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SYNTHESIS, STRUCTURE AND ESR SPECTRUM OF $(Hmorph)_6[(V^{IV},V^{V},Mo_{10})VO_{40}] \cdot 3H_2O$

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Abstract—The title compound has been synthesized from molybdenum(VI) oxide and ammonium vanadate in aqueous solution by adding morpholine (pH 5.8). The X-ray structural investigation shows that the polyoxometalate anion adopts a Keggin-type structure with a central tetrahedral vanadium(V) atom. The other two vanadium atoms are crystallographically disordered over $12MO_6$ octahedral sites. The ESR spectrum clearly indicates that one octahedrally coordinated vanadium atom has the oxidation number +4.

$[Hmorph]_6[(V^{IV},V^{V},Mo_{10})VO_{40}] \cdot 3H_2O$ (morph = morpholine) belongs to the class of so-called "heteropoly blues",[1] the formation of which is often used in analytical chemistry.[2] Such hetero- as well as iso-polyoxoanions containing vanadium, molybdenum or tungsten show the ability to form reduced compounds, but only when the metal atom is coordinated to one terminal oxygen atom.[3]

The ESR spectra of Keggin-type heteropolymolybdates reduced by one electron indicate that this electron is always trapped on an octahedrally but not on a tetrahedrally coordinated metal atom,[4] the same as was observed for the compound described in this paper. The ESR spectrum of the title compound is almost the same as that of the vanadyl complexes with organic ligands, proving clearly that the added electron is localized on the vanadium atom. The same evidence has been found for the analogous structure of $K_3(V_2,Mo_{10})VO_{40} \cdot 13H_2O$.[5] The heteropolyoxometalates in such partially reduced state are of particular interest due to their potential catalytic activity.[6]

EXPERIMENTAL

Reagents and apparatus

All chemicals were of reagent grade and used as purchased from commercial sources. The IR spectrum was recorded in KBr with a FTIR 1600 Fourier-transform spectrophotometer in the 4500–450 cm^{-1} region. Thermogravimetric analysis of water content was obtained on a Mettler TA4000, with a heating rate of 10°C per minute. The ESR spectrum was recorded with a polycrystalline sample on a Varian E-109 spectrometer operating at 100 kHz modulation. DPPH was used as an internal reference. All measurements were made at room temperature.

Preparation and elemental analysis

MoO_3 (1.8 g) was dissolved by heating in a mixture of water (10 cm^3) and morpholine (1 cm^3). A suspension of NH_4VO_3 (2.9 g) in water (30 cm^3)

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was added and then the mixture heated and neutralized to pH 5.8 with 2 M hydrochloric acid. After standing for 20 days, a black stable crystalline product (4 mg, 0.14%) was filtered off and washed with ethanol.

Found: C, 12.8; H, 3.8; N, 4.2; Mo, 40.7; V, 6.0, H_2O, 3.2. Calc. for $C_{24}H_{66}Mo_{10}V_3N_6O_{49}$: C, 12.4; H, 2.9; N, 3.6; Mo, 41.1; V, 6.5; H_2O, 2.3%. IR (cm^{-1}): 3442 (s), 3046 (s), 2850 (m), 1568 (m), 1402 (m), 885 (vs), 768 (vs).

ESR spectrum

The ESR spectrum of powdered $[Hmorph]_6[(V^{IV}, V^{V}, Mo_{10})VO_{40}]\cdot 3H_2O$ exhibits the superposition of two sets of eight hyperfine lines due to the interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$). The parameters calculated from the spectra are $A_{\parallel} = 14.0$ mT, $A_{\perp} = 6.0$ mT, $g_{\parallel} = 1.935$ and $g_{\perp} = 1.984$.

Crystal structure determination

Crystal data. $C_{24}H_{66}Mo_{10}V_3N_6O_{49}$, triclinic, space group $P\bar{1}$, $M = 2335.05$, $a = 11.840(4)$, $b = 15.225(6)$, $c = 18.181(7)$ Å, $\alpha = 76.47(2)^{\circ}$, $\beta = 71.28(2)^{\circ}$, $\gamma = 76.85(2)^{\circ}$, $V = 2976(3)$ Å^3, $Z = 2$, $D_X = 2.61$ g cm^{-3}, $F(000) = 2266$, μ(Mo-K_{α}) = 25.96 cm^{-1}.

A single crystal of dimensions $0.98 \times 0.23 \times 0.20$ mm^3 was used for the data collection on a Philips PW1100 diffractometer with graphite monochromatized Mo-K_{α} radiation ($\lambda = 0.7107$ Å). Four standard reflections measured every 75 min showed no significant crystal decay. 17,110 reflections (16,631 unique) were collected, ($2 \leqslant \Theta \leqslant 30^{\circ}$, $-15 \leqslant h \leqslant 16$, $-20 \leqslant k \leqslant 21$, $0 \leqslant l \leqslant 25$) by ω–2Θ scans. Data were corrected for Lorentz and polarization effects, and also for absorption; ψ scan data with χ set at 90° were taken at the end of data collection, the correction method being that of North *et al.*[7]

The structure was solved by Patterson and successive Fourier syntheses. The refinement was performed by full-matrix least-squares procedure on F_0^2 with anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms attached to the morpholinium cations were positioned geometrically [d(C—H) = 0.97 and d(N—H) = 0.90 Å, U_{iso} from 0.044 to 0.114 Å^2] and included in the structure factor calculations. Hydrogen atoms of water molecules were not located. The values of the reliability indices obtained at the end of refinement were $R(F_0) = 0.054$ for 12,732 reflections with $F_0 \geqslant 4\sigma(F_0)$ and 835 refined parameters, $R_w(F_0^2) = 0.157$, $w = [\sigma^2(F_0) + (0.0985P)^2 + 9.81P]^{-1}$, where $P = 1/3(F_0^2 + 2F_c^2)$, and $S = 1.023$, for 16,571 reflections (60 reflections with $\Delta/\sigma > 5$ were omitted). The largest remaining difference peak was 1.53 e Å^{-3} [0.80 Å from Mo/V(11)]. All calculations were carried out on an IBM PC/AT compatible microcomputer (80486/66 MHz processor) using SHELXS86[8] and SHELXL93[9] programmes. The CSU[10] programme was used to calculate interatomic distances and angles, ORTEP[11] and PLUTON[12] to draw structural schemes.

RESULTS AND DISCUSSION

The ESR spectrum of the title compound is shown in Fig. 1. The anisotropic hyperfine coupling constants and g parameters are close to the ESR

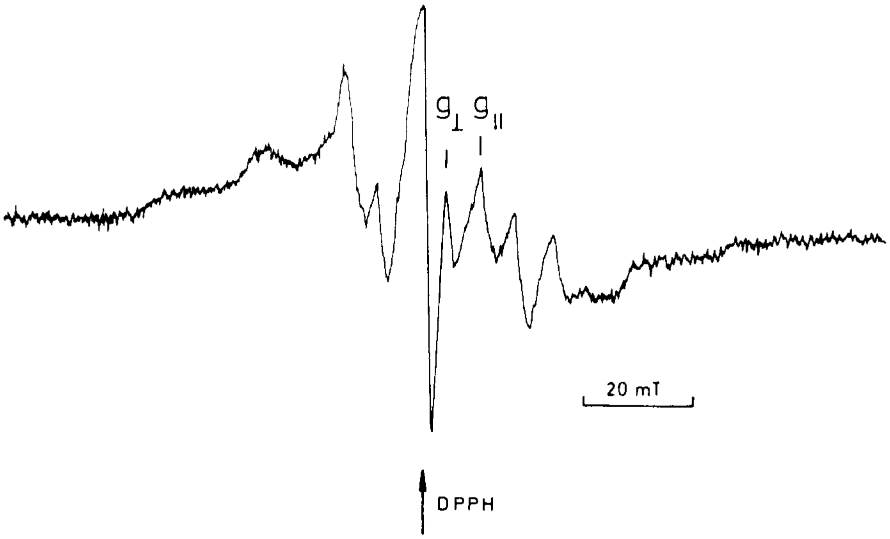

Fig. 1. The ESR spectrum of powdered $[Hmorph]_6[(V^{IV}, V^{V}, Mo_{10})VO_{40}]\cdot 3H_2O$.

parameter values of the oxovanadium ion.[13–16] This suggests that one vanadium ion is $\mathrm{V^{4+}}$, which is in agreement with the molecular formula. The absence of an $\mathrm{Mo^{5+}}$ ESR signal confirms that all the molybdenum atoms are in the oxidation state +6, showing again that $\mathrm{V^{5+}}$ is the more easily reducible ion. The observed values of $g_{\parallel} < g_{\perp}$ and $A_{\parallel} \geqslant A_{\perp}$ indicate a tetragonal distortion of the paramagnetic vanadium species, pointing to the existence of a vanadyl bond responsible for the ESR signals.

The structure of the $[(\mathrm{V^{IV}},\mathrm{V^{V}},\mathrm{Mo_{10}})\mathrm{VO_{40}}]^{6-}$ anion is shown in Fig. 2 and the packing of the molybdovanadate anion with surrounding morpholinium cations and water molecules with all possible hydrogen bondings in Fig. 3. The atomic coordinates, thermal parameters, complete list of interatomic distances and angles, and observed and calculated structure factors have been deposited as supplementary material with the Cambridge Crystallographic Data Centre, from whom copies are available on request.

The molybdovanadate anion has the well-known Keggin structure[17] (α isomer) with a $\mathrm{V^{V}O_4}$ tetrahedron at the centre of 12 surrounding $\mathrm{Mo_6}$ octahedra with a random distribution of $10\mathrm{Mo^{6+}}$, one $\mathrm{V^{4+}}$ and one $\mathrm{V^{5+}}$ ions between 12 metal atom positions. The distances V···Mo/V vary from 3.468(2) to 3.524(2) Å. Whereas three $\mathrm{MO_6}$

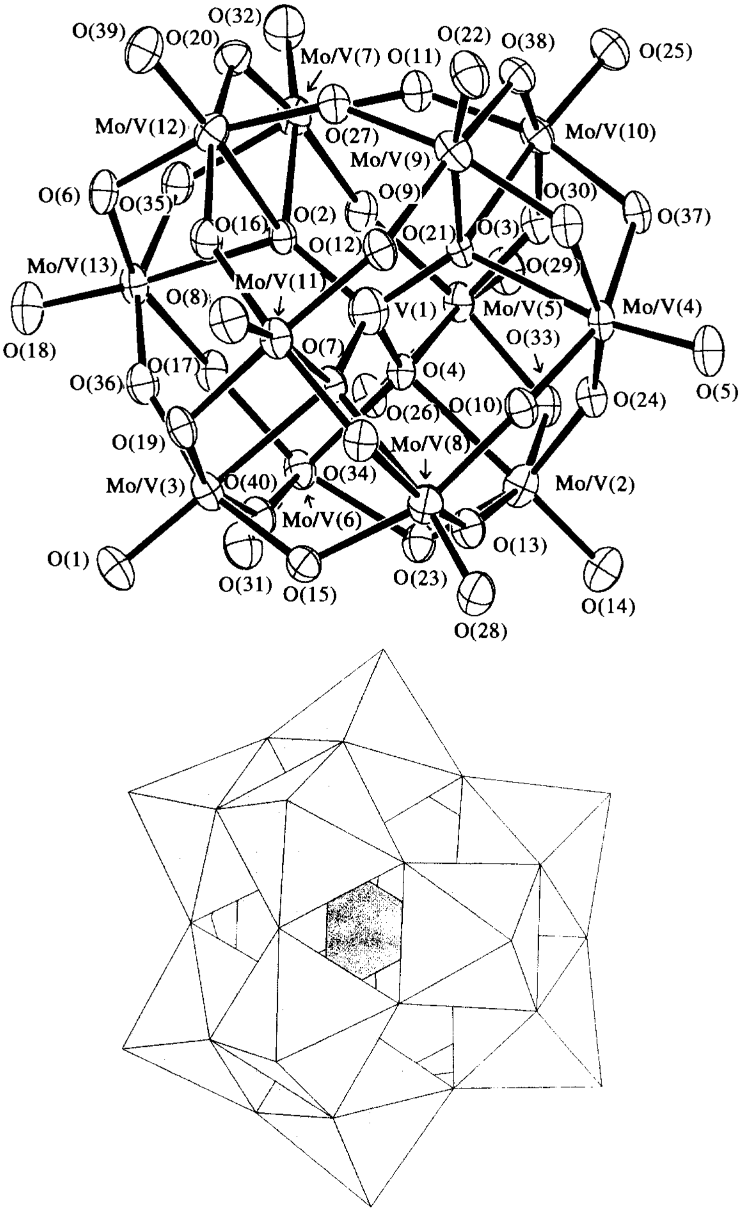

Fig. 2. A perspective view of the $[(\mathrm{V^{IV}},\mathrm{V^{V}},\mathrm{Mo_{10}})\mathrm{VO_{40}}]^{6-}$ anion with the atomic numbering scheme (top). Polyhedral representation of the same anion (bottom).

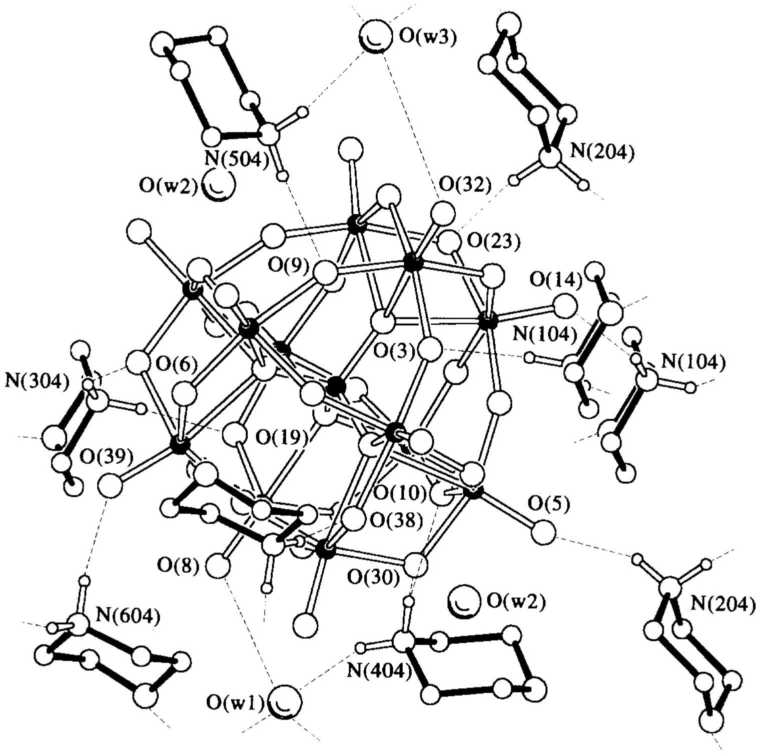

Fig. 3. Molybdovanadate anion with the surrounding morpholinium cations and water molecules. Only atoms involved in the hydrogen bonding are labelled. Hydrogen bonds are denoted by broken lines.

octahedra of the anion share common edges, thus forming the M_3O_{13} units, with the M · · · M distances from 3.289(1) to 3.353(1) Å, four such M_3O_{13} units are linked together by sharing common corners, but at significantly greater M · · · M distances, varying from 3.638(1) to 3.701(2) Å. Such differences in the metal-to-metal distances were not observed in the analogous structure of $K_6[(V_2, Mo_{10})VO_{40}] \cdot 13H_2O$ due to the rotational disorder in the structure, with the anion distributed between two positions interrelated by a 90° rotation.[5] However, such M · · · M distances are comparable with those found in the structure of $Na_3[VMo_{12}O_{40}] \cdot 19H_2O$.[18]

The central VO_4 tetrahedron is almost regular, with V—O bond lengths from 1.626(3) to 1.646(3) Å, and O—V—O angles from 109.0(2) to 110.1(2)°. Owing to the above-mentioned random distribution of Mo^{6+}, V^{4+} or V^{5+} ions within all MO_6 octahedra, any comparison of bond distances and angles with those found in similar structures would be unreasonable. Within each octahedron, the metal-to-oxo-oxygen atom distances vary as follows: one terminal oxo-oxygen atom from 1.662(4) to 1.688(4) Å, four doubly-bridging from 1.846(4) to 2.007(4) Å, and one bridging four metal atoms (one vanadium and three molybdenum/vanadium) from 2.285(3) to 2.333(3) Å. The O—Mo/V—O angles range from 73.3(1) to 103.4(2)°.

The distances given in Table 1 show that all hydrogen atoms from the morpholinium $—NH_2$ groups participate in the N—H · · · O hydrogen bonding between morpholinium cations, molybdovanadate anions and water molecules O(w1) and O(w3). The water molecule O(w2) is situated between two polyoxometalate anions and surrounded by their nine oxygen atoms at distances ranging from 2.834(7) to 3.151(8) Å, connecting them all along the *a*-axis. As can be seen from Table 2, each of the water molecules O(w1) and O(w3) are also surrounded by three oxygen atoms (one from the polyoxo anion and two from morpholinium cations) at distances varying from 2.828(13) to 3.155(15) Å. These approaches are indicative of additional hydrogen bonds between the species present in the crystal structure. Both terminal [O(5), O(8), O(39)] and doubly-bridging [O(3), O(6), O(9), O(10), O(19), O(23), O(30), O(38)] oxygen atoms of the polyoxometalate anion are protonated in such a way.

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Table 1. The N—H···O hydrogen bonding parameters (distances in Å, angles in °) between morpholinium cations, polyoxometalate anions and water molecules

D	H	A	H···A	D···A	∠D—H···A
N(104)	H(105)	O(3$^{(i)}$)	2.050	2.946(5)	174.2(6)
N(104)	H(106)	O(14$^{(ii)}$)	2.016	2.800(6)	144.8(6)
N(204)	H(205)	O(5$^{(iii)}$)	1.985	2.820(6)	153.6(6)
N(204)	H(206)	O(23)	1.952	2.837(6)	167.4(6)
N(304)	H(305)	O(6$^{(iv)}$)	2.240	2.980(8)	139.2(6)
N(304)	H(306)	O(19$^{(iv)}$)	2.094	2.965(6)	162.6(6)
N(404)	H(405)	O(w1)	1.918	2.754(7)	153.7(6)
N(404)	H(406)	O(10$^{(v)}$)	2.294	3.131(6)	154.7(6)
N(404)	H(406)	O(30$^{(v)}$)	2.392	3.092(7)	134.7(6)
N(504)	H(505)	O(w3)	2.164	2.950(11)	145.5(8)
N(504)	H(506)	O(9)	2.182	3.031(7)	157.1(8)
N(604)	H(605)	O(38)	1.892	2.783(8)	170.3(8)
N(604)	H(606)	O(39$^{(vi)}$)	2.010	2.888(7)	164.6(8)

Symmetry code: (i) $2-x$, $1-y$, $1-z$; (ii) x, y, $1+z$; (iii) $2-x$, $1-y$, $-z$; (iv) $1-x$, $-y$, $1-z$; (v) $-1+x$, y, $1+z$; (vi) $2-x$, $-y$, $1-z$.

Table 2. Additional close contacts between oxygen atoms from water molecules, polyoxometalate anions and morpholinium cations (Å)

O(w1)···O(8$^{(i)}$)	3.089(7)
O(w1)···O(101$^{(ii)}$)	2.998(9)
O(w1)···O(201$^{(iii)}$)	2.881(8)
O(w2)···O(1)	3.007(6)
O(w2)···O(17)	3.151(8)
O(w2)···O(18)	3.108(8)
O(w2)···O(30$^{(iv)}$)	2.947(8)
O(w2)···O(31)	3.089(7)
O(w2)···O(36)	3.112(7)
O(w2)···O(37$^{(iv)}$)	2.834(7)
O(w2)···O(38$^{(iv)}$)	2.860(6)
O(w2)···O(40)	3.072(6)
O(w3)···O(32$^{(v)}$)	2.828(13)
O(w3)···O(301$^{(v)}$)	3.155(15)
O(w3)···O(601$^{(v)}$)	3.043(14)

Symmetry code: (i) $-1+x$, y, $1+z$; (ii) $1-x$, $-y$, $2-z$; (iii) x, $-1+y$, $1+z$; (iv) $-1+x$, y, z; (v) $1-x$, $1-y$, $1-z$.

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