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FULL PAPER

Spectroscopic and magnetic investigation of the $K_5[PMo_2VW_9O_{40}]\cdot 24H_2O$ heteropolyoxometalate and its monoprotonated form†

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The $K_5[PMo_2VW_9O_{40}]\cdot 24H_2O$ heteropolyoxometalate complex was synthesized and investigated by means of spectroscopic and magnetic susceptibility measurements. The co-ordination of the vanadium(IV) ion to the monovacant α-$[PMo_2W_9O_{39}]^{7-}$ heteropolyanion results in the shift of the bicentric $\nu_{asym}(M{=}O_a)$ and $\nu_{asym}(M{=}O_d)$ and tricentric $\nu_{asym}(M\text{–}O_{b,c}\text{–}M)$ vibrations (M = W or Mo) in the 700–1100 cm^{-1} region of the IR spectrum of the complex compared to those of the ligand. Two low wavenumber bands in VIS spectrum were assigned to $^2B_2 \longrightarrow {}^2E$ (11310 cm^{-1}) and $^2B_2 \longrightarrow {}^2B_1$ (13710 cm^{-1}) transitions for V^{IV} in an axial C_{4v} environment. The two shoulders at 16150 and 19220 cm^{-1} correspond to $V^{IV}\rightarrow Mo^{VI},W^{VI}$ and $Mo^{V}\rightarrow Mo^{VI},W^{VI}$ transitions, respectively. The UV transitions (38480 and 47680 cm^{-1}) correspond to charge transfer bands. The simulation of the powder EPR spectrum of the sample obtained at room temperature indicates the presence, in the same amounts, of one-electron-reduced species ($g_{\parallel} = 1.922$, $g_{\perp} = 1.972$, $A_{\parallel} = 181$ G, $A_{\perp} = 63$ G) and a monoprotonated two-electron-reduced species with mixed valence V^{IV}, Mo^{V} and Mo^{VI} ($g_{iso} = 1.972$, ΔB_{iso}(p-p) = 450 G). The magnetic parameters ($\mu_{eff} = 2.11\ \mu_B$, $\theta = -59$ K) of the sample and the effective spin $S' = 0.84$ estimated for the two-electron-reduced species suggest the presence of one antiferromagnetic coupling between the V^{IV} and the Mo^{V}–Mo^{VI} pair.

Introduction

Heteropolyanions have won particular attention mainly because of their use in heterogeneous catalysis,[1,2] oxidation[3,4] and acidic processes.[5] Heteropolyoxometalates (HPOM) with mixed addend atoms, like vanadium, molybdenum or tungsten, are also very interesting from the structural point of view.[6,7] The proximity of the lighter vanadium and molybdenum ions in the structure,[6] the presence of anions with mixed valence,[8] unpaired electron delocalization in the HPOM[9,10] or, on the contrary, the presence of trapped electrons on different ions[11,12] are a few structural features leading to different spectroscopic properties and applications of these compounds.

Another aspect refers to the coexistence of reduced and unreduced anions in the same sample. The appearance of these species is determined by the physical and chemical conditions of the synthesis process.[13] Owing to the non-equivalent positions of the addend atoms in the HPOM, the sample could also contain different geometrical isomers.[14,15]

The main goal of this paper is to report some spectroscopic and magnetic investigations on the $K_5[PMo_2VW_9O_{40}]\cdot 24H_2O$ heteropolyoxometalate (V^{IV}-HPOM) and its monoprotonated form. This complex presents an α-Keggin structure[16] (Fig. 1) and derives from the monovacant α-$[PMo_2W_9O_{39}]^{7-}$ anion to which one vanadium ion is added.[17]

Previous X-ray and multinuclear NMR studies on isostructural complexes have indicated that vanadium, molybdenum and tungsten ions are usually octahedrally co-ordinated with the oxygen atoms. The MoO_6 and VO_6 octahedra are adjacent and share a corner oxygen atom.[10]

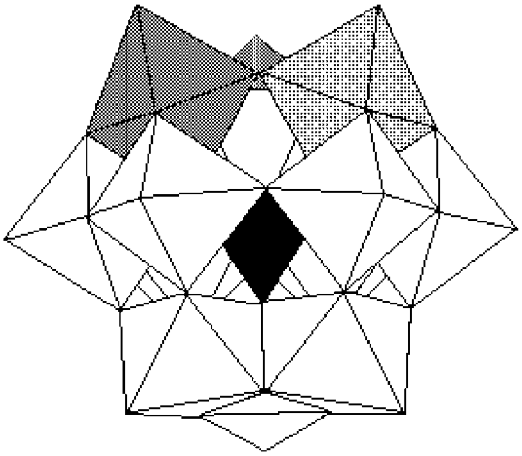

Fig. 1 The structure of the $K_5[PMo_2VW_9O_{40}]\cdot 24H_2O$ heteropolyoxometalate. Shaded octahedra in the "cap" position represent MoO_6 sites. The pointed octahedron represents the VO_6 unit. The empty polyhedra are WO_6 units and the full central tetrahedron is PO_4.

Cadot *et al.*[6] have prepared by electrochemical techniques one- ($V^{V} \longrightarrow V^{IV}$), three- ($V^{V} \longrightarrow V^{IV}$, $2Mo^{VI} \longrightarrow 2Mo^{V}$), and four- ($V^{V} \longrightarrow V^{III}$, $2Mo^{VI} \longrightarrow 2Mo^{V}$) electron-reduced species of the α-$[PMo_2VW_9O_{40}]^{4-}$ anion. The electronic spectrum of the one-electron-reduced anion presents two bands at 16000 and 20900 cm^{-1}; the three-electron-reduced species has a strong absorption at 20400 cm^{-1}, which decreases in intensity for the four-electron-reduced species. The EPR spectra of the powder one-electron-reduced species and its solution revealed signals for V^{IV} in an axially distorted ligand field.[6]

In our synthesis we use from the beginning the vandium(IV) ions from $VOSO_4$. Our spectroscopic and magnetic investigation shows the coexistence in the sample, in the same amount, of the $[PMo^{VI}_2V^{IV}W^{VI}_9O_{40}]^{5-}$ one-electron-reduced species and $[HPMo^{V}Mo^{VI}V^{IV}W^{VI}_9O_{40}]^{5-}$ monoprotonated two-electron-reduced species. The two-electron-reduced species is obtained in the acid medium of the reaction because of reduction of one Mo^{VI} to Mo^{V} by V^{IV} from unchanged $VOSO_4$.[18,19] The reduction of the Mo^{VI} takes place at the same time as the

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† Electronic supplementary information (ESI) available: IR data. See http://www.rsc.org/suppdata/dt/b0/b004871m/

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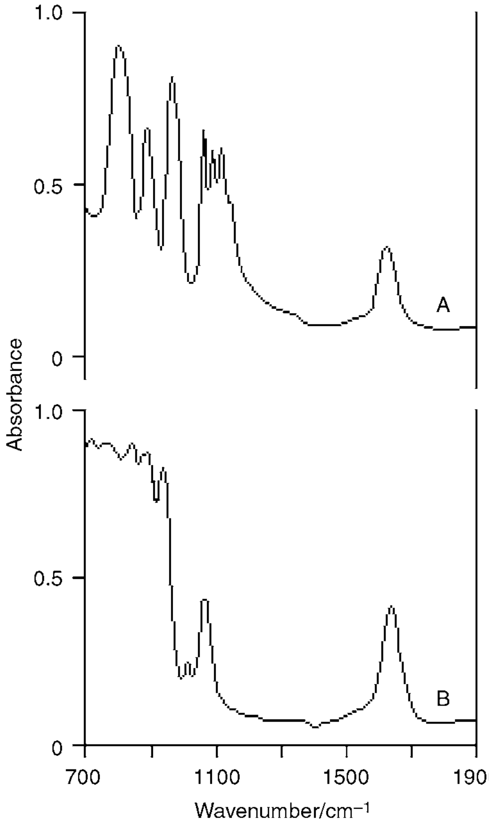

Fig. 2 IR spectra of the V^{IV}-HPOM complex (A) and the ligand (B).

protonation to prevent an increase of the anionic charge. This protonation is by hydrogen from the water used in the synthesis or from the acid medium. The V^{IV} from the reacted $VOSO_4$ leads to the one-electron-reduced species.

Results and discussion

Infrared data

The analysis of the co-ordination mode of the V^{IV} was made by means of comparison between the IR absorption bands of the V^{IV}-HPOM complex with those of the $K_7[PMo_2W_9O_{39}]\cdot 13H_2O$ ligand (see ESI). The positions of the bands, their shape and intensity for the complex and for the ligand differ in the 700–1900 cm^{-1} region (Fig. 2).

The strong shift of the $\nu_{asym}(W{=}O_d)$ (by 28 cm^{-1}) and $\nu_{asym}(Mo{=}O_d)$ (35 cm^{-1}) vibrations in the IR spectrum of the complex is due to the involvement of the $V{=}O_d$ vanadyl group in the co-ordination.[20] These bands are well resolved in the ligand spectrum, but in the complex spectrum they are overlapped to form a single band with a shoulder.[21] Two vibration bands for tricentric $W{-}O_c{-}W$ bonds of the edge-sharing WO_6 octahedra are present in the spectrum of the ligand, while in the complex spectrum only the band with the highest frequency appears.

Electronic spectroscopy

The UV electronic spectra of the V^{IV}-HPOM complex and of the ligand (Fig. 3) present two strong and broad charge transfer bands. The band centered at 47680 cm^{-1} in the ligand spectrum remains unchanged in the complex spectrum and is due to $p_\pi(O_d) \longrightarrow d_{\pi*}(W,Mo)$ transitions.[22] The co-ordination of the vanadium(IV) ion to the heteropolyoxometalate changes the position and the shape of the second band for the $p_\pi(O_{b,c}) \longrightarrow d_{\pi*}(W,Mo)$ transitions. This band is centered at ≈38680 cm^{-1} for the ligand and presents a shoulder at ≈36800 cm^{-1} because of the non-equivalent $M{-}O{-}M'$ bonds (M, M′ = W, Mo). The complex spectrum shows a broad and more intense band, centered at ≈ 38480 cm^{-1}. Its strong shift may be due to the presence of heteropoly reduced species.[23,24]

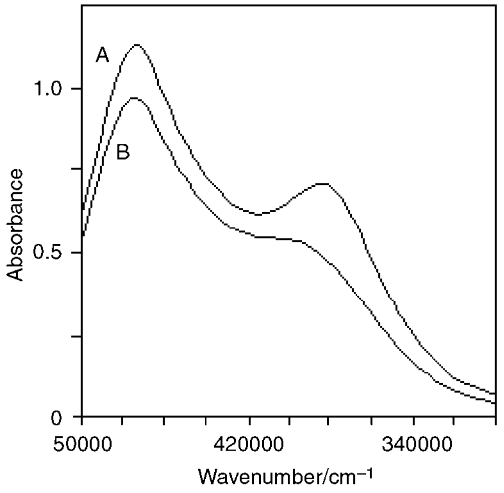

Fig. 3 UV spectra of the V^{IV}-HPOM complex (A) and the ligand (B) obtained in 5×10^{-5} mol l^{-1} aqueous solution.

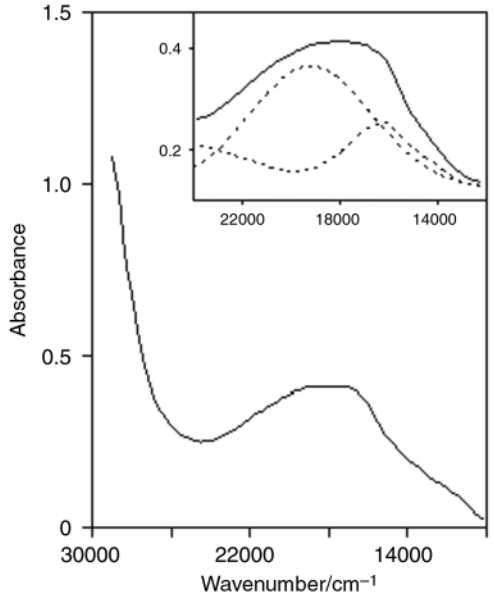

Fig. 4 Visible electronic spectra of the V^{IV}-HPOM complex in 10^{-2} mol l^{-1} aqueous solution. The simulated components (dashed lines) of the main band are presented in the inset.

The visible electronic spectrum of the V^{IV}-HPOM complex (Fig. 4) in aqueous solution shows a strong and very broad band in the 15300–24000 cm^{-1} range and two shoulders at ≈11310 and 13710 cm^{-1}. The low wavenumber shoulders correspond to the so-called I and II bands for d–d transitions in oxovanadium complexes.[25] According to the Ballhausen and Gray molecular orbital theory for the V^{IV} in C_{4v} local symmetry, these bands can be assigned to $^2B_2(d_{xy}) \longrightarrow {}^2E(d_{xz,yz})$ and $^2B_2(d_{xy}) \longrightarrow {}^2B_1(d_{x^2-y^2})$ transitions.[26] These depend upon the character of the vanadium–oxygen double bond $V{=}O_d$ and upon the non-axial ligand field respectively. We note the lowering of the wavenumbers for these transitions when molybdenum atoms substitute some tungsten atoms of the HPOM. Thus, when replacing two W^{VI} in $[PVW_{11}O_{40}]^{4-}$,[27] the decrease of the above d–d transitions is about 700–800 cm^{-1}. In the spectra of the reduced forms of the α-$[PMo_2VW_9O_{40}]^{4-}$ anion obtained by Cadot *et al.*[6] the bands appear at wavenumbers greater than 16000 cm^{-1}, without any band at lower frequencies.

The strong band at higher frequency in our study presents two shoulders at ≈19220 and ≈16150 cm^{-1} (Fig. 4). The first corresponds to the $Mo^V \rightarrow Mo^{VI},W^{VI}$ transition and the other is

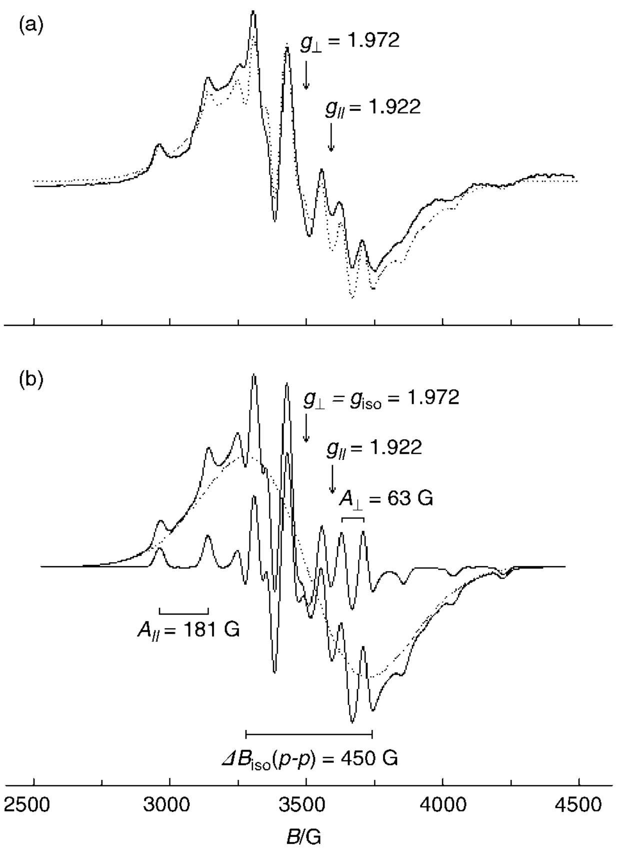

Fig. 5 (a) The experimental EPR spectrum of the powder V^{IV}-HPOM complex, at room temperature (normal line) and its simulated spectrum (dotted line). (b) The components of the simulated spectrum of the complex.

assigned to $V^{IV} \rightarrow Mo^{VI}, W^{VI}$ charge transfer transitions.[6,28] The spectrum is different from those of the one- and three-electron-reduced species previously reported,[6] but similar to those of two-electron-reduced species of similar compounds.[6,29] The appearance of the $Mo^V \longrightarrow W^{VI}$ transition suggests the presence of the two-electron-reduced species in the sample.

EPR spectroscopy

Some EPR parameters of the one-electron-reduced anion at room and liquid nitrogen temperatures have been reported by Cadot *et al.*[6] They obtained an axial spectrum typical for V^{IV}, with resolved hyperfine features.

The now-reported powder EPR spectrum of the complex at room temperature reveals the presence of a new reduced species, as suggested by the electronic studies above. This spectrum (Fig. 5a) is a superposition of one axial component with a resolved vanadium(IV) hyperfine structure and one isotropic and very broad component. The axial spectrum can be described by the spin Hamiltonian (eqn. 1) characteristic for a d^1 system with

$$H = \mu_B[g_\parallel B_z S_z + g_\perp(B_x S_x + B_y S_y)] + A_\parallel S_z I_z + A_\perp(S_x I_x + S_y I_y) \quad (1)$$

C_{4v} symmetry,[30] where $g_\parallel$, $g_\perp$ and $A_\parallel$, $A_\perp$ are the axial principal values of the gyromagnetic and hyperfine tensors respectively, μ_B is the Bohr magneton, B_x, B_y, B_z are the components of the applied magnetic field lengthways of the principal g axes, and S_x, S_y, S_z and I_x, I_y, I_z are the components of the electronic and nuclear spin angular momentum operators, respectively.

The axial spectrum exhibits eight hyperfine components, both in the perpendicular and in the parallel bands, due to hyperfine coupling of the unpaired electron with the nuclear spin ($I = 7/2$) of the ≈99.8% natural abundance ^{51}V isotope. The isotropic broad signal can be attributed either to another one-electron-reduced species[30,31] $[PMo^{VI}_2V^{IV}W_9O_{40}]^{5-}$ or to a monoprotonated two-electron reduced species[30] $[HPMo^V\text{-}Mo^{VI}V^{IV}W_9O_{40}]^{5-}$. In the first case the broadening of the EPR signal is due to delocalization of the vanadium(IV) unpaired electron towards its neighboring Mo^{VI},[32] whereas it is due to a merging effect of the vanadium(IV) ion signal and the signal of the Mo^V–Mo^{VI} delocalized mixed-valence pair in the last case.[33,34]

Table 1 EPR parameters at room temperature and in DMSO–water solution at $T = 100$ K

T/K	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$/G	$\lvert A_\perp \rvert$/G	β_2^2	K
293	1.922	1.972	181	63	0.87	0.78
100	1.929	1.990	179	65	0.83	0.84
100	1.918	2.000	187	80	0.74	1.06

The best fit of the EPR spectrum (Fig. 5b) was made considering the $g_\parallel = 1.922$, $g_\perp = 1.972$, $A_\parallel = 181$ G, $A_\perp = 63$ G and $\Delta B_\parallel(\text{p-p}) = 30$ G, $\Delta B_\perp(\text{p-p}) = 33$ G linewidths for the axial component, $g_{iso} = 1.972$, $\Delta B_{iso}(\text{p-p}) = 450$ G for the isotropic signal and Gaussian type line shapes. The two components contribute equally (50%) to the whole spectrum, suggesting that the one-electron and the monoprotonated two-electron reduced species appear in equal quantity in the sample. The principal axes of g and A tensors were presumed to be coincident for simulation of the axial spectrum, with the $g_\parallel$ direction parallel to the $V{=}O_d$ bond.

The covalence degree of the in-plane V–O $\pi(\beta_2^2)$ bonds was evaluated using the LCAO-MO approach for V^{IV} with antibonding $B_2(d_{xy})$ ground state, in a C_{4v} local symmetry,[26] where

$$\beta_2^2 = \tfrac{7}{6}\left[-\frac{A_\parallel - A_\perp}{P} + (g_\parallel - g_e) - \tfrac{5}{14}(g_\perp - g_e)\right] \quad (2)$$

$P = g_e\mu_B g_N\mu_N\langle r^{-3}\rangle = 0.0128\ \text{cm}^{-1}$ is the dipolar interaction term for the vanadyl ion and $g_e = 2.0023$ is the gyromagnetic factor of the free electron. We have estimated the Fermi contact term from $K = -(A_0/P) - (g_e - g_0)$, where $A_0 = (A_\parallel + 2A_\perp)/3$ and $g_0 = (g_\parallel + 2g_\perp)/2$. The not too high value of the β_2^2 coefficient confirms that the VO_6 and MoO_6 octahedra share a corner, as previous studies of heteropolyoxometalates with vanadyl ion have indicated.[6] The delocalization of the vanadium unpaired electron onto the molybdenum ions *via* O_b and O_c atoms is sustained by the low $K = 0.67$ Fermi contact term and the negative signs of $A_\parallel$ and $A_\perp$, the only situation which gives rise to acceptable values for the molecular orbital coefficients (Table 1).[30]

By freezing the DMSO–water solution of the sample at $T = 100$ K the isotropic component disappears (Fig. 6). The EPR spectrum obtained is axial with two sets of hyperfine lines for two non-equivalent $S = 1/2$ species (Table 1). One of these (1) has EPR parameters near to those of the powder axial species. For the assignment of the second species (2) the powder EPR spectrum at 100 K was recorded. This spectrum is nearly unchanged relative to the room temperature powder spectrum, which suggests that the hopping electron process is not the main cause of broadening of the isotropic signal, but rather the merging effect of the EPR signals for different paramagnetic centers in a two-electron-reduced species present in the powder sample.[33] Species (2) derives from the solid monoprotonated two-electron-reduced species, which becomes deprotonated and only one-electron-reduced in solution. In DMSO–water solution the Mo^V is reoxidized to Mo^{VI} by the oxygen from water. This explains the appearance of the second one-electron-reduced species. The values of these EPR parameters and those found from the powder EPR spectrum indicate distortion of the local symmetry around the vanadium ion in frozen solution.[30] The smaller value of the in-plane π-bonding coefficient β_2^2 for species (2) indicates greater delocalization of the unpaired

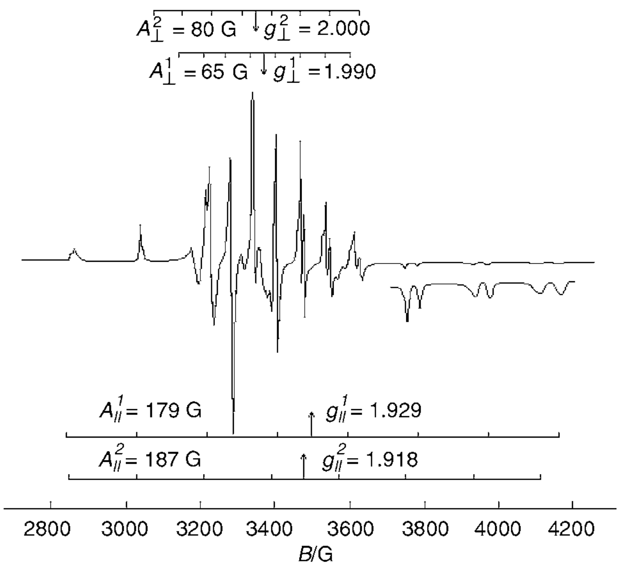

Fig. 6 The V^{IV}-HPOM EPR spectrum in frozen DMSO–water (T = 100 K).

electron from vanadium towards neighboring oxygen atoms and the presence of vanadium and molybdenum ions in close proximity. This shows that for species (2) the in-plane π bonding is stronger than for (1) (the $V–O_{b,c}$ in plane distances are shorter), but the axial vanadyl bond is weaker (the $V{=}O_d$ distance is longer). Therefore, the VO_6 octahedron of species (2) is more distorted than that of (1) because of the compression lengthways on the O_z axis. Species (2) can be a α type isomer as is (1), but with different V–O–Mo angles and bond lengths because of deprotonation,[30] or a β isomer obtained at low temperature in solution, with one of the MoW_2O_{13} units rotated by 60°.[35] In both cases the vanadium atom and at least one molybdenum atom are in close proximity because of the low $\beta_2{}^2$ value.

Magnetic susceptibility measurements

The sample obeys the Curie–Weiss law $\chi = \chi_0 + [C/(T - \theta)]$ within the high-temperature limit (94–260 K).[36] The fitting of the experimental data gives the following values: $\chi_0 = -1113 \times 10^{-6}$ emu mol^{-1}, $\mu_{eff} = 2.11\ \mu_B$ and $\theta = -59$ K. The high value of the diamagnetic correction χ_0 compared to those of other isostructural heteropolyoxometalates[37,38] arises from the presence of the monoprotonated two-electron-reduced species. It is well known that the excess of diamagnetism may be attributed to a ring current of the delocalized electrons, circulating in a loop under the influence of the imposed magnetic field.[36] For the studied sample, the electron of the Mo^V–Mo^{VI} mixed-valence pair is also delocalized onto the V^{IV} through the oxygen bonds, increasing the diamagnetism of the two-electron-reduced species.

This is also supported by its effective spin value estimated from the magnetic moment. The value of the effective magnetic moment can be expressed as a function of the magnetic moments of the one-electron (involving paramagnetic V^{IV}, μ_{1e}) and the monoprotonated two-electron (involving paramagnetic V^{IV} and Mo^V, μ_{2e}) reduced species,[39] eqn. (3) where f_{1e} and f_{2e} are

$$\mu_{eff} = (f_{1e}\mu_{1e}{}^2 + f_{2e}\mu_{2e}{}^2)^{1/2} \qquad (3)$$

the molar fractions of the reduced species and are both equal to 0.5, as obtained from the powder EPR spectrum. The values of the magnetic moments for the one-electron and two-electron-reduced species are given by: $\mu_{1e} = (g_\parallel + 2g_\perp)3\cdot\sqrt{S(S+1)}$ ($g_\parallel$ = 1.922, $g_\perp$ = 1.972, S = 1/2) and $\mu_{2e} = g_{iso}\sqrt{S'(S'+1)}$ (g_{iso} = 1.972, S' is the effective spin), respectively. By substituting these expressions in μ_{eff} we have obtained S' = 0.84. According to the general tendency of pairing of electrons in two-electron-reduced species,[34] this effective spin corresponds to the excited triplet of the antiferromagnetic coupled V^{IV}–Mo^V pair.[30] This is supported by the negative value of the Curie temperature.[40]

Conclusion

The IR investigations of $K_5[PMo_2VW_9O_{40}]\cdot 24H_2O$ indicate co-ordination of the vanadyl group in the monolacunary region of the α-$[PMo_2W_9O_{39}]^{7-}$ anion and the presence of different isomers in the sample. The vanadium(IV) ion is six-co-ordinated by oxygen atoms in a C_{4v} local environment and has a $^2B_2(d_{xy})$ ground state. The appearance of the intervalence charge transfer $Mo^V \rightarrow W^{VI}$ transition at ≈19220 cm^{-1} in the VIS spectrum suggests the presence of a monoprotonated two-electron-reduced species in the sample. The EPR spectra of the sample obtained at room temperature and at 100 K indicate the coexistence of one- and two-electron-reduced species in the same amount. The V^{IV} and the Mo^V–Mo^{VI} pair are antiferromagnetically coupled in the second species. In frozen DMSO–water solution the monoprotonated species become deprotonated.

Experimental

Physical measurements

Infrared spectra were recorded on a Carl Zeiss Jena model UR-20 spectrophotometer in the 4000–400 cm^{-1} range, using KBr discs, electronic spectra in aqueous solutions within a range of λ = 200–800 nm on a standard Specord UV-VIS spectrophotometer. The EPR spectra on powdered solids were obtained at room temperature and 100 K at *ca.* 9.6 GHz (X band) using a JEOL-JES-3B spectrometer. The spectrum of solution in DMSO–water was also recorded at 100 K using the same instrumentation. The magnetic susceptibility measurements were performed using a Faraday type balance in the temperature range 77–290 K.

Synthesis of $K_5[PMo_2VW_9O_{40}]\cdot 24H_2O$

The monovacant $K_7[PMo_2W_9O_{39}]\cdot 13H_2O$ heteropolyoxometalate was prepared according to the method of Contant and co-workers.[17] A solution of $VOSO_4$ (0.219 g, 1.34 mmol) in 10 ml distilled water was added to a solution of $K_7[PMo_2W_9O_{39}]\cdot 13H_2O$ (4.040 g, 1.34 mmol) in 50 ml acetate buffer solution (pH 4.7) at 60 °C, with vigorous stirring for 30 minutes. After cooling at room temperature, KCl (Sigma-Aldrich) solution was added to the blue heteropolyoxometalate complex solution. A dark blue precipitate was collected on a medium frit, dried under vacuum for 30 minutes, washed with saturated KCl solution and dried under vacuum again. The chemical analysis was carried out by atomic absorption methods after decomposition by boiling with 6 M NaOH solution. Yield: 3.08 g (72%) (Found: K, 6.15; Mo, 5.95; P, 0.95; V, 1.60; W, 51.85; H_2O, 13.48. Calc. for $H_{48}K_5Mo_2O_{64}PVW_9$: K, 6.12; Mo, 6.00; P, 0.97; V, 1.59; W, 51.77; H_2O, 13.51%).

Acknowledgements

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