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Spectroscopic investigation of tetranuclear clusters encapsulated in some polyoxometalate complexes

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The sandwich-type $Na_6[Fe_4(H_2O)_2(AsW_9O_{34})_2]\cdot 20H_2O$ (**1**) and $Na_{10}[Co_4(H_2O)_2(AsW_9O_{34})_2]\cdot 25H_2O$ (**2**) complexes were prepared and investigated through spectroscopic (FT–IR, UV–VIS, ESR) methods and magnetic susceptibility measurements. The stretching vibration ν_{as}(W–O_c–W) band is shifted in the IR spectra with 13 cm^{-1} and 12 cm^{-1} for (**1**) and (**2**) respectively, towards higher energies comparative to the $Na_9[AsW_9O_{34}]\cdot 11H_2O$ ligand spectrum due to the involvement of the oxygen atoms at the coordination metallic ions. The opposite shift of ν_{as}(W–O_e–W) and ν_{as}(W–O_c–W) vibrations bands shows the coordination of each metallic ion at oxygen atoms from the belt region. The UV electronic spectra of the sandwich-type complex and of the ligand contain two bands characteristic for the ligand to metal change transfer in the heteropolyoxometalates frame. The more intense band corresponding to the $p_\pi(O_t) \rightarrow d_{\pi^*}(W)$ transitions is centred at 49100 cm^{-1} (**L**), 49150 cm^{-1} (**1**) and 49300 cm^{-1} (**2**). This is in agreement with the coordination of the Co (II) and Fe (III) ions in the lacunary region of the ligand and not to the terminal oxygen atoms. The Gaussian deconvolution of the visible spectrum for complex (**1**) in aqueous solution shows the presence of a band centered at 29340 cm^{-1} assigned to the $^6A_{1g}(S) \rightarrow {}^4E_g(D)$ transition for the Fe (III) ions in O_h distorted symmetry. Information about the local environment of Co (II) ions have been obtained by means of d–d transitions from the visible electronic spectrum performed in aqueous solution. Two bands of the Co complexes, at 16000 cm^{-1} and 19400 cm^{-1} are assigned to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (υ_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (υ_3) transitions. The ESR spectrum of complex (1) shows the antiferromagnetic coupling of Fe (III) ions and the octahedral local symmetry around the metallic ions. The ESR spectrum of the Co complex obtained at T= 80 K contain a single very large signal centered at 3250 G. The linewidth of the signal indicate the presence of the coupling between the chrome ions and the almost isotropic shape of this is due to a higher symmetry (O_h) around the Co (II) ions. In the temperature range 77 – 290 K the molar magnetic susceptibility follows a Curie – Weiss behavior. The obtained effective magnetic moment are μ_{eff} = 9.51 μ_B for (**1**) and μ_{eff} =7.88 μ_B for (**2**), the value of Curie constant being θ = –15.1 K (**1**) respectively –7.0 K (**2**).

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1. Introduction

The remarkable and unusual chemical properties of the polyoxometalates complexes (high charges and ionic masses, electron exchange characteristics, oligomeric cluster structures, high solubility, etc.) lead to impressive uses in material research, analysis, chemical catalysis and medicine [1-4]. During the last years, sandwich-type heteropolyoxometalates encapsulating clusters of early transition metals have received much attention both from applied and fundamental research perspectives. The great advantage of these complexes is the possibility of varying either the type of the metallic cluster (its structural topology and the nature of the transition metals) or the heteroatom [5,6]. The metallic cluster is usually encapsulated between two Keggin or Dawson – Wells trivacant fragments [7-9].

Heteroatoms P (V), As (V), Si (IV) and Ge (IV) are tetrahedral coordinated by oxygen atoms in these fragments and the fourth oxygen acting toward the lacunary region is involved in coordination to the metallic cluster.

In this paper we report the synthesis and physical properties of sandwich-type compounds of composition $Na_6[Fe_4(H_2O)_2(AsW_9O_{34})_2]\cdot 20H_2O$ (**1**) and $Na_6[Co_4(H_2O)_2(AsW_9O_{34})_2]\cdot 25H_2O$ (**2**) (Fig. 1) complexes. In order to obtain information about the co-ordination and the local symmetry of the metallic ions FT–IR and UV–VIS measurements were performed. Precious information on the spin state of the metallic cluster and the type of metal-metal coupling was provided by the ESR and magnetic susceptibility measurements.

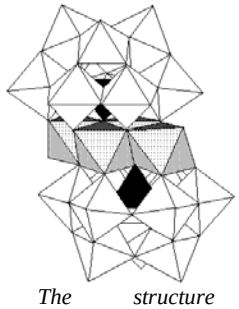

Fig. 1. The structure of the $Na_6[M^{n+}{}_4(H_2O)_2(AsW_9O_{34})_2]^{(18-4n)-}$ heteropolyanion, M=Fe (III), Co (II) (Empty polyhedra are WO_6 octahedra, the black triangles are AsO_4 tetrahedra and the shaded units are MO_6 octahedra).

2. Experimental section

All chemicals were of reagent grade and used as received. $Na_9[AsW_9O_{34}]\cdot 11H_2O$ have been synthesized as previously described. For both complexes, the total number of water molecules has been checked by TG studies.

2.1 Synthesis of $Na_6[Fe_4(H_2O)_2(AsW_9O_{34})_2]\cdot 20H_2O$ (1)

5.36 g (2 mmol) $Na_9[AsW_9O_{34}]\cdot 11H_2O$ was dissolved in 15 mL of distilled water at 70 ^{0}C. After complete dissolution of the salt, 1,60 g (4 mmol) of $Fe(NO_3)_3\cdot 9H_2O$ in 10 ml of distilled water was slowely added with sirring. The mixture was heated to 70 °C for 15 min. The resulting yellow-orange solution (pH = 6.5) was filtered through a sintered-glass frit and allowed to cool at room temperature. After ten days yellow-orange poweder was obtained by filtration and washed with NaCl 2 M, ethanol and ether. The powder was allowed to crystallize after dissolution in hot water (450 mg/5mL). After ten days, yellow-orange microcrystals were collected. Yield: 3,63 g (62%).

2.2 Synthesis of $Na_{10}[Co_4(H_2O)_2(AsW_9O_{34})_2]\cdot 25H_2O$ (2)

5.36 g (2 mmol) $Na_9[AsW_9O_{34}]\cdot 11H_2O$ was dissolved in 15 mL of distilled water at 70 ^{0}C. After complete dissolution of the salt, 1,16 g (4 mmol) of $Co(NO_3)_2\cdot 6H_2O$ in 10 ml of distilled water was slowely added with sirring. The mixture was heated to 70 °C for 15 min. The resulting pink solution (pH = 6.7) was filtered through a sintered-glass frit and allowed to cool at room temperature. After eight days pink poweder was obtained by filtration and washed with NaCl 2 M, ethanol and ether. The powder was allowed to crystallize after dissolution in hot water (550 mg/5mL). After few days, pink microcrystals were collected. Yield: 4.28 g (72%).

Physical-chemical measurements

FT-IR spectra were recorded on a Jasco FT/IR 610 spectrophotometer in the 4000–400 cm^{-1} range, using KBr pellets.

Electronic spectra in the visible range were performed in aqueous solutions on an ATI Unicam-UV-Visible spectrophotometer with Vision Software V 3.20.

EPR spectra on powdered solids were recorded at room (9.617 GHz) and 80 K (9.699 GHz) temperatures in the X-band using a Bruker ESP 380 spectrometer. All g values have been estimated with a $\pm$ 0.002 precision.

The magnetic susceptibility measurements were made using a Faraday type balance in the temperature range 77-290 K.

3. Results and discussion

3.1 FT-IR spectra

Information about the coordination mode of the Fe (III) and Co (II) ions to the trivacant Keggin fragments have been obtained by comparing the FT-IR spectra of the metallic complexes (**1**) and (**2**) with those of the $Na_9[AsW_9O_{34}]\cdot 11H_2O$ ligand.

The positions of the bands, their shape and intensity for the complexes and for the ligand differ in the 400–1000 cm^{-1} region (Fig. 2). Table 1 present some selected vibration bands for the ligand and for the synthesized compounds.

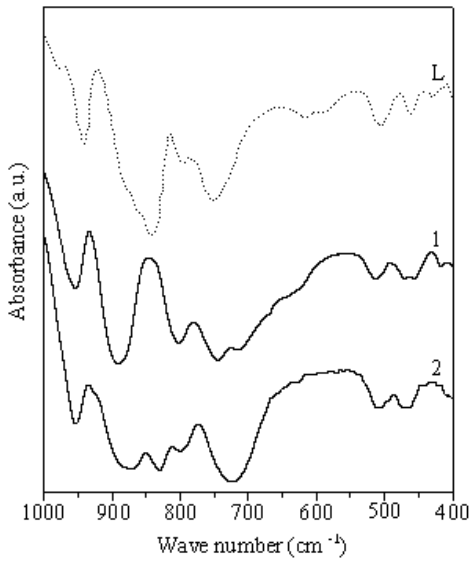

*Fig. 2. FT-IR spectra of the ligand (**L**) and Fe (III) (**1**) and Co (II) (**2**) complexes.*

The band due to the stretching frequency of the $\upsilon_{as}(W–O_t)$ bond is shifted toward higher frequencies with 6 cm^{-1} (**1**) and 8 cm^{-1} (**2**) which indicates the non-participation of the terminal atoms of oxygen to the coordination at metallic ions, as well as the stability of the polyoxowolframic trilacunar fragments.

The bands due to the $\upsilon_{as}(As–O_a)$ and $\upsilon_{as}(W–O_c–W)$ stretching vibrations are superposed and are shifted with 13 cm^{-1} for the complex (**1**) and with 12 cm^{-1} for (**2**) towards higher frequencies given the ligand [10,11].

In the Fe complex, the band $\upsilon_{as}(W–O_e–W)$ due to the stretching vibration of the tricentric bonds is split into two components both for the complex and ligand. The first two bands are insignificant shift with 7 cm^{-1}comparatively with the ligand and the third band is shift with 32 cm^{-1} towards lower energies as a consequence of the participation of oxygen O_e atoms at the coordination of Fe (III) ions [12].

*Table 1. FT-IR data (cm^{-1}) for the ligand (**L**), Fe (III) (**1**) and Co (II) (**2**) complexes [a].*

Bands	**L**	**1**	**2**
ν_{as} (W=O_t)	979 sh 945 s,sp	956 s	954s
ν_{as}(As-O_a)+ν_{as}(W-$O_{c,e}$-W)	878 vs,sh	892 vs,vb	890 s,sh 775 s,sh
ν_{as} (W-$O_{c,e}$-W)	843 vs	840 sh,b	830vs,sp
ν_s (W-O_e-W)	795 s 752 s	802 s 745 vs	799s 724vs,vb
ν_s(W-O_b-W)		720 s	724vs,vb
δ(W-$O_{c,e}$-W)	508 m	515 m	510 w 505 m
ν_s(As-O_a)	463 m	472 m 459 m	465 m 455 m

[a] *w, weak; m, medium; s, strong; ws, very strong; sh, shoulder; b, broad; sp, sharp O_a is the oxygen which links the As and W atoms, $O_{c,e}$ connect corner and edge-sharing octahedra, respectively, O_t is a terminal oxygen*

3.2 Electronic spectroscopy

The UV electronic spectra of the sandwich-type complex and of the ligand contain two bands characteristic for the ligand to metal change transfer in the heteropolyoxometalates frame. The more intense band corresponding to the $p_\pi(O_t) \rightarrow d_{\pi^*}(W)$ transitions is centred at 49100 cm^{-1} for (**L**), 49150 cm^{-1} for (**1**) and 49300 cm^{-1} for (**2**). This is in agreement with the coordination of the Co (II) and Fe (III) ions in the lacunary region of the ligand and not to the terminal oxygen atoms. The broader band centred at 39732 cm^{-1} in the ligand spectrum belongs to the $p_\pi(O_{c,e}) \rightarrow d_{\pi^*}(W)$ change transfer transition in the tricentric bonds. This absorption band appears at 38000 cm^{-1} and 39400 cm^{-1} in the UV spectra of the Fe (III) and respectively Co (II) complexes (Fig. 3).

The absorption band due to tricentric W-$O_{c,e}$-W bonds lead two shoulders at 40000 cm^{-1} and 36014 cm^{-1} in the UV spectrum of the Fe (III) complex. This splitting suggests the lower of the symmetry for the polyoxowolframic fragments and the appearance of the distortion in the complexes.

Three bands appear in the visible electronic spectrum in aqueous solution for the Co (II) complex at 8100 cm^{-1}, 16000 cm^{-1} and 19400 cm^{-1} which are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ [13] (Fig. 4).

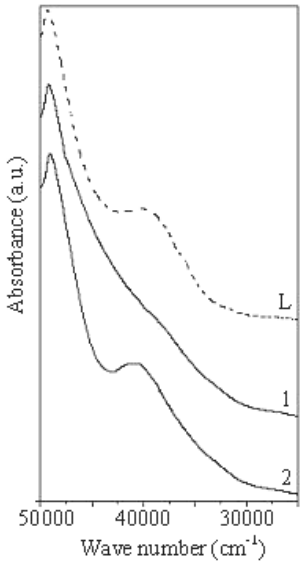

*Fig. 3. The UV spectra of the ligand (**L**) and complexes.*

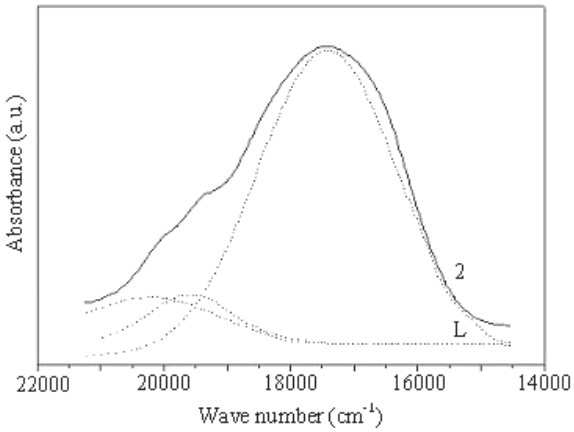

Fig. 4. Visible spectrum of the Co (II) complex (solid line) and the Gaussian component (dashed line).

Electronic spectrum of the Fe (III) - complex obtained in the visible range contains one absorption band up to 30000 cm^{-1} for the Fe (III) $\rightarrow$ O charge transfer transition. The Gaussian deconvolution of the spectrum shows the presence of a band centered at 29340 cm^{-1}. Taking into account the geometry of the complex similar to that of other sandwich-type HPOM with four 3d transition ions, this band was assigned to the $^6A_{1g}(S) \rightarrow {}^4E_g(D)$ transition of the Fe (III) ions in O_h distorted symmetry.

3.3 ESR spectra

The ESR spectrum of the complex (1) obtained at T= 80 K contains an intense signal at g ≈ 4.3 with indicate that at this temperature the complex is characterized by one S ≥ 5/2 spin state [14]. The signals from ≈ 295 G, 790

G, 950 G are due to the states state resulting by the coupling of the Fe (III) ions (Fig. 5).

The polycrystalline ESR spectrum of the complex (**2**) obtained at T= 80 K contain a single very large ($\Delta B(p\text{-}p) \approx$ 2100 G) pseudo-isotropic signal centered at B ≈ 3250 G. The linewidth of the signal indicate the presence of the coupling between the Co (II) ions and the almost isotropic shape of this is due to a higher symmetry around the metallic ions. The shape of this signal is not modified at T= 293 K. By raising the temperature, the linewidth of signal decreases, witch indicates the presence of small Co (II) – Co (II) superexchange interactions [14-16].

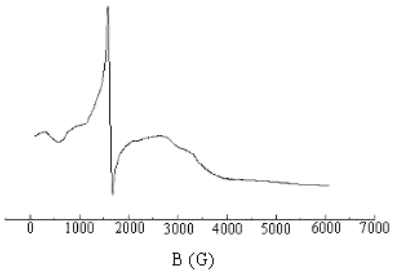

Fig. 5. The ESR spectrum of the $a_6[Fe_4(H_2O)(AsW_9O_{34})_2]\cdot 20H_2O$ complex at T = 80 K.

3.4 Magnetic susceptibility measurements

Temperature dependence of the reciprocal molar susceptibility $1/\chi_m$ for the complex (**2**) is presented in Fig. 6 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 behavior of the susceptibility data intermediates between the effective moments of the spin state characterized by S = 4, S = 5 for (**1**) and S =3, S = 4 for (**2**). This assumption was used to calculate the effective magnetic moment μ_{eff} = 9.51 for (**1**) and μ_{eff} =7.88 μ_B for (**2**)).

The Curie-Weiss behavior and the negative value of the Curie-Weiss temperature (θ = –15.1 K respectively – 7.0 K) are in good agreement with the presence of antiferromagnetic coupled Fe (III) and Co (II) ions [17-20].

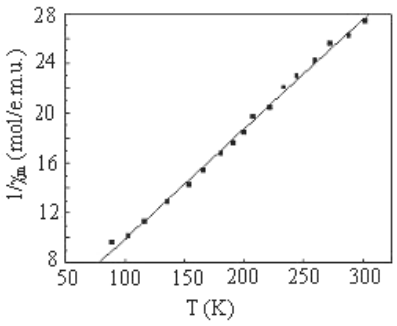

*Fig. 6. Temperature dependence of the reciprocal molar magnetic susceptibility of the (**1**) complex. Solid line is the best fit of the experimental data with a Curie-Weiss behavior.*

4. Conclusions

Spectroscopic and magnetic investigation of the sodium/potassium salt of $[M_4(H_2O)_2(AsW_9O_{34})_2]^{6-}$ heteropolyanion confirms the sandwich – type structure of this complex and the encapsulation of the tetranuclear Fe(III), Co(II) cluster between two trivacant Keggin units. The shift of the $\nu_{as}(W\text{–}O_e\text{–}W)$ and $\nu_{as}(W\text{–}O_c\text{–}W)$ vibration bands for the bonds from edge and corner-sharing octahedral respectively in the complex FT–IR spectrum compared to the ligand spectrum indicated the coordination of the M_4 ions in the lacunary region of the AsW_9O_{34} fragments. The charge transfer into the terminal $W{=}O_t$ bonds is unaffected by the metal ions. UV spectra show that ions coordination to the ligand intensifies the charge transfer into the heteropolymetalate framework. The LMCT bands (M→O) In the VIS spectrum are direct proof of the existence of metal – oxygen bonding. The local symmetry around the metallic centers is octahedral distorted. The geometry of the metallic clusters favors the antiferromagetic interactions.

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