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NEW PERSPECTIVES IN POLYOXOMOLYBDATES CHEMISTRY CONTAINING LARGE $\{Mo_{132}\}$ CLUSTERS

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ABSTRACT. The new $(NH_4)_{60}\{U_3\subset\{(Mo^{VI})Mo_5^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2^{V}O_4(SO_4\}_{30}]{\cdot}308H_2O$ spherical cluster was synthesized as ammonium salt and investigated by means of elemental analyses, FT-IR, Raman, UV-Vis and EPR spectroscopy and by magnetic measurements. The results suggest the binding of uranium cations to the SO_4^{2-} ligands and the quasi-cubic local symmetry around the uranium ions.

Keywords: *Uranium (IV), metal clusters, IR, Raman, UV, Vis, RES spectroscopies, magnetic susceptibility.*

INTRODUCTION

Over the past twelve years, the chemistry of the giant spherical polyoxometallate clusters has brought about spectacular changes, due to the synthesis and characterization of giant molecules with the new structures displaying a high level of symmetry and remarkable topological and electronic properties.

In 1998, Müller and his team [1] presented a very large spherical mixed-valance polyoxometallate cluster, i.e. $[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$, abbreviated as $\{Mo_{132}\}$, $[Mo^{VI}_{72}Mo^{V}_{60}]$ or $[Mo_{11}]_{12.}$ The new dodecameric cluster was named “giant ball” (giant sphere).

The central Mo^{VI} atoms of the 12 $[(Mo^{VI})Mo^{VI}_5]$ pentagons define the 12 corners, while the 30 $[Mo^{V}_2]$ linkers, i.e. the $[Mo^{V}_2O_4]^{2+}$ units, define the 30 edges of an icosahedron. This corresponds to the formulation $[(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_6]_{12}\ [Mo^{V}_2O_4(CH_3COO)]_{30}]^{42-}$ or $[(Mo^{VI})Mo^{VI}_5]_{12}[(Mo^{V}_2)]_{30} \equiv (pentagon)_{12}(linker)_{30}$. Based on a topological concept, the molecule can also be formulated as $[(Mo^{VI})^{0}(Mo^{VI}_{5})^{I}(Mo^{VI}_{5})^{II}]_{12}$. This formulation takes formally into account the fact that the Mo atoms of each rather stable $[Mo^{V}_2]$ belongs to the two adjacent $[Mo_{11}]$ groups.

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The cluster can be considered as being built up of 12 [Mo_{11}] units with central [MoO_7] pentagonal - bipyramidal groups, so that the fivefold symmetry axes are retained in the resulting spherical structure, which shows an overall icosahedral symmetry (I_h) [2]. The spherical nanocapsule of the type $\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}$ has 20 sizeable pores of the $\{Mo_9O_9\}$ type finely sculpturable cavity interiors. A water cluster consisting of two shells, an outer $\{H_2O\}_{60}$ Archimedian solid and an inner $\{H_2O\}_{20}$ dodecahedron, is located inside the capsule.

The giant sphere species can act as hosts for cations forming new types of compounds in terms of structure and properties [3-5a]. $\{Mo_{132}\}$ exhibits a nanometer-size cavity, presenting new perspectives for novel host-guest chemistry. The most interesting challenge will be to fill the cavities of the “opened” ball-type $\{Mo_{132}\}$ cluster, which exist as a lacunary-type system, with a variety of different guests, and also to place molecules inside the cavity of the ball-shaped clusters, which show a different reactivity to the discrete ones.

The different cations (substrates) can be fixed at a well-defined position above the $\{Mo_9O_9\}$ type pores (Rb^+), below the pores (Ce^{3+}, Na^+/Mo) and especially in the channels (urea H^+/Na^+, Cs^+, Gua H^+/Urea$^+$ [6-10].

In this paper we described the synthesis of a new, very large cluster from the $\{Mo_{132}\}$ series which corresponds to the formula $(NH_4)_{60}\{U_3\subset\{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2{}^{V}O_4(SO_4)\}_{30}]\cdot 308H_2O$ and which is abbreviated as $\{Mo_{132}\text{-}U^{IV}\}$. The new cluster was investigated by vibrational (FT-IR, Raman), electronic (UV-VISNIR) spectroscopy, magnetic susceptibility measurements, as well as EPR spectroscopy.

RESULTS AND DISCUSSIONS

The reaction of U^{4+} ions with $\{Mo_{132}$-sulphate$\}$ in water can be described by eq. (1). The isolation of the products as ammonium salts resulted in relatively good yields of the complex.

$$3U^{4+} + [\{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2{}^{V}O_4(SO_4)\}_{30}]^{72-} \rightarrow \\ \{U_3\subset\{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2{}^{V}O_4(SO_4)\}_{30}]^{60-} \qquad (1)$$

Chemical analysis

The elemental analysis found is in good agreement with the calculated composition of the complex.

Vibrational spectra

FT-IR spectrum

The vibration bands of the FT-IR spectrum (in cm^{-1}) (Fig. 1) and their assignments are the following: 1622(m) δ_{HOH}, 1400(m) $\delta_{NH_4}{}^+$, 1190(w), 1136(w) and 1045(w) $\nu_{3(SO_4),}$ 968(s) and 936(m) $\nu_{as}(Mo\text{-}O_t)$, 856(m), 802(vs), 729(vs)

ν_{as}(Mo-O_{br} -Mo), 571((s) and 474(m) δ(Mo-O_{br}-Mo), where O_t, O_{br} are terminal oxygen atoms and bridged oxygen atoms, respectively.

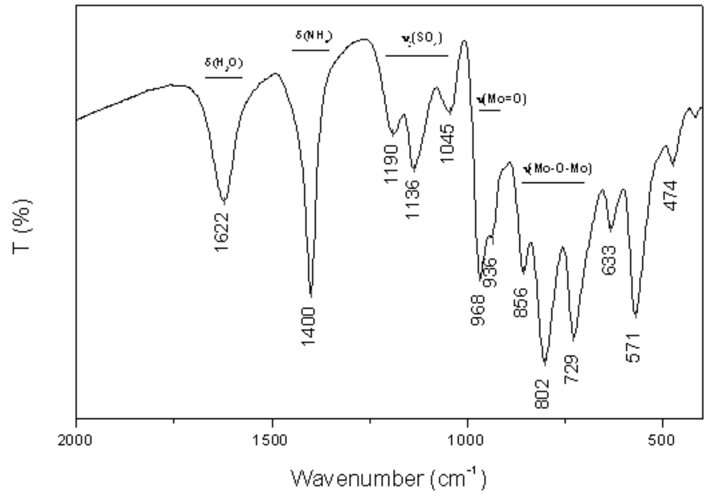

Figure 1. FT-IR spectrum of {Mo_{132}-U^{IV}} cluster.

The five anti-symmetric stretching vibrations ν_{as}(Mo-O_t) and ν_{as}(Mo-O_{br}-Mo) characteristic to Mo-O bonds are recorded in the range of 700-1000 cm^{-1} [11]. The spectroscopic data indicate the polyoxometalate nature of the {Mo_{132}–U^{IV}} cluster, and the binding of uranium cations to the SO_4^{2-} ligands, because the frequency values of the coordinated sulfate group in the infrared spectrum are similar to the spectrum of the {Mo_{132}} type spherical clusters [9].

Raman spectrum

The vibration bands of Raman spectrum (Fig. 2) (in cm^{-1}) are: 974(m) $\nu_{s\,(SO4)}$, 946(m) ν_s(M=O_t), 876(vs) and 838(vs) ν_s(Mo-O_{br}-Mo), 378(w), 312(w).

The three characteristic medium, strong and very strong bands, registered at 946, 876 and 838 cm^{-1}, are assigned to the ν_s(Mo-O_t), ν_{as}(Mo-O_t), and ν_s(Mo-O_{br}-Mo) vibrations, respectively. The last two bands in the Raman spectrum of {Mo_{132}-U^{IV}} compound are due to the splitting process of the band from 878 cm^{-1} of the {Mo_{132}-sulphate} cluster. This splitting is due to the distortions in the MoO_6 octahedra upon coordination of the uranium(IV) ions [12].

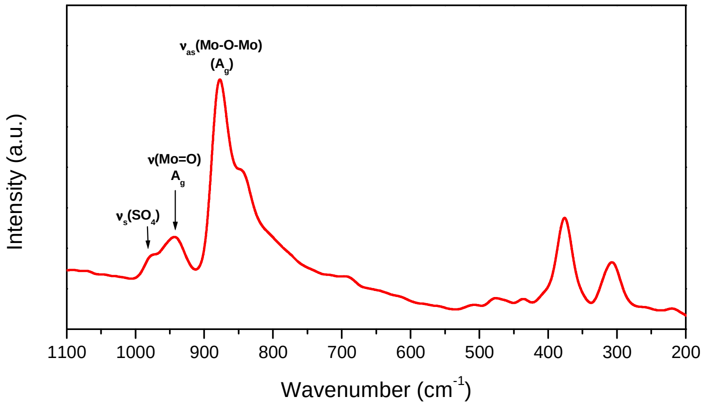

Figure 2. Raman spectrum of the {Mo_{132}-U^{IV}} cluster.

Electronic spectra

UV spectrum

The absorption bands (in nm/cm^{-1}) and their assignments are: ν_1 between 229.5/43572 (sh) and 267/37453 (sh) (CT) Mo-O_{br}-Mo and ν_2 at 208.5 / 47961 (CT) Mo-O_t.

The UV spectra of polyoxometallate clusters generally exhibit two charge-transfer (CT) bands, characteristic to the polyoxoanionic framework and assigned to oxygen-to-metal-transitions [13, 14].

In the UV spectrum of the {Mo_{132}-U^{IV}} cluster, the broad ν_1 CT band is reduced to two shoulders at 229.5/43572 (sh) and 267/37453 (sh), due to the $d\pi$-$p\pi$-$d\pi$ transitions from the three center Mo-O_{br}-Mo modes. Due to the $d\pi$-$p\pi$ transitions of the Mo-O_t bonds, the sharper ν_2 CT band has the maximum value positioned at 208.5 nm (47961 cm^{-1}). The in-spectrum presence of the two shoulders indicates that the cluster anion has nonequivalent Mo–O_{br}–Mo bonds, caused by the U^{IV} ion coordination.

Vis-NIR spectrum

In polyoxometallates with reduced addenda, new intervalence charge-transfer (IVCT) bands arise in the visible and NIR domains. In most cases, three IVCT bands are observed, marked by A, B and C [15, 16]. For the {Mo_{132}-U^{IV}} cluster, the reduced addendum is the Mo^V metal centre, which yields in the presence of the homo-nuclear IVCT $Mo^V \rightarrow Mo^{VI}$ C band. The recorded spectrum shows a strong absorption over the entire visible domain, which extends in NIR and accounts for the dark brown color of the substance, in both solid state and solution.

The absorption bands (in nm/cm^{-1}) and their assignments are: 457/21881 homo-nuclear IVCT band C $Mo^{V} \rightarrow Mo^{VI}$ (Fig. 3a) (this band is present also in Mo_{132}-sulphate at 455/21978), 795.5/12570 and 1143/8748 (hetero-nuclear IVCT bands A and B, $U^{IV} \rightarrow Mo^{VI}$) (Fig. 3 b).

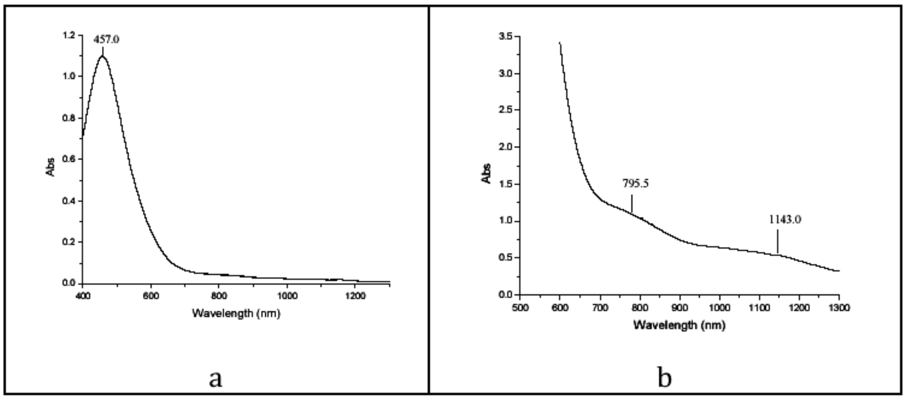

Figure 3. Vis-NIR absorption electronic spectrum of $\{Mo_{132}\text{-}U^{IV}\}$ in aqueous solution ($c=5\cdot10^{-4}$ mol L^{-1}). a-homo-nuclear IVCT band,C; b-hetero-nuclear IVCT bands A, B.

The heteronuclear broad A IVCT band, located in NIR at 1143 nm (8748 cm^{-1}), as well as the B IVCT band, recorded at 795.5 nm (12570 cm^{-1}) and the intense homo-nuclear C IVCT band cover the f-f electron transfer (ET) bands, characteristic to the U^{4+} ion (of f^2 electron configuration) in cubic field. These ET bands, specific to the $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^1I_6$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^1D_2({}^1G_4)$ and $^3H_4 \rightarrow {}^3P_0$ transitions, would have been expected at approximately 423, 496, 565, 647 and 689.6 nm (23600, 20160, 17670, 15440 and 14500 cm^{-1}). [17]

Magnetic susceptibility measurements

The monomeric character of the $\{Mo_{132}\text{-}U^{IV}\}$ cluster is confirmed by the magnetic susceptibility measurements. In the temperature range of 135÷290 K, the values of the magnetic susceptibility corresponds to a Curie-Weiss behavior. The magnetic susceptibility data were corrected for diamagnetic and temperature-independent paramagnetic (TIP) contributions, both calculated from the tabulated values from the diamagnetic cluster ($\chi_0=2.73\cdot10^{-3}$ emu/mol). Figure 4 shows the dependence of the reverse of the molar susceptibility (χ-χ_0) *vs* temperature.

The experimental data were fitted using the following equation [18]:

$$\chi_m = \frac{N\mu_B^2 \mu_{eff}^2}{3kT} + \chi_0 \tag{1}$$

The obtained effective magnetic moment is $\mu_{eff} = 2.83\,\mu_B$ and indicates that the uranium ion is in the oxidation state +4 [19]. Such low value is obtained when the uranium(IV) ion is in a high symmetry environment, particularly in a local cubic symmetry, with $^3H_4$ ground state. [20]

At relatively low temperatures, the uranium ions are well separated and do not interact. The nine-fold degenerated ground state $^3H_4$ of the uranium $5f^2$ electrons split into Γ_1, Γ_3, Γ_4 and Γ_5 levels by the eightfold cubic crystal field of oxygen ions around the uranium ion. The temperature-independent para-magnetism is big enough (χ_0=2.73·10^{-3} emu/mol). This value suggests that Γ_1 is the lowest level [18]. This is in accordance with the fact that for this uranium(IV) complex we have not obtained any electron paramagnetic spectrum at room temperature and liquid nitrogen temperature.

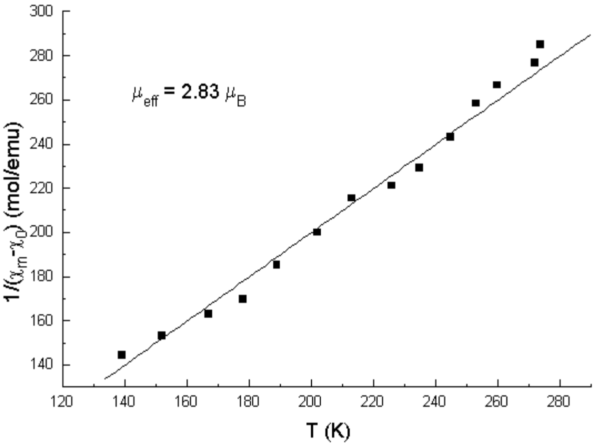

Figure 4. The 1/χ *vs* T curve for {Mo_{132}-U^{IV}} cluster.

EPR spectrum

The powder EPR spectrum of the compound {Mo_{132}-U^{IV}} obtained in X band at room temperature (Fig. 5) exhibits the most intense signals in the 3250–3400 G region.

The main values of the gyro-magnetic tensor, slightly decreased below the free electron g_0 = 2.0023 value, indicate that the obtained spectrum is the contribution both of U^{IV} and Mo^V ions. [21]. The fine structure of the EPR spectrum can be interpreted by considering one S_{eff} =1 effective spin for the uranium(IV) ion and a Γ_5 sublevel of the $^3H_4$ multiplet as ground state [22, 23].

The shape of the ESR spectrum can be interpreted by considering one S_{eff} =1 effective spin state of the uranium (IV) non–Kramers ion. In a cubic crystalline field, the degeneracy of the ground state $^3H_4$ is partially removed to $\Gamma_1(1)$, $\Gamma_4(3)$, $\Gamma_3(2)$, $\Gamma_5(3)$ levels. The lowest level is either Γ_5 or Γ_1, but only the first of them is EPR active [24].

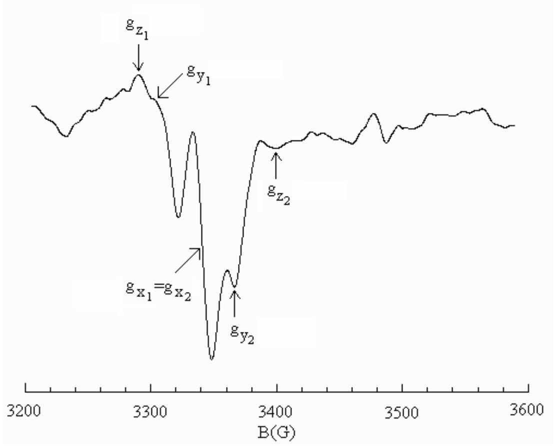

Figure 5. EPR spectrum of the $\{M_{132}\text{-}U^{IV}\}$ cluster at room temperature.

Owing to the fact that we have obtained an EPR spectrum even at room temperature, we conclude that the Γ_5 multiplet is energetically the lowest and may be described by an effective S_{eff} = 1 spin.

The resonance B values of the fine structure signals (B_{z_1} = 3284 G, B_{y_1} = 3306 G, B_{x_1} = B_{x_2} = 3342 G, B_{y_2} = 3366 G, B_{z_2} = 3408 G) indicate a small orthorhombic distortion from the cubic symmetry. The main values of the gyromagnetic tensor g (g_x = 1.922, g_y = 1.940, g_z = 2.005) and the zero-field splitting parameters ($D = 18.31 \cdot 10^{-4}$ cm^{-1}, $E = 5.99 \cdot 10^{-4}$ cm^{-1}) were calculated with the usual procedure for S = 1 systems. [24] This result confirms that every U^{IV} ion is surrounded by eight oxygen ions, arranged like a basis for anti-prismatic configurations. The orthorhombic EPR spectrum proves that the 5f electrons are trapped at the uranium sites, indicating the dominance of the spin-orbit coupling.

CONCLUSIONS

The paper reports the synthesis and structural investigation of the new $(NH_4)_{60}\{U_3\subset\{(Mo^{VI})Mo_5^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2^{V}O_4(SO_4)\}_{30}]\cdot 308H_2O$ nano-sized inorganic cluster.

The vibration bands of the FT-IR and Raman spectra are characteristic to the $\{Mo_{132}\}$ spherical clusters framework.

The UV spectrum shows two charge-transfer (CT) bands recorded at 229.5 - 267 and 208.5 nm, specific to the polyoxometalate edifice.

The Vis-NIR spectrum exhibits three inter-valence charge-transfer (IVCT) bands, owing to the presence of the Mo^{V} metal centre, as a reduced addendum. The Mo^{V} - Mo^{VI} homo-nuclear IVCT band and U^{IV} - Mo^{VI} hetero-nuclear IVC bands are recorded at 457, 795.5 and 1143 nm. These bands were superposed over the f – f electron transfer bands characteristic to the U^{4+} ions.

Magnetic susceptibility measurements demonstrate that the uranium ions are well separated and display no interaction. The obtained effective magnetic moment is $\mu_{eff} = 2.83\mu_B$ and it indicates that the uranium ion is in the oxidation state +4 in a high symmetry environment, particularly in a cubic local symmetry, with $^3H_4$ ground state.

The EPR spectral data indicate a small orthorhombic distortion from the cubic symmetry for U^{IV} ions and confirms that every U^{IV} ion is surrounded by eight oxygen ions, arranged like the basis for anti-prismatic configurations.

Based on these results, we propose in Fig. 6 a schematic representation of the uranium ions coordination to the ligand, similar to the one related to Ce^{III} ions, as shown in the literature [9].

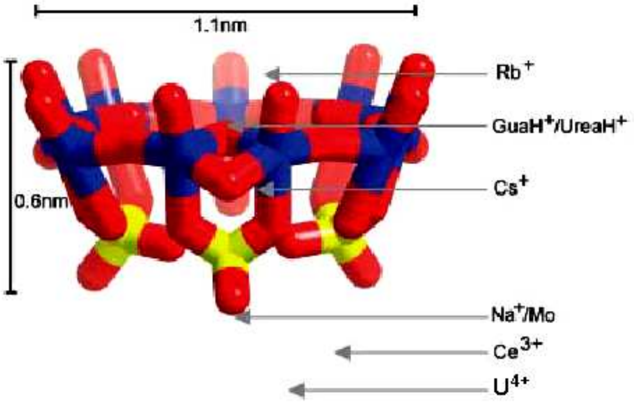

Figure 6. The relative positions of all the fixed substrates in one of the 20 channels [9], color code: Mo blue, O red, S yellow, other respective substrates/cations in different color.

Three U^{IV} cations are disordered over 30 equivalent positions forming an icosidodecahedron, where each underoccupied uranium center is coordinated symmetrically in a bidentate fashion to two O atoms of a SO_4^{2-} bidentate ligand and by four O atoms of the $\{H_2O\}_{60}$ - type shell, as well as two O atoms of the $\{H_2O\}_{20}$ - type shell as ligands, thus forming an anti-prismatic - type coordination [10].

EXPERIMENTAL SECTION

Materials

Reagent grade chemicals were used and all syntheses and studies were carried out in distilled water.

Syntheses

The ammonium salt of the novel uranium(IV) cluster $\{Mo_{132}\text{-}U^{IV}\}$ was prepared in two steps, as follows:

Synthesis of $(NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}] \cdot 300\ H_2O$
abbreviated as $\{Mo_{132} – acetate\}$

The substance was prepared according to the procedure described in the literature [1] and was characterized by FT-IR spectrum.

Synthesis of $(NH_4)_{60}\{U_3 \subset \{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2{}^{V}O_4(SO_4\}_{30}] \cdot 308H_2O$
abbreviated as $\{Mo_{132}\text{-}U^{IV}\}$

A sample of $U(SO_4)_2$ (10.0 g. 23.2 mmol) was added after 1.5 hours to a refluxing solution of $\{Mo_{132}$ – acetate$\}$ (5.0 g., 0.18 mmol) and amomonium sulphate (15 g. 113.5 mmol) in H_2O (400 mL). The resulting solution was refluxed for 30 minute and filtered hot. After three days, dark brown crystals of $\{Mo_{132}\text{-}U^{IV}\}$ appeared, which were collected by filtration over a syntherized glass frit, washed with ice-cold-2-propanol, and dried in air. Yield: 4.40 g (0.146 mmol) 78% based on $\{Mo_{132}$ -acetate$\}$.

Elemental analyses (%) calcd: U 2.37, N 2.78, S 3.18, Mo 42.02; found: U 2.12, N 2.90, S 3.26, Mo 42.00.

Methods and instrumentation

ICP-AES (Inductive Coupled Plasma Atom Emission Spectroscopy) was used for the elemental analysis of uranium and molybdenum. The nitrogen and sulphur were analyzed with a Vario EL device. The crystallization water content was determined by means of the difference between the initial sample and the weight of sample after being heated for 30 minutes at 120^{o}C.

A FTIR-JASCO 610 spectrophotometer was used to record IR spectra for samples pelleted in KBr.

Raman spectra were performed on a Bruker FTIR IFS 66 with a Raman FRA 106 unit spectrophotometer (λ_e=1064 nm), using solid compound powders.

UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer in aqueous solutions having concentrations of 10^{-5} M and 10^{-3} M.

EPR spectra were performed on powder of the compound, at room temperature, at 9.4 GH (X band) using a standard JOEL-JES-3B equipment.

Magnetic susceptibility measurements were performed in the 135-290 K temperature range with a Faraday balance.

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