

**TETRANUCLEAR Cu(II) CLUSTER ENCAPSULATED IN ONE ARSENIC(V)
HETEROPOLYOXOTUNGSTATE. SPECTROSCOPIC AND MAGNETIC
INVESTIGATION**

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Abstract

Na₁₀[Cu₄(H₂O)₂(AsW₉O₃₄)₂]-23H₂O heteropolyoxometalate was synthesized and investigated by elemental analyses, thermogravimetry, FT-IR, VIS and EPR spectroscopy and magnetic susceptibility techniques. Measurements performed in the present study were used to investigate changes of Keggin units, to evaluate the local symmetry around the Cu ions and to identify the nature of Cu-Cu interactions.

Results of FT-IR investigations showed that asymmetric stretching frequencies (ν_{asym}) corresponding to O connecting As and W atoms $\nu_{\text{asym}}(\text{W}-\text{O}_a)$ and to O connecting corner and edge-sharing octahedra $\nu_{\text{asym}}(\text{W}-\text{O}_{c,e}-\text{W})$ were shifted. $B_1(d_{x^2-y^2}) \rightarrow E(d_{xz,yz})$ and

$B_1(d_{x^2-y^2}) \rightarrow B_2(d_{xy})$ transitions in the VIS spectrum of the complex were broad. EPR parameters (g , D and E) were estimated using the Kambe model for a tetranuclear cluster of Cu(II) ions. These measurements were used to investigate the ground state (1,1,0) and the excited states (1,1,1) and (1,0,1) of the complex. Magnetic susceptibility data for temperatures ranging from 77 to 273 K were used to calculate the effective magnetic moment.

Spectroscopic investigations demonstrated that Cu(II) ions coordinate to AsW₉O₃₄ units, W–O_c–W tricentric bonds in the complex are not equivalent and Cu(II) ions form distorted O_h symmetry with CuO₆ and CuO₅O* local units. Antiferromagnetic coupling between Cu(II) ions was also identified by magnetic susceptibility measurements.

Key words: polyoxometalate, clusters, Cu, spectroscopy, magnetic susceptibility

Introduction

Sandwich-type heteropolyoxometalates (HPOM) in which four *d-electron* transition metal ions link two trivacant Keggin or Dawson-Wells fragments form tetranuclear clusters. Several studies^{1,2} reported that these clusters are characterized by high magnetic spin, having catalytic and antiviral activity. Quite a number of different heteroatoms and metal ions can be used to form tetranuclear clusters.³⁻⁶ Usually,

transition metal ions encapsulated in the heteropolyoxometalate compounds are coupled due to ferro- or antiferro- magnetic interactions.⁷⁻⁹

Different studies investigated the properties and structure of several heteropolyoxometalate complexes in the presence of Cu(II) transition metal ion. Gomez-Garcia et al.⁹ investigated the properties of the $\text{K}_8\text{Na}_2[\text{Cu}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 16\text{H}_2\text{O}$ and $\text{Na}_{16}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{P}_2\text{W}_{15}\text{O}_{56})_2] \cdot 44\text{H}_2\text{O}$ sandwich-type compounds with four Cu(II) ions and phosphorous as heteroatom, demonstrating that two trivacant Keggin and/or Dawson-Wells fragments encapsulate a centrosymmetric rhomb-like Cu_4O_{16} unit formed by four edge-sharing CuO_6 octahedra. It was also reported⁹ that two of the Cu(II) ions coordinate to water molecules in apical positions, while Cu(II) ions are antiferromagnetically coupled. The Kambe model for two exchange constants J' and J with $J'/J > 2$ was used in the above-mentioned study to describe the Cu_4 clusters. Bi et al.¹⁰ reported that distortion of Cu_4O_{16} cluster is smaller in the case of the Dawson-Wells structure $\text{Na}_{16}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{As}_2\text{W}_{15}\text{O}_{56})_2] \cdot 47\text{H}_2\text{O}$ compared to phosphorus species.¹⁰ Jahn-Teller distortions of the CuO_6 group were identified in a study investigating the structure of the $\text{K}_8\text{Na}_2[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 32\text{H}_2\text{O}$ complex.⁴

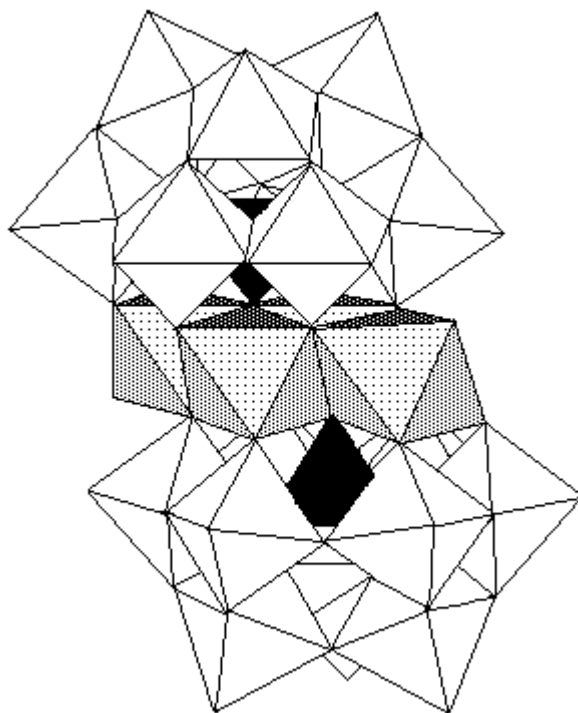


Figure 1. Polyhedral representation of Cu(II)–HPOM complex. Empty polyhedra represent WO_6 octahedra, black triangles represent AsO_4 tetrahedra and hatched polyhedra represent CuO_6 octahedra.

In the present study, FT-IR, VIS and EPR spectroscopy and magnetic susceptibility techniques were used to investigate the sandwich-type $\text{Na}_{10}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]\cdot 23\text{H}_2\text{O}$ heteropolyoxotungstate (Cu(II)–HPOM) (Figure 1). This complex derives from two $\text{AsW}_9\text{O}_{34}$ trilacunary Keggin fragments connected by a Cu_4O_{16} group of four coplanar CuO_6 octahedra sharing edges.³ Keggin units changes, local symmetry around the Cu ions and Cu-Cu interactions were determined and evaluated for the investigation of changes occurred in the complex due to the presence of Cu(II) ions. Coordination of Cu(II) ions to $\text{AsW}_9\text{O}_{34}$ units and distorted O_h symmetry formed by Cu(II) and CuO_6 and CuO_5O^* local units were demonstrated by spectroscopy. This study also demonstrates that coupling between Cu(II) ions is antiferromagnetic for the complex investigated by magnetic susceptibility techniques.

Results and discussion

Infrared data. Complex and $\text{Na}_8(\text{HAsW}_9\text{O}_{34})_2\cdot 11\text{H}_2\text{O}$ ligand FT-IR spectra were compared (Figure 2) to obtain information about coordination of Cu(II) cluster to trilacunary Keggin fragments in the sandwich-type heteropolyoxometalate.

All antisymmetric stretching frequencies characterizing bonds involving tungsten ions were shifted ($1\div 17\text{ cm}^{-1}$) in the complex spectrum with respect to their corresponding frequencies in the ligand spectrum (Table 1). The relative small shift of the $\nu_{\text{asym}}(\text{W}=\text{O}_t)$ vibration band from 943 cm^{-1} in the ligand spectrum to 954 cm^{-1} in the complex spectrum is due to the fact that the terminal O_d atoms at the heteropolyoxometalate surface are not involved in the co-ordination to Cu(II) ions.⁴ The vibration frequencies of the $\text{As}-\text{O}_a$ bonds are not observed, being masked by the $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ bands.⁴

FT-IR spectrum of the ligand presents two vibration bands (at 877 and 888 cm^{-1}), corresponding to tricentric $\text{W}-\text{O}_e-\text{W}$ bonds of the edge-sharing WO_6 octahedra. Vibration bands at 877 and 888 cm^{-1} suggest presence of two nonequivalent tricentric $\text{W}-\text{O}_e-\text{W}$ bonds. A single band, at 883 cm^{-1} , is present in the complex FT-IR spectrum.^{11,12} Tricentric $\text{W}-\text{O}_c-\text{W}$ bonds in the corner-sharing WO_6 octahedra region, changes into one vibration (at 839 cm^{-1}) in the ligand spectrum and into two vibrations (at 822 and 848 cm^{-1}) in the complex spectrum. Presence of broad bands instead of individual components is typical for HPOM with transitional metals. However,

behaviour of the $\nu_{\text{asym}}(\text{W}-\text{O}_c-\text{W})$ bands in the complex spectrum indicates the nonequivalence of $\text{W}-\text{O}_c-\text{W}$ bonds, linking octahedra from the equatorial and polar regions of the trilacunary Keggin fragments.¹¹

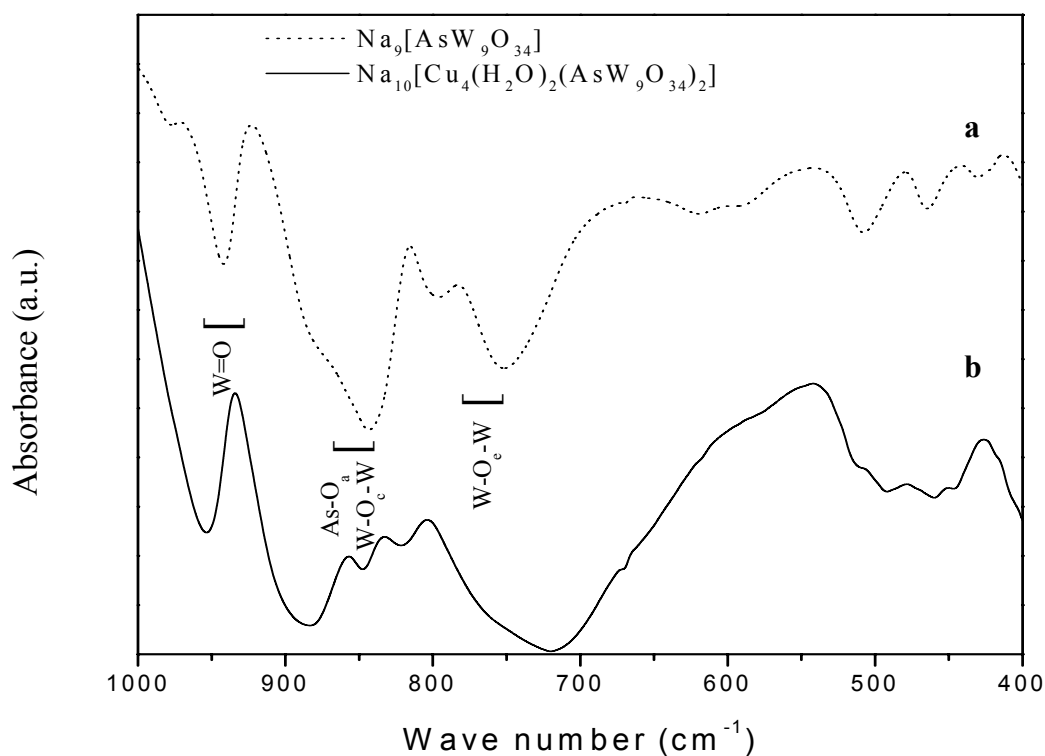


Figure 2. FT-IR spectra. FT-IR spectrum of the ligand is presented in Figure 2a, while in Figure 2b is presented the FT-IR spectrum of the Cu(II)–HPOM complex.

$\text{W}-\text{O}_a$ bonds, which connect WO_6 octahedra to AsO_4 units, have two vibrations, both in the complex and ligand spectrum. One of the frequencies, characterizing these two vibrations, is shifted 16 cm^{-1} , towards higher frequencies, in the complex FT-IR spectrum. This is due to coordination of Cu_4 cluster in the lacunary region of the ligands.¹³

The water molecules present a very broad band with two shoulders, characterizing the stretching vibrations $\nu_{\text{asym}}(\text{OH})$ (Figure 2, Table 1). This indicates coexistence of crystallization and coordinated water molecules.¹⁴ The centre of the band is significantly shifted (140 cm^{-1}) towards higher wavenumbers, as shown in the FT-IR spectrum of the

complex compared to the ligand spectrum (Figure 2). Water molecules bounded directly to two Cu(II) ions produce this frequency shift.

Table 1. FT-IR data (cm^{-1}) for the ligand and Cu(II)–HPOM complex.

Band ^a	Ligand	Complex
$\nu_{\text{asym}}(\text{W}-\text{O}_a)$	721 vs,sp ^b	720 vs,br
	746 vs,sh	762 vs,sh
$\nu_{\text{asym}}(\text{W}-\text{O}_c-\text{W})$	839 s,sh	822 s,sp
		848 s,sp
$\nu_{\text{asym}}(\text{W}-\text{O}_e-\text{W})$	877 s,sp	883 vs,sp
	888 s,sh	
$\nu_{\text{asym}}(\text{W}=\text{O}_t)$	943 s,sp	954 s,sp
$\delta(\text{H}_2\text{O})$	1616 w,br	1624 w,br
$\nu_{\text{asym}}(\text{OH})$	3505 m,sh	3700 m,sh
	3420 s,vbr	3560 s,vbr
$\nu_{\text{sym}}(\text{OH})$	3250 m,sh	3330 m,sh

^a O_a is the oxygen which links the As and W atoms; $\text{O}_{c,e}$ connect corner and edge-sharing octahedra; O_t represents terminal oxygen. ^b w–weak, m–medium, s–strong, sh–shoulder, br–broad, sp–sharp, vs–very strong, vbr–very broad.

Electronic spectroscopy. The visible region of the electronic spectrum of the Cu heteropolyoxometalate shows a very broad band presenting a shoulder (Figure 3). Two components, centred at 11588 cm^{-1} and 10026 cm^{-1} , were obtained by Gaussian deconvolution of the spectrum. These components can be assigned to $\text{B}_1(\text{d}_{x^2-y^2}) \rightarrow \text{E}(\text{d}_{xz,yz})$ and $\text{B}_1(\text{d}_{x^2-y^2}) \rightarrow \text{B}_2(\text{d}_{xy})$ transitions of Cu ions having octahedral distorted symmetry. Previous studies^{15,16} reported Cu_4O_{16} clusters encapsulated in heteropolyoxometalates, the local units being CuO_6 and CuO_5O^* for two pairs of opposite Cu(II) ions.

EPR spectroscopy. Complex EPR spectra recorded in the X band at room and liquid nitrogen temperatures (Figure 4) can be interpreted by taking into account the geometry of Cu(II) cluster. According to VIS investigations, the centrosymmetric rhomb-like structure of the tetrameric cluster facilitates overlapping of the ground state orbitals $\text{d}_{x^2-y^2}$ of the Cu(II) ions.

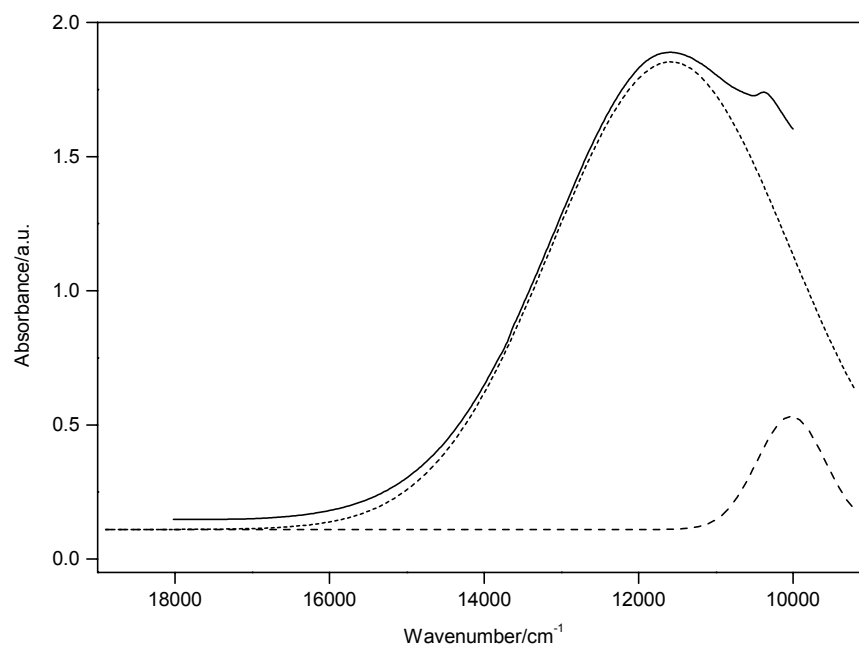


Figure 3. Electronic spectrum and its Gaussian deconvolution. The electronic spectrum of the Cu(II)–HPOM complex in the visible range is presented with solid line and its Gaussian components obtained by deconvolution are presented with dashed lines.

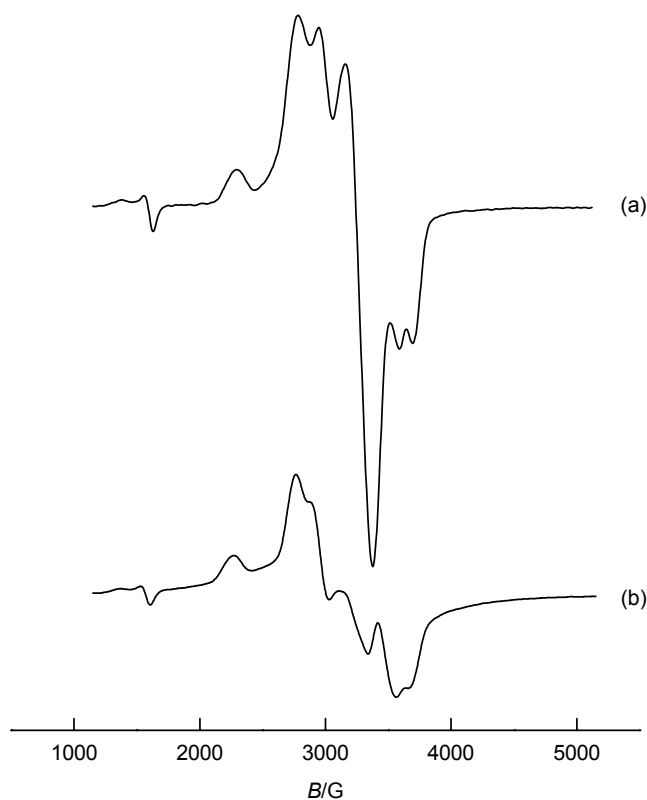


Figure 4. EPR spectra. Powder EPR spectrum of the Cu(II)–HPOM complex recorded at $T = 80$ K is presented in Figure 4a and that recorded at $T = 293$ K is presented in Figure 4b. Both EPR spectra in Figure 4 were recorded in the X band.

EPR spectra were interpreted in terms of the antiferromagnetic coupling between the Cu(II) ions.⁹ The signal at half-field (≈ 1570 G) proves the presence of exchange coupled Cu(II) ions and it is assigned to $\Delta M_S = \pm 2$ transitions.¹⁷ The other signals, present in the spectra, are typical for one spin state ($S = 1$). These signals are due to isotropic antiferromagnetic interactions between S_1 , S_2 , S_3 and S_4 electronic spin angular momentum operators characterizing the Cu(II) ions.

Behavior of the cluster, according to its geometry (Figure 5), can be described by the J and J' exchange constants.^{7,18,19} Based on the Kambe model,²⁰ the energies of the states are:

$$E(S, S_{13}, S_{24}) = -J[S(S+1) - S_{13}(S_{13}+1) - S_{24}(S_{24}+1)] - J'[S_{24}(S_{24}+1) - 3/2] \quad (1)$$

S_{13} , S_{24} and S represent the quantum spin numbers corresponding to the electronic spin angular momentum operators ($S_{13} = S_1 + S_3$, $S_{24} = S_2 + S_4$ and $S = S_{13} + S_{24}$).

The nature of the ground state of the cluster depends on the J'/J ratio.⁹ If $J'/J < 1$, the ground state is (0,1,1) followed by the excited (1,1,1), (1,1,0), (0,0,0), (1,0,1) and (2,1,1) states. For $1 < J'/J < 2$, the order of the energy levels is: (0,1,1), (1,1,0), (0,0,0), (1,1,1), (1,0,1) and (2,1,1) and for $J'/J > 2$, this order becomes: (1,1,0), (0,0,0), (0,1,1), (1,1,1), (1,0,1) and (2,1,1).⁹ EPR measurements performed in the present study were based on calculation of the EPR parameters and estimation of the J'/J ratio.

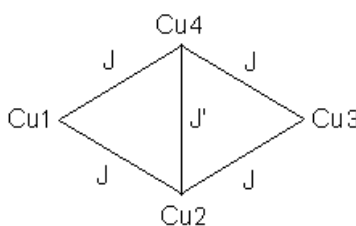


Figure 5. Representation of exchange pathways for the Cu_4 cluster. Cu1 and Cu3 coordinate in apical positions to water molecules.

EPR spectrum of the complex, recorded at a temperature (T) of 293 K, was interpreted²¹ using a spin Hamiltonian comprising the Zeeman and zero field splitting terms:

$$H = \mu_B B g S + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (2)$$

Based on the positions of the signals, this spectrum was simulated using the g , axial (D) and rhombic (E) zero field splitting parameters calculated and a Lorentzian line shape with $\Delta B_{x,y} = 100$ G and $\Delta B_z = 145$ G line widths. The values of the EPR parameters used to simulate this spectrum were: $g_x = 2.114$, $g_y = 2.030$, $g_z = 2.292$, $D = 0.029$ cm⁻¹, $E = 0.0049$ cm⁻¹ (Figure 6d). Position and shape of the signals on the spectrum were reproduced correctly, except for the signal at ≈ 3235 G. Any attempt to obtain this signal in the simulated spectrum by varying EPR parameters failed. This suggested that this signal corresponds to a different spin state.

Geometry of Cu₄O₁₆ cluster is slowly dependent on the type of the Keggin fragments (e.g. type of heteroatoms) encapsulating the cluster. EPR parameters characterizing this different spin state were searched around the values already reported⁹ for phosphorus based heteropolyanions. EPR behaviour of this state was described using the rhombic g and D tensors with the following components: $g_x = 2.055$, $g_y = 2.205$, $g_z = 2.330$ and $D = 0.068$ cm⁻¹, $E = 0.0008$ cm⁻¹ (Figure 6c).

Intensity of the signal at ≈ 3235 G decreases strongly when the temperature is varied from 80 to 293 K compared to the other signals in the spectrum. This indicates that the (c) component in the spectrum corresponds to a lower spin state when compared to the (d) component. However, both states are characterized by the same spin ($S = 1$). To reproduce the relative intensities of the signals in the experimental spectrum obtained at 293 K, the two components (c) and (d) were summed up in the 7:13 ratio. According to the Boltzmann distribution,²² the EPR component corresponding to the excited state cannot have a higher contribution to the entire spectrum. This indicates that (d) spectrum originates in, at least, two excited states ($S = 1$).

Area of the integrated spectrum of the complex varies with the temperature. This area (I) decreases with temperature. In the case of two spectra of the complex, one recorded at 293 K (I_{293}), and the other one recorded at 80 K (I_{80}), this area decreases with an I_{80}/I_{293} ratio of approximately 0.83. This indicates that the cluster presents an EPR inactive spin state ($S = 0$) populated below 80 K, spin state situated between the ground state and the first excited state ($S = 1$). At higher temperatures, the higher excited states ($S = 1$) are populated to the prejudice of the lower excited state ($S = 0$) and hence contribute to the *whole* EPR spectrum, increasing its integrated intensity. This is in accordance with the order of the energy levels⁹ for $J'/J > 2$.

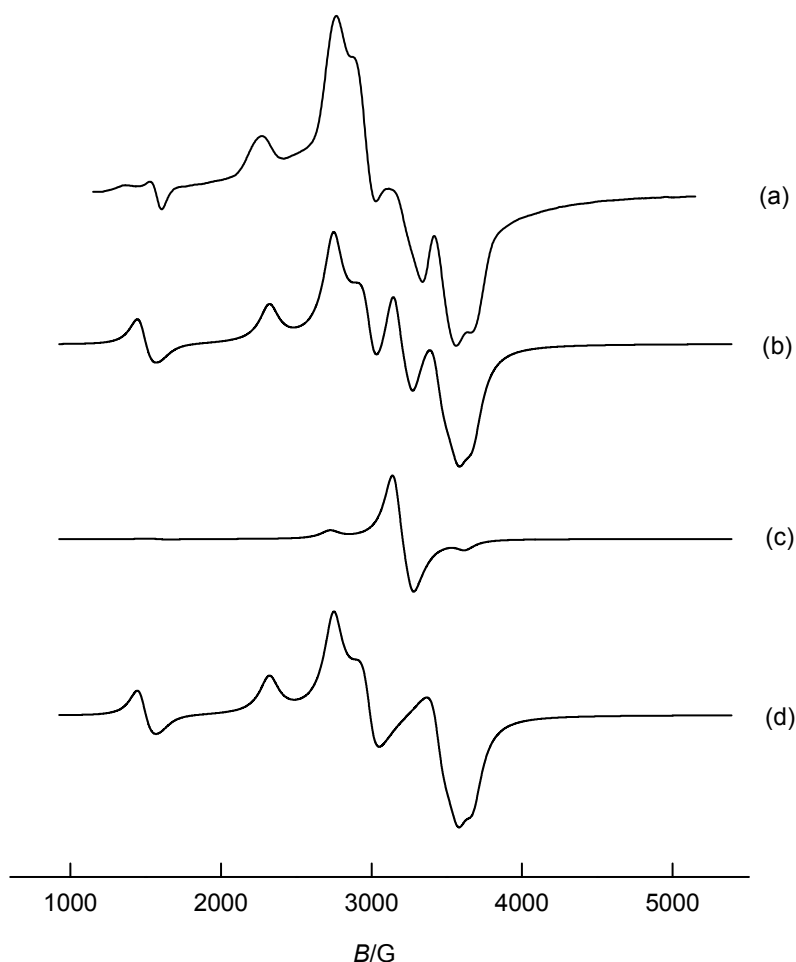


Figure 6. Experimental and simulated EPR spectra. Experimental EPR spectrum of the Cu(II)–HPOM complex recorded at $T = 293$ K is shown in Figure 6a. The simulated spectrum in Figure 6b represents the sum of the components presented in Figure 6c and 6d.

Magnetic susceptibility measurements. Temperature dependence of the reciprocal molar susceptibility $1/\chi_m$ for the Cu(II)–HPOM complex is presented in Figure 7 for temperatures ranging from 77 to 273 K.

Diamagnetic contribution corrections of the magnetic susceptibility data were performed using the Pascal values. It was assumed that a Curie-Weiss behaviour of the susceptibility data¹⁷ intermediates between the effective moments of the spin states characterized by $S = 1$ and $S = 2$. This assumption was used to calculate the effective magnetic moment ($\mu_{\text{eff}} = 4.57 \mu_B$). The Curie-Weiss behaviour and the negative value of the Curie-Weiss temperature ($\theta = -94$ K) are in good agreement with the presence of antiferromagnetic coupled Cu(II) ions and with the energy levels diagram scheme determined from the EPR spectrum.

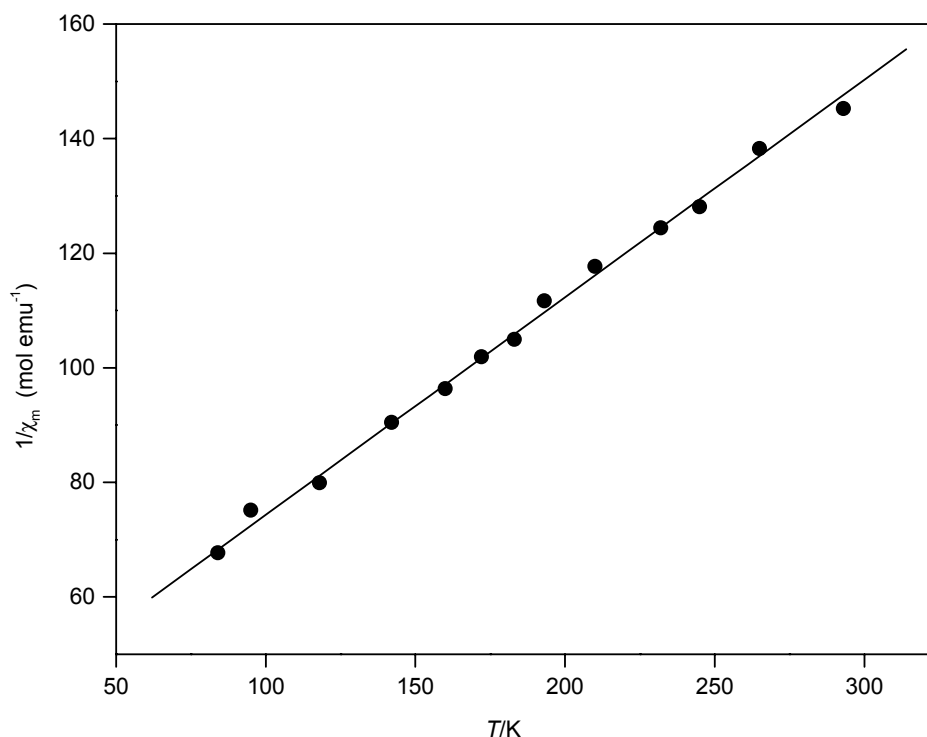


Figure 7. Variation of reciprocal molar susceptibility of the Cu(II)-HPOM complex with respect to temperature. Solid line represents the best fit of the experimental data with a Curie-Weiss behaviour.

Conclusions

To characterize the $\text{Na}_{10}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 23\text{H}_2\text{O}$ complex, a sandwich-type heteropolyoxometalate with transition metal cluster, spectroscopic (FT-IR, VIS, EPR) and magnetic susceptibility techniques were used.

The shift of the $\nu_{\text{asym}}(\text{W}-\text{O}_{\text{c,e}}-\text{W})$ and $\nu_{\text{asym}}(\text{W}-\text{O}_{\text{a}})$ stretching frequencies in the FT-IR spectrum of the complex compared to the ligand spectrum suggests coordination of Cu(II) ions to the lacunary region of the Keggin units. The strong shift of the $\nu_{\text{asym}}(\text{OH})$ band (140 cm^{-1}) in the complex FT-IR spectrum proves the presence of water molecules coordinated directly to two Cu(II) ions. Each metal ion is surrounded by six oxygen atoms in a distorted O_h symmetry and has a $d_{x^2-y^2}$ orbital in ground state.

Zero field splitting parameters characterizing the ground (1,1,0) and the excited (1,1,1) and (1,0,1) states and the relationship between the two exchange parameters J' and J were estimated by EPR.

The magnetic susceptibility measurements performed for temperatures ranging from 77 to 273 K indicated the presence of antiferromagnetically coupled Cu(II) ions.

Experimental

Measurements. Tungsten, copper, sodium and bismuth were identified by atomic absorption. The water content was determined by thermal analysis performed using a METTLER-TGA/SDTA 851°STAR[®]Software derivatograph. FT-IR spectra were recorded on a Jasco FT/IR 610 spectrophotometer in the 4000–400 cm^{-1} range, using KBr pellets. Electronic spectroscopy studies in the VIS range were performed for the sample dissolved in aqueous solutions, using an ATI Unicam-UV-Visible spectrophotometer with Vision Software V 3.20. EPR spectra on powdered solids have been recorded at room temperature and 80 K at ca. 9.6 GHz (X-band) using a Bruker ESP 380 spectrometer. The magnetic susceptibility measurements were performed using a Faraday type balance for temperatures ranging from 77 to 273 K.

Synthesis of the $\text{Na}_8[\text{HAsW}_9\text{O}_{34}]\cdot 11 \text{ H}_2\text{O}$ ligand. 69.2 g (200 mmol) $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ was dissolved in 85 mL of distilled water by stirring. To this solution, 7.3 g (22 mmol) of $\text{Na}_3\text{AsO}_4\cdot 7\text{H}_2\text{O}$, followed by 27 mL of glacial acetic acid (pH adjusted to 7.5), were added and this mixture was refluxed for 2 h. The resulting hot solution was filtered by gravity filtration through paper. The mixture was then cooled down to the room temperature for 2 days, a white precipitate being formed. The solid was collected on a sintered-glass frit and dried under aspiration. Yield: 47.85 g (81%). Anal. Calcd for $\text{Na}_8\text{AsW}_9\text{O}_{45}\text{H}_{23}$: Na 7.68, W 58.65, As 3.00, H_2O 7.92. Found: Na 7.73, W 58.77, As 3.07, H_2O 7.84.

Synthesis of the $\text{Na}_{10}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]\cdot 23 \text{ H}_2\text{O}$ complex. 5.3 g (2 mmol) $\text{Na}_8[\text{HAsW}_9\text{O}_{34}]\cdot 11\text{H}_2\text{O}$ was dissolved in 15 mL distilled water at 70 °C. After complete dissolution of salt, 0.8 g (4 mmol) $\text{Cu}(\text{CH}_3\text{CO}_2)_2\cdot \text{H}_2\text{O}$ was slowly added to 10 mL distilled water while stirring. This mixture was heated to 70 °C for 15 min. The resulting pale green solution (pH = 6.8) was filtered through a sintered-glass frit and it was allowed to cool down to room temperature. Three days later, the pale green powder was obtained by filtration and washed with NaCl 2 M, ethanol and ether. The powder was allowed to crystallize after dissolution in hot water (400 mg/5mL). After six days, pale green microcrystals were collected. Yield: 3.91 g (71%). Anal. Calcd for $\text{Na}_{10}\text{As}_2\text{W}_{18}\text{Cu}_4\text{O}_{116}\text{H}_{50}$: Na 4.19, Cu 4.64, W 60.37, As 2.73, H_2O 8.19. Found: Na 4.12, Cu 4.69, W 60.25, As 2.67, H_2O 8.30.

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Povzetek

Pripravili smo heteropolioksometalat $\text{Na}_{10}[\text{Cu}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]\cdot 23\text{H}_2\text{O}$ in ga karakterizirali z elementno analizo, termogravimetrijo, FT-IR, VIS in EPR spektroskopijo in merjenjem magnetne susceptibilnosti. FT-IR spektri imajo asimetrično nihanje kisikovega mosta med As in W atomi in med dvema W atomoma. Bakrovi(II) ioni so koordinirani na $\text{AsW}_9\text{O}_{34}$ enote, $\text{W}-\text{O}_c-\text{W}$ niso ekvivalentne. Geometrija Cu(II) ionov je popačen oktaeder. Meritve magnetne susceptibilnosti kažejo na antiferomagnetno sklopitev med Cu(II) ioni.