

Dedicated to Professor Victor-Emanuel Sahini  
on the occasion of his 80th anniversary

## COMPLEXES OF THE TRILACUNARY KEGGIN ARSENO(V)POLYOXOTUNGSTATE WITH IRON (III), COBALT (II) AND NICKEL (II)

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Three new complexes of the trilacunary  $B\alpha$ -[As<sup>V</sup>W<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> Keggin polyoxometalate with M<sup>n+</sup> transition metal cations (M= Fe<sup>III</sup>, Co<sup>II</sup> and Ni<sup>II</sup>) have been synthesized. The complexes, which correspond to the formula  $Na_{(18-4n)}[M^{(n+)}_4(H_2O)_2(AsW_9O_{34})_2]$ , were investigated by FT-IR, UV-VIS, EPR spectroscopy and magnetic susceptibility measurements.

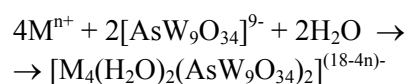
The FT-IR spectra of complexes exhibit a new  $\nu_s(W-O_b-W)$  band, due to the presence of two trilacunary units, connected by bridging oxygen atoms. The results prove that the 4 : 2 complexes have a sandwich-type structure, with a M<sub>4</sub> cluster encapsulated between two trilacunary Keggin units. Two water molecules are linked to two M atoms. The magnetic investigations reveal a weak antiferromagnetic coupling of the four M metal centers.

### INTRODUCTION

Lacunary polyoxometalates are usually synthesized from their complete precursor structure by the removal of one or more MO<sub>6</sub> octahedra.<sup>1-3</sup> They exhibit an increased reactivity towards metal ions, thus forming a broad variety of complexes in which the polyoxoanion framework remains unchanged.<sup>4</sup>

Trilacunary  $B\alpha$ -[X<sup>V</sup>W<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> Keggin polyoxotungstates form with transition metal cations sandwich-type complexes, in which the metal-to-ligand ratio is 4 : 2. Although complexes of the trilacunary [PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> polyoxometalate have been widely investigated, there are relatively few papers concerning the isostructural [AsW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> polyoxometalate acting as a ligand. Complexes of the trilacunary [As<sup>V</sup>W<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> arseno(V)polyoxometalate with p metal cations,<sup>5</sup> transition metal cations,<sup>6-12</sup> copper-β alanine,<sup>13</sup> rare earth cations<sup>14-16</sup> and with organotin fragments<sup>17</sup> have been reported, so far.

This work reports the synthesis, investigation and characterization of three new complexes of the  $B\alpha$ -[As<sup>V</sup>W<sub>9</sub>O<sub>34</sub>]<sup>9-</sup> ligand, having a trilacunary Keggin structure, with M<sup>n+</sup> transition metal cations (M= Fe<sup>III</sup>, Co<sup>II</sup> and Ni<sup>II</sup>). The 4 : 2 complexes, which correspond to the formula  $[M^{(n+)}_4(H_2O)_2(AsW_9O_{34})_2]^{(18-4n)-}$ , are obtained according to the following reaction:



The complexes were investigated and characterized by FT-IR, UV-VIS, EPR spectroscopy and magnetic susceptibility measurements. This allowed for determining subsequently the behavior of the encapsulated transition metal ions, their coordination by the Keggin fragments, the corresponding local symmetry and the type of metal-metal interactions.

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## RESULTS

The following abbreviations will be used: i) for the anions: **L** or  $\text{AsW}_9$  for  $\text{Ba}[\text{As}^{\text{V}}\text{W}_9\text{O}_{34}]^{9-}$ , **1** for  $[\text{Fe}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{6-}$ , **2** for  $[\text{Co}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$  and **3** for  $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{10-}$ ; ii) for the salts:  $\text{Na}_9$ **L** for  $\text{Ba}\text{-Na}_9[\text{AsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ ,  $\text{Na}_6$ **1** for  $\text{Na}_6[\text{Fe}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 20\text{H}_2\text{O}$ ,  $\text{Na}_{10}$ **2** for  $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 25\text{H}_2\text{O}$  and  $\text{Na}_{10}$ **3** for  $\text{Na}_{10}[\text{Ni}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2] \cdot 22\text{H}_2\text{O}$ .

### Chemical analysis

$\text{Na}_6$ **1** found (calculated): Na 2.65 (2.68), As 2.85 (2.91), Fe 4.40 (4.35), W 64.30 (64.37),  $\text{H}_2\text{O}$  7.08 (7.00);

$\text{Na}_{10}$ **2**: Na 4.20 (4.18), As, 2.77 (2.73), Co 4.35 (4.32), W 60.37 (60.15),  $\text{H}_2\text{O}$  8.22 (8.19);

$\text{Na}_{10}$ **3**: Na 4.30 (4.23), As 2.78 (2.75), Ni 4.30 (4.32), W 60.90 (60.83),  $\text{H}_2\text{O}$  7.32 (7.28).

### FT-IR spectra

FT-IR spectra of polyoxometalates exhibit generally contributions of the polyoxoanion framework.<sup>18</sup> The characteristic IR vibration bands of  $\text{Na}_6$ **1**,  $\text{Na}_{10}$ **2** and  $\text{Na}_{10}$ **3** complexes, as compared to those of the  $\text{Na}_9$ **L** ligand, are displayed in Table 1.

### Electronic spectra

UV spectra exhibit the two charge transfer bands of the polyoxometalate anion.<sup>19</sup> The UV bands of the **1**, **2** and **3** complexes, as compared to those of the **L** ligand, are listed in Table 2.

Table 1

Principal vibration bands observed in the FT-IR spectra ( $\text{cm}^{-1}$ )

Vibration	$\text{Na}_9$ <b>L</b>	$\text{Na}_6$ <b>1</b>	$\text{Na}_{10}$ <b>2</b>	$\text{Na}_{10}$ <b>3</b>
$\nu_{\text{as}}(\text{W}=\text{O}_i)$	945 s, sp	955 s	954 s	953 s
$\nu_{\text{as}}(\text{As}-\text{O}_i)$	878 vs, sh	892 vs, vb	890 s, b	890 vs
$\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$	833 vs, b	840 sh, b	850 vs, sp	849 s, b
$\nu_s(\text{W}-\text{O}_e-\text{W})$	795 s 752 s	802 s 745 vs	799 s	788 s, vb
$\nu_s(\text{W}-\text{O}_b-\text{W})$	-	720 s	724 vs, vb	723 vs, vb
$\delta(\text{W}-\text{O}_c, e-\text{W})$	508 m	515 m	510 w 505 m	512 m
$\nu_s(\text{As}-\text{O}_i)$	463 m	472 m 459 m	465 m 455 m	468 m

Notations: m, medium; s, strong; vs, very strong; sh, shoulder; b, broad; vb, very broad; sp, sharp;  $\text{O}_i$  is an internal oxygen which links As and W atoms,  $\text{O}_{c,e}$  connects corner and edge-sharing octahedra,  $\text{O}_b$  is a bridging oxygen between W atoms from two ligand units,  $\text{O}_t$  is a terminal oxygen.

Table 2

Charge transfer bands observed in the UV absorption spectra ( $\text{cm}^{-1} / \text{nm}$ )

Band	<b>L</b>	<b>1</b>	<b>2</b>	<b>3</b>
$\nu_2$ : $\text{W}-\text{O}_t$	49 100 / 204	49 150 / 203	49 300 / 203	49 250 / 203
$\nu_1$ : $\text{W}-\text{O}-\text{W}$	39 732 / 252	40 000 / 250 sh 36 015 / 278 sh	39 400 / 254	39 435 / 254

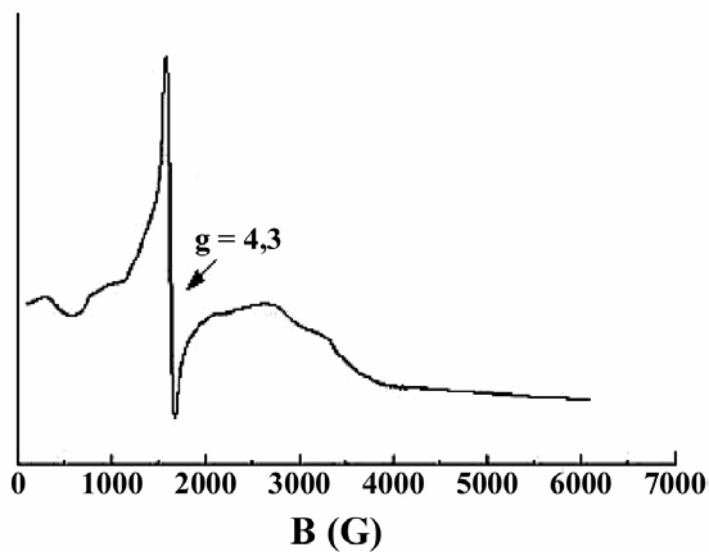
Visible spectra only show electron transfer bands of the  $\text{M}^{n+}$  transition metal ions coordinated by the ligand. The absorption bands of the **1**, **2** and **3** complexes recorded in the visible range ( $\text{cm}^{-1} / \text{nm}$ ), as compared to those of the corresponding  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  aqua-cations in octahedral field from the literature (in brackets),<sup>20</sup> are:

**1**:  $\nu_3 = {}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g$ : - (24 600 / 406 and 24 300 / 412);  $\nu_2 = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ : - (19 700 / 508);  $\nu_1 = {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ : - (12 600 / 794);

**2**:  $\nu_3 = {}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ : 20 230 / 494 sh and 19 585 / 511 sh (19 400 / 515);  $\nu_2 = {}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ : 17 420 / 574 (16 000 / 625);  
**3**:  $\nu_3 = {}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ : 23 265 / 430 (25 300 / 395);  $\nu_2 = {}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ : 12 415 / 805 (13 500 / 741) and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^1\text{E}_{1g}$ : 14 200 / 704 sh (15 400 / 649).

### Electron paramagnetic resonance spectra

EPR signals are due to the presence of the  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  paramagnetic transition metal ions. Figure 1 displays the EPR spectrum of  $\text{Na}_6$ **1**.

Fig. 1 – EPR spectrum of Na<sub>6</sub>1 at 80 K.

### Magnetic susceptibility measurements

Results of magnetic susceptibility measurements for the Na<sub>6</sub>1, Na<sub>10</sub>2 and Na<sub>10</sub>3 complexes are presented in Table 3.

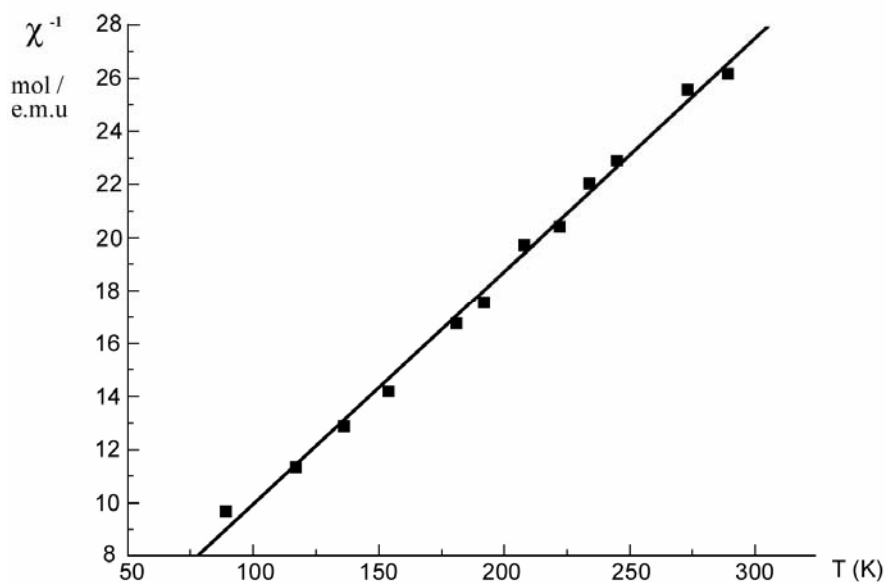
The temperature dependence of the reciprocal magnetic susceptibility for Na<sub>6</sub>1 is shown in Figure 2.

Table 3

Magnetic data

Substance	$10^6 \chi_m$ (emu mol <sup>-1</sup> )	$\mu_{\text{ef}}$ ( $\mu_B$ )	$\theta$ (K)
Na <sub>6</sub> 1	-1392	9.51	-15.1
Na <sub>10</sub> 2	-1485	7.88	-7.0
Na <sub>10</sub> 3	-1472	6.09	-28.4

Notations:  $\chi_m$  molar magnetic susceptibility,  $\mu_{\text{ef}}$  effective magnetic moment,  $\theta$  Curie-Weiss temperature.

Fig. 2 – The  $\chi_m^{-1}$  vs. T curve for Na<sub>6</sub>1.

## DISCUSSION

Similarity of FT-IR spectra for ligand **L** and for complexes **1**, **2** and **3** shows that vibration bands are mainly due to the polyoxotungstate structure. The shift of the  $\nu_{\text{as}}(\text{As-O}_i)$  antisymmetric stretching vibration, the main band of the ligand, towards higher energies in complexes indicates that the coordination increases the cohesion of the trilacunary ligand structure.<sup>18</sup> The tiny shift of the  $\nu_{\text{as}}(\text{W=O}_t)$  stretching vibration in the spectra of complexes, as compared to the ligand, can be explained by the fact that terminal  $\text{O}_t$  atoms are not involved in the coordination of  $M$  transition metal ions. On the other hand, the larger shift of the  $\nu(\text{W-O}_{\text{c,e}}-\text{W})$  stretching vibrations, for the bonds from the belt and cap areas, indicates the coordination of  $M$  metal ions by  $\text{O}_c$  and  $\text{O}_e$  oxygen atoms from corner-sharing and edge-sharing octahedra.<sup>21</sup>

The complexes exhibit a new band, due to the  $\nu_s(\text{W-O}_b-\text{W})$  vibration, proving the presence of two ligand units connected by bridging  $\text{O}_b$  atoms. The other new  $\nu(\text{M-O}_{\text{c,e}})$  bands, expected in the 500–300  $\text{cm}^{-1}$  range, are masked by the stronger vibration bands of the ligand in this area.

UV spectra of the ligand and complexes are also very similar, evincing that the charge transfer inside the polyoxotungstate structure is not significantly affected by coordination.<sup>19</sup> However, the molar absorption coefficient of the  $\nu_2$  band, which is proportional to the number of  $\text{W}$  atoms, is almost twice greater in complexes than in the ligand ( $\epsilon \approx 1.40 \cdot 10^5$  vs.  $0.75 \cdot 10^5$   $\text{L mol}^{-1} \text{cm}^{-1}$ ). These values also indicate the existence of two **L** trilacunary ligand units in the **1**, **2** and **3** complexes.

Visible spectra of complexes **2** and **3** show the characteristic d-d electron transfer bands of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions in octahedral field. However, the expected transition bands are not found in the spectrum of complex **1**.<sup>20</sup> The very low intensity d-d transitions of the  $d^5$   $\text{Fe}^{3+}$  ion, forbidden by the Laporte and spin selection rules, are totally masked by the  $\nu_1$  charge transfer band, which extends from UV into the visible range. This indicates that  $\text{Fe}^{3+}$  ions are involved in the charge transfer in complex **1**.

EPR spectra were interpreted by considering the geometry of the rhomboedral  $M_4$  tetranuclear cluster, encapsulated between two **L** units. Spectrum of  $\text{Na}_6\mathbf{1}$ , recorded at 80 K, exhibit an intense signal at  $g \approx 4.3$ , which corresponds to the high state  $S = 5/2$  of  $\text{Fe}^{3+}$ . Signals at  $B \approx 295$ , 790 and 950 G are due to higher spin states, as a result of the coupling of  $\text{Fe}^{3+}$  ions.<sup>22</sup>

EPR spectrum of  $\text{Na}_{10}\mathbf{2}$  at room temperature, centered at  $\approx 3250$  G, is strongly affected by noise. This signal is probably due to the coupled  $\text{Co}^{2+}$  ions.<sup>23</sup> At 80 K, the spectrum becomes very broad and offers no supplementary information.

For  $\text{Na}_{10}\mathbf{3}$  at 80 K, where all spin states, *i.e.*  $S = 0, 1, 2, 3, 4$ , are populated, the spectrum shows an asymmetric signal at  $\approx 585$  G and a weak signal at  $\approx 3500$  G. The signal at  $\approx 585$  G corresponds to the excited  $S = 3$  and  $S = 4$  states and proves an antiferromagnetic coupling of  $\text{Ni}^{2+}$  ions.<sup>24</sup>

Magnetic susceptibility measurements indicate a paramagnetic behavior with a weak antiferromagnetic exchange. Diamagnetic corrections were calculated by using Pascal values. The calculated effective magnetic moments,  $\mu_{\text{ef}}$ , correspond to spin states between  $S = 3$  and 4 for  $\text{Na}_6\mathbf{1}$ , between  $S = 4$  and 5 for  $\text{Na}_{10}\mathbf{2}$  and  $S = 5$  for  $\text{Na}_{10}\mathbf{3}$ .<sup>25,26</sup> These states are in agreement with the energy level diagrams determined from EPR spectra. The temperature dependence of  $\chi_m^{-1}$ , the reciprocal molar susceptibility, demonstrates a Curie-Weiss behavior in the temperature range 77–290 K. The Curie-Weiss behavior and the negative values of the  $\theta$  Curie-Weiss temperature are in good agreement with a weak antiferromagnetic coupling of the  $M^{n+}$  metal centers. The exchange interactions between the  $M^{n+}$  metal centers are mediated *via*  $M\text{--O--}M$  pathways between the  $\text{MO}_6$  octahedra.

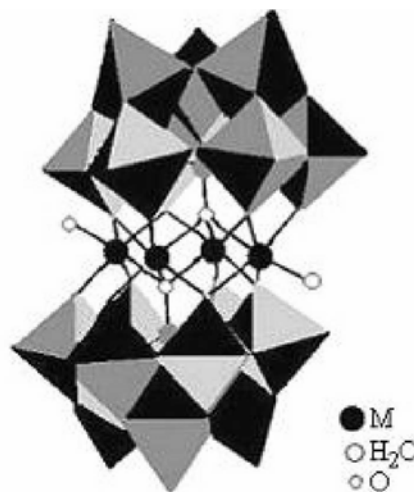


Fig. 3 – Structure of the  $[\text{M}_4(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{34})_2]^{(18-4n)-}$  complexes in combined polyhedral and ball-and-stick representation.

As shown, the investigation of the **1**, **2** and **3** complexes support their sandwich-type structure, with two trilacunary  $\text{B}\alpha\text{-As}^{\text{V}}\text{W}_9\text{O}_{34}$  Keggin units ligated to a group of four metal-centered octahedrons sharing edges and making a  $\text{M}_4\text{O}_{14}(\text{H}_2\text{O})_2$  fragment, see Figure 3.

## EXPERIMENTAL

### Synthesis

The Na<sub>9</sub>L ligand was prepared according to Finke.<sup>27</sup> Then, 10 mL of an aqueous solution containing 1.60 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 1.16 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or 1.12 g NiSO<sub>4</sub>·7H<sub>2</sub>O (4 mmol) was added at 70 °C, under stirring, to a 15 mL aqueous solution containing 5.36 g Na<sub>9</sub>L (2 mmol). The mixture was subsequently stirred for 15 min. Next, the solution was filtered and cooled to room temperature. Microcrystals of Na<sub>6</sub>1 (yellow), Na<sub>10</sub>2 (blue) or Na<sub>10</sub>3 (yellow) precipitated after 3-4 days and were collected by filtration, then washed with NaCl solution (2 mol dm<sup>-3</sup>), ethanol and ether; eventually they were recrystallized from hot water. Yield: 3.63 g (62% based on Fe) for Na<sub>6</sub>1, 4.28 g (72% based on Co) for Na<sub>10</sub>2 and 3.89 g (65% based on Ni) for Na<sub>10</sub>3.

### Investigation

Elemental analysis of As, W, Fe, Co and Ni was performed by OES-ICP with a BIRD 2070 spectrophotometer. Na was determined by FEP with an Eppendorf flame photometer. Water content was determined by dehydration at 350 °C.

Vibrational spectra were recorded in the 4000-200 cm<sup>-1</sup> range on a Jasco FT/IR 610 spectrophotometer, using KBr pellets.

Electronic spectra in aqueous solution were recorded in the 190-1000 nm range on an ATI Unicam-UV-Visible spectrophotometer, by means of a Vision Software V 3.20.

EPR spectra were obtained with a Bruker ESP 380 spectrometer.

Magnetic susceptibility was measured in the 77-290 K temperature range, with a Faraday type balance.

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