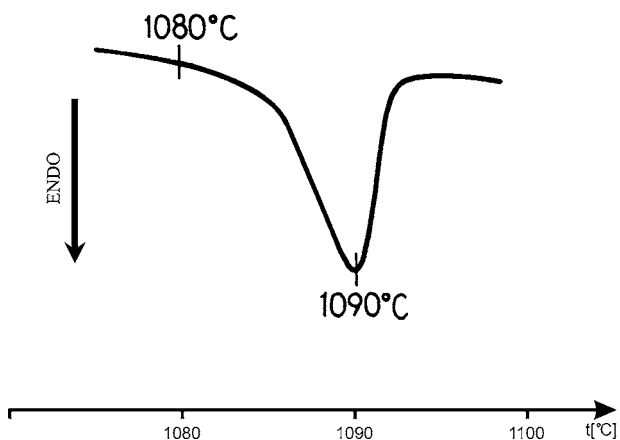


Figure 2 DTA curve of  $\text{Co}_{2.5}\text{VMoO}_8$ .

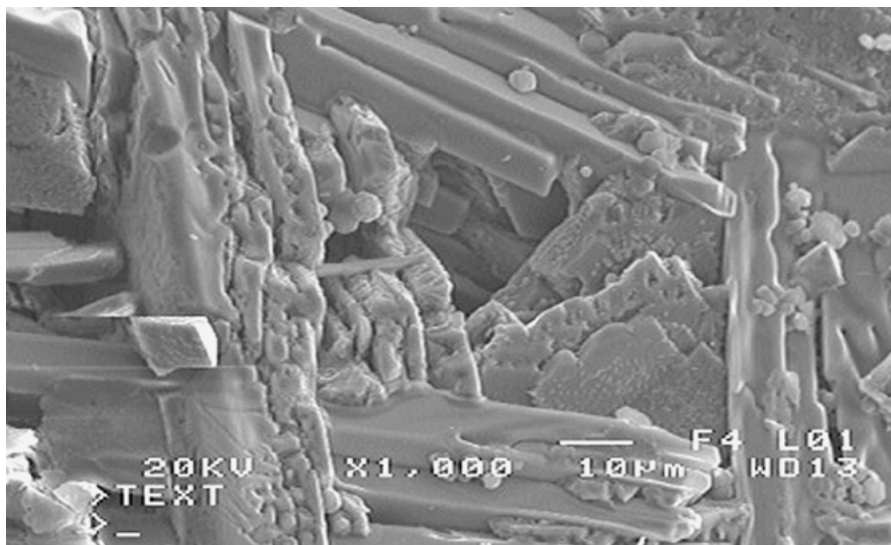


Figure 3 SEM image of the melting products of  $\text{Co}_{2.5}\text{VMoO}_8$ .

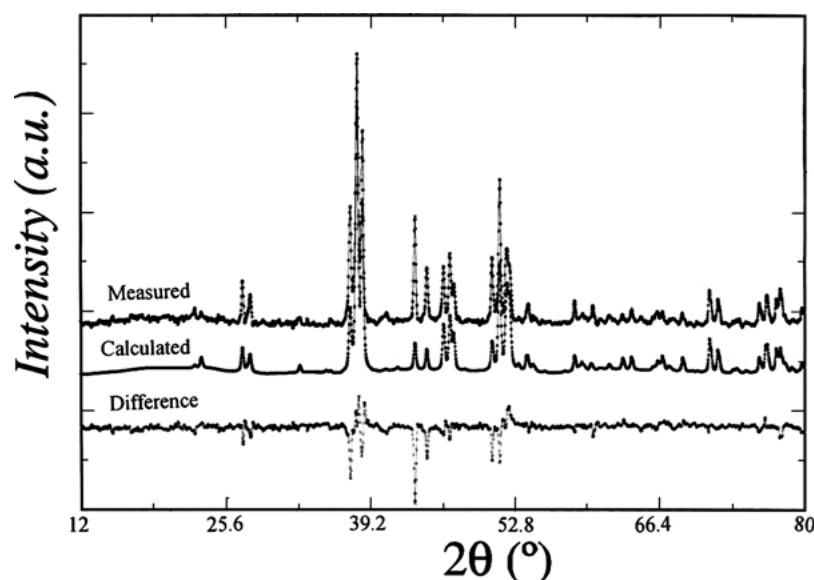


Figure 4 Measured and calculated XRD pattern of  $\text{Co}_{2.5}\text{VMoO}_8$ .

$\text{Co}_{2.5}\text{VMoO}_8$  were determined by indexing with the use of the program POWDER [17]. They amounted to  $a = 0.505138$  nm,  $b = 1.03660$  nm,  $c = 1.74149$  nm, and  $Z = 6$ . Next they were refined by the pattern matching and Rietveld refinement procedure. Agreement factors for both stages of the refinement are given in Table I. The small difference between them proves a good quality of the structure refinement in comparison to the pattern matching. Both stages show good quality by themselves as their  $R$  indices are distinctly below 10%. The discrepancies between the fitted model and the experimental diffractogram are mainly due to counting statistics (non-linear background approximation) and deficiencies of the peak shape description (asymmetric reflections approximation).

TABLE I Reliability factors for the 2 steps of the refinement

	$R_p$ (%)	$R_{wp}$ (%)	$R_{exp}$ (%)
Pattern matching	3.18	4.25	2.76
Structure refinement	3.85	5.08	2.77

The refined parameters of the pattern matching are compiled in Table II. The refined cell parameters are within 0.15% deviation from the previously found ones [9]. Atomic co-ordinates from the refinement of the

TABLE II Experimental details, cell parameters and instrument parameters for  $\text{Co}_{2.5}\text{VMoO}_8$

Data collection	
Wavelengths	0.178892 nm, 0.179278 nm
Angular range	$10.00^\circ \leq 2\theta \leq 80.00^\circ$
Step width	$0.02^\circ 2\theta$
Counting time	10 s
Profile and cell parameters	
$a$	0.50453(3) nm
$b$	1.03448(5) nm
$c$	1.73925(9) nm
Volume	$0.907770$ nm <sup>3</sup>
Space group	Pnma
Total number of reflections	389
Pseudo-Voigt parameter ( $\eta$ )	0.67(1)
Halfwidth parameters (U, V, W)	0.07(1), $-0.09(1)$ , 0.049(3)
Asymmetry parameter	$-0.030(6)$
Zero-point ( $z_0$ )	$-0.077(3)$

TABLE III Fractional atomic coordinates and site occupancy parameters of  $\text{Co}_{2.5}\text{VMoO}_8$

Atom	$x/a$ ( $\sigma x$ )	$y/b$ ( $\sigma y$ )	$z/c$ ( $\sigma z$ )	Occupancy
Co(1)	0.2617 (8)	0.4262 (3)	0.4711 (2)	1
Co(2)	0.3960 (8)	0.25	0.7467 (2)	0.5
Co(3)	0.2569 (13)	0.25	0.2992 (3)	0.375
V(1) + Mo(1)	0.7216 (8)	0.25	0.5541 (2)	0.25 + 0.25
V(2) + Mo(2)	0.7684 (7)	0.4714 (2)	0.3404 (2)	0.5 + 0.5
O(1)	0.6710 (21)	0.25	0.6535 (3)	0.5
O(2)	0.4024 (19)	0.25	0.5170 (10)	0.5
O(3)	0.8661 (11)	0.6245 (7)	0.3139 (6)	1
O(4)	0.9317 (24)	0.1192 (9)	0.5409 (9)	1
O(5)	0.5880 (17)	0.4896 (16)	0.4255 (4)	1
O(6)	0.5666 (13)	0.3687 (12)	0.2857 (7)	1
O(7)	0.0631 (22)	0.3956 (14)	0.3648 (5)	1

The overall isotropic temperature factor =  $2.3(3) \text{ \AA}^2$ .

structure are given in Table III. Their standard deviations are less than 1%, that means that the positions of the atoms are quite exactly determined, even in the case of the light atoms of oxygen. Selected bond lengths and angles are compiled in Tables IV and V.

The successful refinement of the  $\text{Co}_{2.5}\text{VMoO}_8$  structural model based on the  $\text{Mg}_{2.5}\text{VMoO}_8$  structure [6]

proved that both compounds are isostructural. Vanadium and molybdenum have been found in a tetrahedral environment, while there are three crystallographically different cobalt positions. Two of cobalt atoms are octahedrally co-ordinated, while the third  $\text{CoO}_6$  polyhedron is shaped like a trigonal prism. A three-dimensional framework structure results from the connection of the co-ordination polyhedra. The Co(1) and Co(3) polyhedra have two vertices in common with each adjacent Co(1) or Co(3) polyhedron respectively. The Co(2) octahedra share three vertices with each adjacent Co(2) octahedron. Thus all Co octahedra are linked in chains running in three different di-rections: Co(1) chains are parallel to the  $y$  axis, Co(2) chains are parallel to the  $x$  axis, while Co(3) chains are parallel to the  $xz$  plane and are sloped by approximately  $45^\circ$  to the  $z$  axis. The  $\text{VO}_4/\text{MoO}_4$  tetrahedra share neither edges nor vertices. The V(1)/Mo(1) tetrahedra connect the Co(1) and Co(2) chains. The Mo(2)/V(2) tetrahedra connect Co(1), Co(2), and Co(3) chains simultaneously. Two Co(1) octahedra, linked by a V(1)/Mo(1) tetrahedron and connected to a Co(3) octahedron by two Mo(2)/V(2) tetrahedra, form a distorted 6-member ring, which is a part of a channel running parallel to the  $x$  axis.

TABLE IV Selected bond lengths for the structure of  $\text{Co}_{2.5}\text{VMoO}_8$  (in nm)

Atom	Atom	Bond	Atom	Atom	Bond	Atom	Atom	Bond	Atom	Atom	Bond	Atom	Atom	Bond
Co(1)	O(4)	0.211	Co(2)	O(3)	0.212	Co(3)	O(6)	0.200	V(1)/Mo(1)	O(2)	0.173	Mo(2)/V(2)	O(7)	0.173
	O(5)	0.194		O(3)	0.212		O(6)	0.200		O(1)	0.175		O(3)	0.172
	O(5)	0.214		O(1)	0.207		O(7)	0.213		O(4)	0.173		O(6)	0.175
	O(7)	0.213		O(1)	0.213		O(7)	0.213		O(4)	0.173		O(5)	0.175
	O(2)	0.211		O(3)	0.213		O(6)	0.215						
	O(4)	0.223		O(3)	0.213		O(6)	0.215						

TABLE V Selected bond angles in the structure of  $\text{Co}_{2.5}\text{VMoO}_8$  (in degrees)

Co(1)	O(5)1	O(2)2	99.3	Co(2)	O(1)1	O(3)2	81.3	Co(3)	O(6)1	O(6)2	75.7	V(1)/Mo(1)	O(4)1	O(4)2	102.6	Mo(2)/V(2)	O(3)1	O(7)2	103.6
	O(5)1	O(4)3	167.9		O(1)1	O(3)3	81.3		O(6)1	O(7)3	89.3		O(4)1	O(2)3	121.2		O(3)1	O(5)3	106.0
	O(5)1	O(7)4	95.4		O(1)1	O(3)4	94.3		O(6)1	O(7)4	148.9		O(4)1	O(1)4	102.7		O(3)1	O(6)4	125.4
	O(5)1	O(5)5	84.6		O(1)1	O(3)5	94.3		O(6)1	O(6)5	128.3		O(4)2	O(2)3	121.2		O(7)2	O(5)3	106.7
	O(5)1	O(4)6	91.7		O(1)1	O(1)6	172.7		O(6)1	O(6)6	85.2		O(4)2	O(1)4	102.7		O(7)2	O(6)4	110.9
	O(2)2	O(4)3	81.7		O(3)2	O(3)3	75.6		O(6)2	O(7)3	148.9		O(2)3	O(1)4	103.4		O(5)3	O(6)4	102.9
	O(2)2	O(7)4	111.0		O(3)2	O(3)4	175.5		O(6)2	O(7)4	89.3								
	O(2)2	O(5)5	85.1		O(3)2	O(3)5	104.6		O(6)2	O(6)5	85.2								
	O(2)2	O(4)6	162.6		O(3)2	O(1)6	92.9		O(6)2	O(6)6	128.3								
	O(4)3	O(7)4	95.5		O(3)3	O(3)4	104.6		O(7)3	O(7)4	90.2								
	O(4)3	O(5)5	83.5		O(3)3	O(3)5	175.5		O(7)3	O(6)5	124.6								
	O(4)3	O(4)6	84.7		O(3)3	O(1)6	92.9		O(7)3	O(6)6	76.0								
	O(7)4	O(5)5	163.6		O(3)4	O(3)5	75.0		O(7)4	O(6)5	76.0								
	O(7)4	O(4)6	81.1		O(3)4	O(1)6	91.6		O(7)4	O(6)6	124.6								
	O(5)5	O(4)6	82.5		O(3)5	O(1)6	91.6		O(6)5	O(6)6	69.8								

TABLE VI Bond-valence values  $\nu_{ij}$  according to Brese and O'Keeffe [18]

Ligand	Co(1)	Co(2)	Co(3)	V(1)/Mo(1)	Mo(2)/V(2)	Total valence
O(1)		0.356/0.302		1.163/1.541		1.82/2.20
O(2)	0.321			1.203/1.593		1.85/2.24
O(3)		0.304/0.304			1.649/1.245	2.27/1.86
O(4)	0.320/0.232	0.315/0.315		1.204/1.594		1.76/2.15
O(5)	0.509/0.299			1.204/1.594		
O(6)			0.434/0.434		1.540/1.162	2.35/1.97
			0.292/0.292		1.519/1.147	2.25/1.87
O(7)	0.309		0.308/0.308		1.596/1.205	2.21/1.82
$\Sigma$ (total valence)	1.99	1.90	2.07	4.77/6.32	6.30/4.76	

TABLE VII Partial contributions ( $\delta$ -ECoN's) to the effective coordination number [14, 15]

Ligand	Co(1)	Co(2)	Co(3)	V(1)	Mo(2)		
O(1)		1.124/0.951		0.967			
O(2)	0.895			1.010			
O(3)		0.994/0.994			1.057		
		0.957/0.957					
O(4)	0.893/0.579			1.011/1.011			
O(5)	1.390/0.823				0.969		
O(6)			1.219/1.219		0.952		
			0.800/0.800				
O(7)	0.856		0.853/0.853		1.015		
$\Sigma$	5.44	5.98	5.74	4.00	3.99		
Ligand	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)
Co(1)		0.698/698		0.700/0.412	0.997/0.455		0.541
Co(2)	0.824/0.657		0.521/0.489				
Co(3)						0.888/0.494	0.538
V(1)	1.261	1.283		1.288			
Mo(2)			1.303		1.193	1.246	1.304
$\Sigma$	2.74	2.68	2.31	2.40	2.65	2.63	2.38

The bond-valence values according to Brese and O'Keeffe [18] as well as the partial contributions to the effective co-ordination number calculated by the program MAPLE4 [14, 15] are given in Tables VI and VII respectively. The bond valences were calculated by using the formula:  $v_{ij} = \exp[(R_{ij} - d_{ij})/b]$ , where  $d_{ij}$  is the bond length between two atoms  $i$  and  $j$ ,  $b$  is commonly taken as a universal constant equal to  $0.37 \text{ \AA}$ , and  $R_{ij}$  is the bond-valence parameter taken from the tables of Brese and O'Keeffe [18]. We have obtained the expected valences within 6% deviation from the ideal values of 2, 5, and 6 for Co, V, and Mo respectively. The calculated valences of V are underestimated by ca. 0.25, while the calculated valences of Mo are overestimated by ca. 0.3. This is caused by the fact that the V/Mo–O bonds are shorter than the expected Mo–O bond length value, but they are longer than the expected V–O bond length value. For oxygen atoms the values of the valences are quite symmetrically distributed around 2 and never reach less than 1.5 or more than 2.5. The values of the effective coordination numbers are generally underestimated. We have obtained the expected values within 9.5% deviation from the ideal coordination number of 6 for Co and of 4 for V and Mo. For oxygen atoms the effective coordination number never reaches the expected value of 3 and is spread symmetrically around 2.5.

The values of the Co–O, V–O, and Mo–O bond lengths in each polyhedron are within 9.5% deviation from the ideal values of  $0.214 \text{ nm}$  [19],  $0.1715 \text{ nm}$  [19], and  $0.177 \text{ nm}$  [19] respectively. The expected M–O bond lengths were calculated by summing the values of ionic radii with taking the co-ordination number into account. The Co(1) octahedra and V/Mo tetrahedra are quite strongly distorted with respect both to the bond lengths and angle. On the other hand, the Co(2) octahedra are the most regular, what is caused probably by the fact that the environment of Co(2) is the most symmetric in the whole structure.

The IR spectrum of  $\text{Co}_{2.5}\text{VMoO}_8$  (Fig. 5) confirms the general features of its structure. The spectrum exhibits one broad band with its extremum at  $775 \text{ cm}^{-1}$

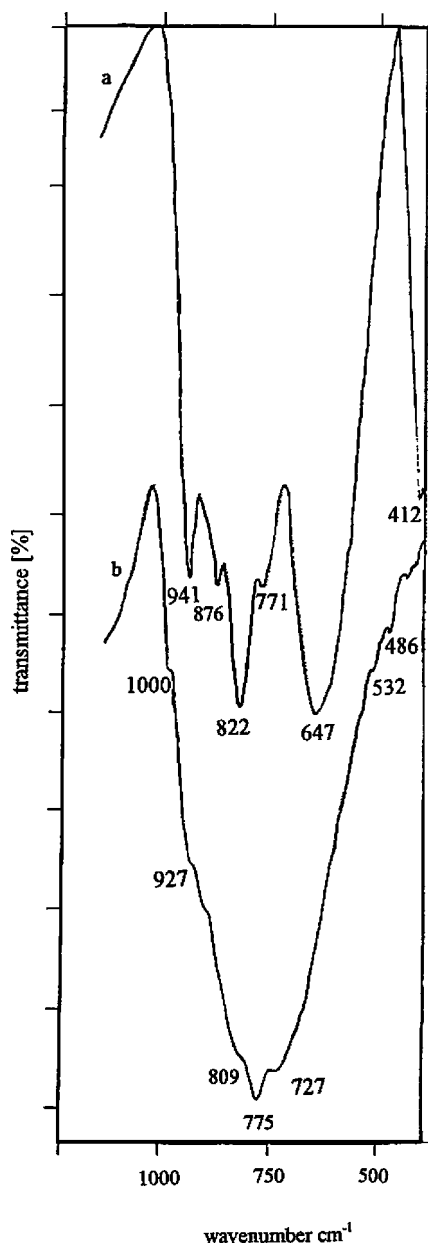


Figure 5 IR spectrum of (a) mixture of  $\text{Co}_3\text{V}_2\text{O}_8$  and  $\text{CoMoO}_4$  at a molar ratio 1:2 and (b)  $\text{Co}_{2.5}\text{VMoO}_8$ .

and with eight shoulders at 1000, 927, 895, 809, 727, 532, 486 and 440  $\text{cm}^{-1}$ . The shoulder occurring at 1000  $\text{cm}^{-1}$  corresponds to the vibrations of the shortest bond Mo(2)/V(2)-O(3) in the (Mo/V) $\text{O}_4$  tetrahedra. The shoulders of 927, 895, 809 and 727  $\text{cm}^{-1}$  correspond to the vibrations of the other Mo/V-O bonds [21–23]. The shoulders occurring at 532, 486 and 440  $\text{cm}^{-1}$  are due to the vibrations of the Co-O bonds. The distinct simplicity of the spectrum is caused by the fact that this is a so called three-dimensional structure.

## References

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