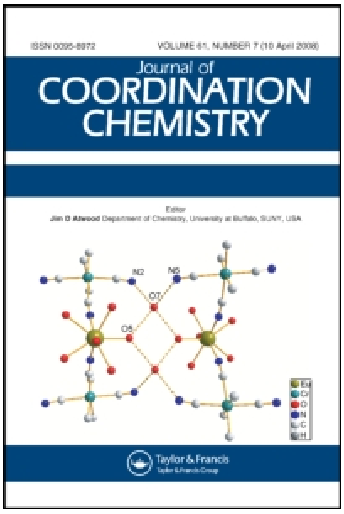

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Synthesis of Molybdovanadates Coordinated by Oxalato Ligands. The Crystal Structure of $K_6[Mo_6V_2O_{24}(C_2O_4)_2]\cdot 6H_2O$

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SYNTHESIS OF MOLYBDOVANADATES COORDINATED BY OXALATO LIGANDS. THE CRYSTAL STRUCTURE OF $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$

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The oxalato complex of a polyoxomolybdovanadate, $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ has been obtained by reaction of potassium molybdate, ammonium vanadate and tartaric or ascorbic acid. Such conversion of dicarboxylate into oxalate ions indicates the catalytic role of molybdenum. Complexes of analogous composition also were obtained in the reactions of MoO_3, V_2O_5 and potassium oxalate, or M_2CO_3 ($M = Rb$, Cs) and oxalic acid. The centrosymmetrical molybdovanadate anion $[Mo_6V_2O_{24}(C_2O_4)_2]^{6-}$ consists of six MoO_6 and two VO_6 edge-sharing octahedra to give the γ-$[Mo_6O_{26}]^{4-}$ structure. All complexes were characterized by powder and single crystal X-ray analyses, ESR and IR spectra and TG and DSC measurements.

Keywords: Molybdenum; Vanadium; Carboxylic acids; Catalysts; Crystal structure

INTRODUCTION

Most of the early transition metal polyoxoanions have structures based on close-packed oxygen arrays with interstitial metal centres so that their chemistry offers a rare opportunity to study chemical transformations on well-defined metal oxide surfaces [1–4]. In the past decade an interest in such polyoxometalates has been prompted by their industrial application as redox catalysts and their facile reoxidation by molecular oxygen resulted in their use in a variety of oxidation reactions. Another attractive feature of such polyoxometalates is the possibility of altering their properties by systematic changes in composition. For example, the redox potentials of polyoxometalates can be manipulated by replacing molybdenum(VI) or tungsten(VI) with vanadium(V).

As a part of our research on polyoxometalates coordinated by carboxylato ligands [5], we describe a new series of alkali metal molybdovanadates coordinated by a bidentate oxalate ion prepared by the conversion of dicarboxylato ions such as tartarate and ascorbnate to oxalate ions.

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EXPERIMENTAL

Reagents and Apparatus

All chemicals were of reagent grade and used as received from commercial sources. IR spectra were recorded in KBr with an FTIR 1600 Fourier-transform spectrophotometer in the range 4500–450 cm^{-1}. ESR spectra were measured at 293 K using a Varian E-109 spectrometer operating at 100 kHz and equipped with dual sample cavity. As a *g*-factor standard, 2,2-diphenyl-1-picrylhydrazyl (DPPH, $g = 2.0036$) was used. Molybdenum and vanadium were determined according to a literature method [6]. Carbon and hydrogen analyses were provided by the Analytical Services Laboratory of the Ruder Bošković Institute in Zagreb. The pH measurements were carried out using a Mettler MP220 pH meter.

Preparation of $M_6[Mo_6V_2O_{24}(C_2O_4)_2]\cdot 6H_2O$, $M = K$, Rb, Cs

(a) MoO_3 (1 mol), V_2O_5 (0.5 mol) and $K_2C_2O_4\cdot H_2O$ (1 mol) were suspended in water (30 cm^3). With heating at 90°C for 1 h, the resulting suspension became yellow. Unreacted oxides were filtered off, leaving a clear yellow solution. After one hour at the room temperature the yellow crystals which formed filtered off and dried *in vacuo*. Yield: 1.33 g, 78%. *Anal.* Found: V, 6.2; Mo, 36.2; C, 3.3; H, 1.0. Calc. for $C_4H_{12}K_6Mo_6V_2O_{38}$: V, 6.5; Mo, 36.4; K, 14.8; C, 3.1; H, 0.8%. IR(cm^{-1}): 3329(m), 1690(s), 1394(s), 1248(w), 988(s), 936(s), 899(s), 863(m), 799(s), 719(s), 654(s).

The same product was obtained in the reaction of K_2MoO_4, (1 mol), NH_4VO_3, (3 mol) and ascorbic acid, $C_6H_8O_6$, (1 mol) or in the reaction of K_2MoO_4, (1 mol), NH_4VO_3, (3 mol) and tartaric acid, $C_4H_6O_6$ (1 mol) in water (30 cm^3). The pH of the solution containing ascorbic acid was 6.45, and of that with tartaric acid 4.27 at 300 K. After approximately two weeks, in both cases, yellow crystals were obtained. They were filtered off and dried *in vacuo*. Yield: 0.10 g, 15% (reaction with ascorbic acid); 0.09 g, 21% (reaction with tartaric acid).

(b) M_2CO_3 ($M =$ Rb or Cs), (1 mol), MoO_3 (1 mol), V_2O_5 (0.5 mol) and $H_2C_2O_4\cdot 2H_2O$ (1 mol) were suspended in water (30 cm^3). With heating at 90°C for 1 h, the suspension became orange. Unreacted oxides were filtered off. The pH of the resulting yellow solution was 5.08 (for $M =$ Rb) and 4.85 (for $M =$ Cs) at 300 K. After approximately 1 day, the yellow polycrystalline product was filtered off and dried under vacuum.

$Rb_6[Mo_6V_2O_{24}(C_2O_4)_2]\cdot 6H_2O$, Yield: 0.25 g, 45%. *Anal.* Found: V, 5.4; Mo, 31.2; C, 2.4; H, 1.0. Calc. for $C_4H_{12}Rb_6Mo_6V_2O_{38}$: V, 5.5; Mo, 31.0; Rb, 27.6; C, 2.6; H, 0.6%. IR(cm^{-1}): 3361(m), 1686(m), 1387(m), 987(m), 934(s), 901(s), 861(m), 798(w), 711(s), 644(s).

$Cs_6[Mo_6V_2O_{24}(C_2O_4)_2]\cdot 6H_2O$, Yield: 0.20 g, 45%. *Anal.* Found: V, 4.5; Mo, 27.0; C, 2.2; H, 0.9. Calc. for $C_4H_{12}Cs_6Mo_6V_2O_{38}$: V, 4.6; Mo, 26.9; Cs, 37.2; C, 2.2; H, 0.6%. IR(cm^{-1}): 3414(m), 1688(s), 1382(m), 981(m), 929(s), 899(s), 855(m), 795(m), 721(s), 655(s).

TG and DSC Measurements

All thermal decompositions were recorded at a heating rate of 10°C min^{-1} in a dynamic atmosphere with a flow rate of 200 $cm^3\,min^{-1}$. Aluminium crucibles were used under argon or oxygen. For all experiments the temperature range was 30–600°C. A Mettler TG 50 thermobalance was used to obtain thermogravimetric data. Calorimetric measurements were undertaken on a Mettler DSC 30 instrument.

X-ray Diffraction

X-ray diffraction data were obtained using CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å) on a Philips PW 3710 powder diffractometer. Data were collected in the $3 < 2\theta < 65°$ range in the θ–2θ step scan mode with $\Delta 2\theta = 0.02°$ and $t = 12$ s.

Single-crystal X-ray Structure Analysis

$C_4H_{12}Mo_6V_2K_6O_{38}$, $M_r = 1580.26$, monoclinic, space group $I2/a$, $a = 13.812(2)$, $b = 12.183(1)$, $c = 21.147(2)$ Å, $\beta = 92.617(9)°$, $V = 3554.7(7)$ Å^3, $Z = 4$, $D_{calc} = 2.953$ g cm^{-3}, $F(000) = 3008$, $\mu(\mathrm{MoK}_\alpha) = 3.374$ mm^{-1}. A single crystal of $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ of dimensions 0.10 × 0.12 × 0.16 mm was used for data collection. All data were collected on a Philips PW1100 diffractometer with graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.7107$ Å). The structure was solved by the heavy atom method and refined on F^2 by full-matrix least-squares calculations. Intensity data were not corrected for absorption. All computations were performed on an IBM ThinkPad microcomputer using SHELXS 97 [7] and SHELXL 97 [8] programmes. Molecular drawings were prepared using ORTEP-III [9].*

RESULTS AND DISCUSSION

In an attempt to synthesize polyoxomolybdovanadates coordinated by ascorbic and tartaric acids, the potassium salt of molybdovanadate coordinated by oxalate ion was obtained. The formula of the complex, $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$, was confirmed by chemical analysis, IR and ESR spectra, thermogravimetric analysis and X-ray structure analysis. Complexes of analogous compositions were isolated in reactions with potassium oxalate, and with rubidium and caesium carbonate and oxalic acid. Our attempts to prepare lithium and sodium complexes were unsuccessful, most probably due to the small size of these cations. During the reactions vanadium(V) was reduced to V(IV) as confirmed by ESR spectra clearly indicative of the presence of the latter (Fig. 1). As partial reduction of V(V) to V(IV) occurs only at the crystal surface the concentration of paramagnetic V(IV) is very low. Paramagnetic (V^{4+}) concentration was determined by double integration of the spectrum compared with a double standard Varian strong pitch [10].

Although the mechanism of the conversion of ascorbic or tartaric acid into oxalate, catalysed by molybdenum, involves several intermediates and rearrangements, the oxidative decarboxylation might be essentially represented by Scheme 1.

Some examples for such conversions, e.g. malonate and malate into oxalate in aqueous solution of peroxomolybdate(VI), are known in the literature [11–13]. However, to now there has been no an adequate explanation for such a reaction.

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*Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153572. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

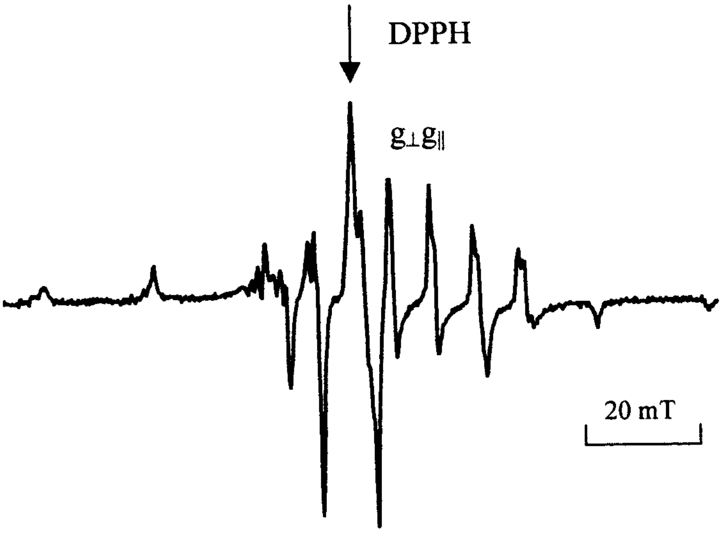
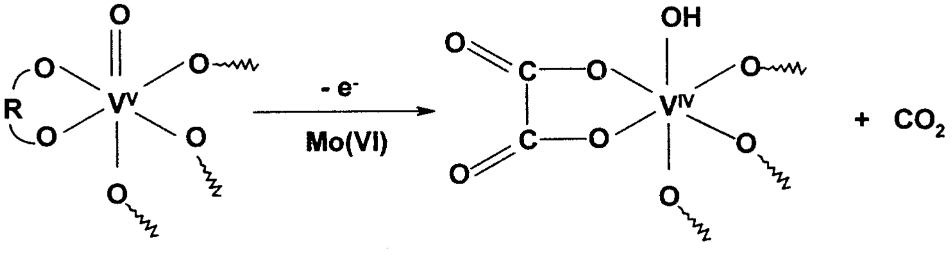


FIGURE 1 ESR spectrum of $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ obtained by reaction of K_2MoO_4 and NH_4VO_3 with tartaric and ascorbic acids.



SCHEME 1 R: other tartaric or ascorbic acid residues.

TG and DSC Analysis

The thermal behaviour of the investigated molybdovanadates are consistent with their formula, analytical data and the crystal structure determination. The TG study in argon atmosphere reveals two main processes, dehydration and pyrolitic decomposition. All molybdovandates start to release water molecules very slowly as soon as heating commences implying the presence of weakly bonded water molecules of crystallization. The weight loss corresponds to six water molecules. The resulting anhydrous molybdovandates are stable to higher temperatures, when decomposition begins with loss of carbon monoxide and carbon dioxide, most probably resulting in the formation of intermediate oxalate–carbonate molybdovandates and finally $M_6[Mo_6V_2O_{26}]$.

As previously observed in the decomposition of oxalato complexes of molybdenum(VI) and vanadium(V) in an argon atmosphere, molybdenum undergoes partial reduction to probably Mo(V) [14], and in like manner V(V) to V(IV) [15]. The thermal decomposition of molybdovanadates follows the same scheme of reduction. However, DSC studies in flowing nitrogen produce non-reproducible curves, mostly due to extensive base line drift. The most noticeable feature of the DSC curves consists of an exothermic peaks at around 370 and 460°C. Final solid products were characterized by powder X-ray diffraction and IR spectroscopy.

Crystal Structure of $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$

The structure of the $[Mo_6V_2O_{24}(C_2O_4)_2]^{6-}$ anion is shown in Fig. 2 and selected interatomic distances are listed in Table I. The crystal structure of $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ is built up of potassium cations, centrosymmetric $[Mo_6V_2O_{24}(C_2O_4)_2]^{6-}$ anions and water molecules. The molybdovanadate anion consists of six MoO_6 and two VO_6 edge-sharing octahedra with two oxalato ligands bonded to the vanadium ions as bidentates, essentially the same as in the anion found in the structure of the corresponding ammonium salt

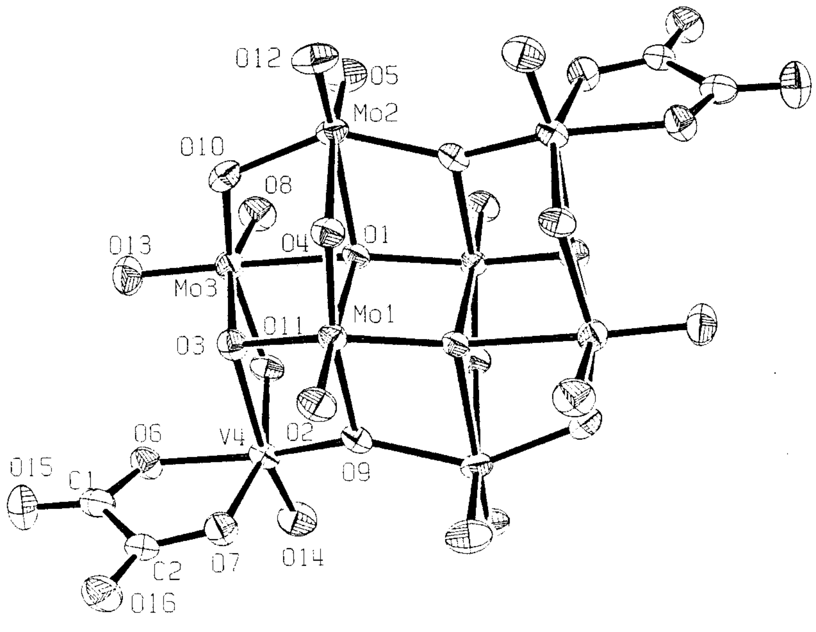


FIGURE 2 ORTEP illustration of the structure of the centrosymmetrical $[Mo_6V_2O_{24}(C_2O_4)_2]^{6-}$ anion.

TABLE I Selected M–O interatomic distances (Å)[a] for $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$

$V–O_t$	1.595(4)
$V–O_b$	1.778(4)
$V–O_{3b}$	1.836(4)–2.413(4)
$V–O_{oxalate}$	2.007(4)–2.010(4)
$Mo–O_t$	1.704(4)–1.716(4)
$Mo–O_b$	1.748(4)–2.358(4)
$Mo–O_{3b}$	1.953(4)–2.230(4)
$Mo–O_{4b}$	2.403(4)

[a] O_t = terminal oxo-oxygen atom, O_b = bridging oxygen atom, O_{3b} = triply-bridging oxygen atom, O_{4b} = quadruply bridging oxygen atom.

$(NH_4)_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ [16]. It adopts the γ-$[Mo_8O_{26}]^{4-}$ type structure with two additional terminal positions, thus satisfying octahedral coordination of all metal ions [17]. The coordination octahedra are significantly distorted with angles at the metal atoms ranging for ∠O–Mo–O from 70.75(14) to 105.3(2)°, and for ∠O–V–O from 72.27(16) to 102.1(2)°. The metal ions are shifted from the centres of the octahedra towards the terminal oxygen atoms due to the metal-to-terminal oxygen double bond and repulsion between neighbouring, positively charged, metal ions. Consequently, the bond lengths between metal and oxygen atoms differ significantly depending upon the type of M–O bond. In the MoO_6 octahedra the $Mo = O_t$ bonds lengths vary from 1.704(4) to 1.716(4) Å, while those between Mo and bridging O atoms range from 1.748(4) to 2.358(4) Å. In the VO_6 octahedron $V = O_t$ is 1.595(4) Å while the distances between V and shared O atoms vary from 1.778(4) to 2.413(4) Å. The $V–O_{oxalato}$ bond lengths are 2.007(4) and 2.010(4) Å. Powder X-ray diffraction patterns of the isomorphous potassium, rubidium and caesium salts indicate minor structural differences, these certainly being due to the size of cations.

IR spectra of all three molybdovanadates were as expected for such compounds [18]. Observed strong bands at 1690 and 1394 cm^{-1} in $K_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$, at 1686 and 1387 cm^{-1} in $Rb_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ and at 1688 and 1382 cm^{-1} in $Cs_6[Mo_6V_2O_{24}(C_2O_4)_2] \cdot 6H_2O$ are due to ν(CO) stretching, involving coordinated oxalate ligands. Other strong absorptions in the ranges 988–934 cm^{-1} and 721–799 cm^{-1} arise from $M = O$ (M =Mo or V) stretching. These values are in accord with the structural findings.

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