Journal of Alloys and Compounds 323/324 (2001) 743–747

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Spectroscopic and magnetic investigation of one sandwich-type uranium(IV)–polyoxometalate with Ge(IV) as heteroatom

C. Craciun, L. David*

Department of Physics, 'Babes-Bolyai' University, 1 Kogalniceanu, RO-3400 Cluj-Napoca, Romania

Abstract

The sandwich-type $Na_{14}[(UO)_3(GeW_9O_{34})_2]\cdot 23H_2O$ uranium(IV)–polyoxometalate was prepared and investigated by FT-IR, UV–Vis spectroscopy and magnetic susceptibility measurements. The coordination of the uranium ions to the polyoxometalate is indicated by the appearance in the FT-IR spectrum of the complex of the ν_{as}(U–O) antisymmetric stretching vibration bands at 1069 and 1126 cm^{-1} and by the shifts of ν_{as}(W–O$_{b,c}$–W), ν_{as}(W=O$_d$), ν_{as}(W–O$_a$) in the 700–960 cm^{-1} region. The visible electronic spectrum of the complex indicates a $^3H_4$ electronic ground state of uranium ions and a quasicubic local symmetry around them. The $^3P_0$, $^1D_2(^1G_4)$, $^3P_1$, $^1I_6$ and $^3P_2$ electronic levels are situated at 15 000, 16 000, 18 480, 19 600 and 23 920 cm^{-1}, respectively above the ground state. The p_π–d_π electronic transitions into the W=O bonds appear at 46 000 cm^{-1} for the ligand and 45 760 cm^{-1} for the complex and d_π–p_π–d_π transitions into tricentric W–O–W bonds at 41 600 cm^{-1} for the ligand and 38 800 cm^{-1} for the complex in the UV electronic spectra. The inverse of the magnetic susceptibility corrected by diamagnetism follows a Curie–Weiss behavior with the effective magnetic moment $\mu_{eff}=4.40\mu_B$ and the Curie temperature $\theta=-73$ K, corresponding to one $S=1$ ground state.

Keywords: Clusters; Electronic states; Exchange and superexchange; Light absorption; Magnetic measurements

1. Introduction

Polyoxometalates have won particular attention mainly because of their use in catalysis, medicine and materials science [1–3].

Although all polyoxometalates are ultimately decomposed to monomeric species in basic solutions, control of pH leads in many cases to lacunary structures [4]. Further condensation of these species can arise in the presence of transition metals, lanthanide or actinide ions, which link the lacunary units [5]. This condensation takes place because the starting building block is actually an 'unsaturated' species [6]. The capacity of heavy atoms to fill the vacancies of the polyoxometalates already has applications for stocking radioactive waste [7].

The main goal of this paper is the report of some spectroscopic (FT-IR and UV–Vis) and magnetic investigations on the $Na_{14}[(UO)_3(GeW_9O_{34})_2]\cdot 23H_2O$ polyoxometalate (U^{IV}–POM) (Fig. 1). Every α-A-$[GeW_9O_{34}]^{9-}$ trilacunary Keggin unit functions as a bidentate ligand for every uranium atom. The uranium atoms are connected by

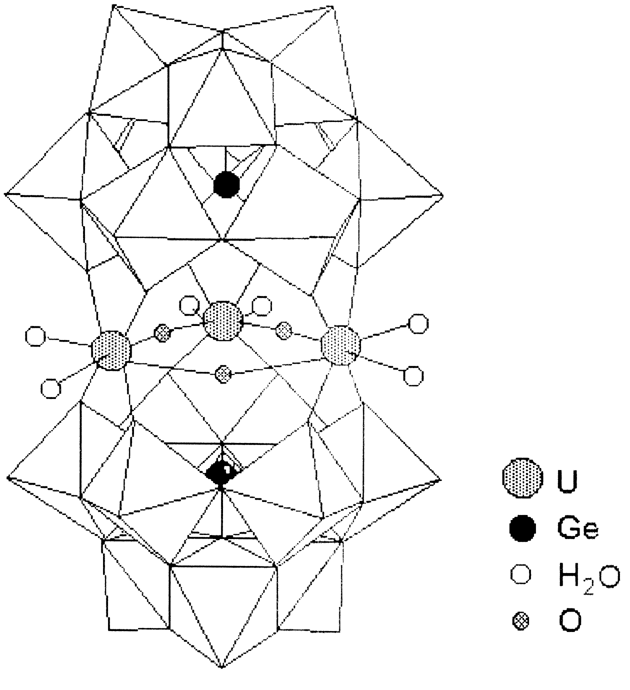

Fig. 1. The structure of the $Na_{14}[(UO)_3(GeW_9O_{34})_2]\cdot 23H_2O$ complex.

---

*Corresponding author. Tel.: +40-64-405-300; fax: +40-64-191-906.
E-mail address: leodavid@phys.ubbcluj.ro (L. David).

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01073-8

oxygen bridges. Two water molecules also coordinate every heavy atom, so the uranium coordination number is eight.

2. Experimental

The polyoxometalate ligand $Na_{10}[GeW_9O_{34}]\cdot14H_2O$ and the $Na_{14}[(UO)_3(GeW_9O_{34})_2]\cdot23H_2O$ complex were prepared as previously reported [8]. FT-IR spectra were recorded on an Equinox 55 Bruker Spectrophotometer on KBr pellets, in the 4000–400 cm^{-1} range. Electronic spectra were taken in aqueous solutions within a range of $\lambda=200$–800 nm using ATI Unicam-UV–Visible Vision Software V 3.20. The magnetic susceptibility measurements were made using a Faraday type balance in the temperature range of 120–290 K.

3. Results and discussion

3.1. FT-IR Spectra

In order to obtain information about the changes appearing in the lacunary polyoxometalate units after the uranium ions coordination, we have compared the FT-IR spectra of the $Na_{10}[GeW_9O_{34}]\cdot14H_2O$ ligand (used for the complex preparation) and the $Na_{14}[(UO)_3(GeW_9O_{34})_2]\cdot23H_2O$ uranium–polyoxometalate compound. The 400–1250 cm^{-1} region of the FT-IR spectra are given in Fig. 2 and some vibration bands are presented in Table 1.

Vibrations corresponding to the trilacunary Keggin heteropolyanion appear in the 450–1000 cm^{-1} region [9]. The additional bands at 1069 and 1126 cm^{-1} in the U^{IV}–POM FT-IR spectrum (Fig. 2) can be attributed to ν_{as}(U–O) vibrations and thus confirms the coordination of the uranium ions to the ligand through the oxygen atoms [10].

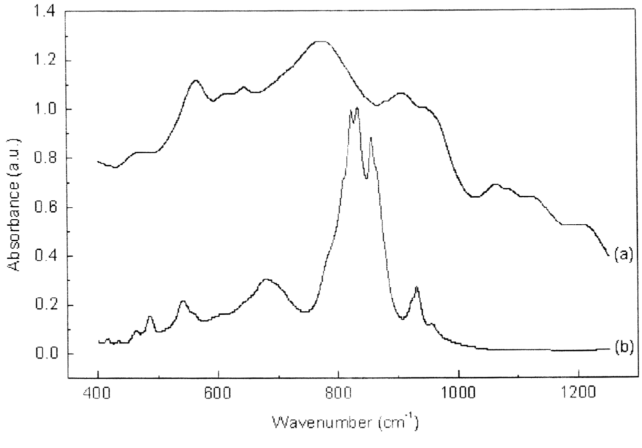

Fig. 2. FT-IR spectra (400–1250 cm^{-1} region) (a) U^{IV}–POM complex; (b) polyoxometalate ligand.

Table 1
FT-IR data for the ligand and U^{IV}–POM complex[a]

Band	Ligand (cm^{-1})	Complex (cm^{-1})
δ(O–Ge–O)	466 w,b	467 w,b
ν_s(W–O$_{b,c}$–W)	489 w,b	–
ν_s(Ge–O$_{b,c}$–W)	545 w,b; 609 w,b	567 m,sp; 619 m,b
ν_{as}(W–O$_a$)	651 w,sh; 684 w,b	647 m,b
ν_{as}(W–O$_c$–W)	785 w,sh	777 s,b
ν_{as}(Ge–O)	811 m,sh; 824 s,sp; 835 s,sp	–
ν_{as}(W–O$_b$–W)	857 s,sp; 865 s,sh	885 m,sh
ν_{as}(W=O$_d$)	926 w,sh; 932 w,sp; 958 vw,b	911 m,sh; 947 m,b
ν_{as}(U–O)	–	1069 w,b; 1126 w,sh
δ(HOH)	1653 w,sh; 1684 w,sp; 1699 w,sh	1559 w,sh; 1624 w,sp
ν_{as}(OH)	3038 w,sh; 3155 m,sh; 3254 m,sh; 3325 m,b; 3390 m,sh; 3535 w,sh	2746 w,sh; 3145 m,vb; 3310 m,vb; 3584 w,sh

[a] w, weak; m, medium; s, strong; sh, shoulder; b, broad; sp, sharp; vw, very weak; vb, very broad.

The tricentric ν_{as}(W–O$_b$–W) and ν_s(Ge–O$_{b,c}$–W) vibrations appear at higher frequency in the complex spectrum which indicate the strengthening of these bonds (Table 1). The increase in the force constants between sharing-corner WO_6 octahedra and those between the heteropolyoxometalate frame and the central GeO_3 units in the complex increases its stability [11]. On the other hand, the ν_{as}(W–O$_c$–W) band is slowly ($\approx$8 cm^{-1}) shifted toward lower frequencies, thus suggesting the decrease of the bonding strength between edge-sharing octahedra of the trilacunary Keggin units. Consequently, the coordination of the uranium atoms to the Keggin fragments decreases the strength of the 'intra' bridges between edge-sharing octahedra, inside a M_3O_{13} set (the cap region of the Keggin unit) and increases the strength of the 'inter' bridges between corner-sharing octahedra from the cap and belt regions, respectively [12]. This is due to the complexation of the uranium atoms in the lacunary regions of the two Keggin units.

The three type of W=O$_d$ bonds of the ligand, differing by their positions in the Keggin unit (two in the six WO_6 octahedra equatorial region and one in the polar region), have different stretching vibration frequency (Table 1). For the complex, the spectrum presents two broad ν_{as}(W=O$_d$) bands, shifted symmetrically by $\approx$15 cm^{-1} to lower and higher frequencies.

The GeO_3 pyramidal group of C_{3v} symmetry presents three ν_{as}(Ge–O) vibration bands for the ligand. In the complex spectrum, these bands are overlapped by the ν_{as}(W–O$_b$–W) and ν_{as}(W–O$_c$–W) vibrations. This effect has been previously reported for complete Keggin structures [13], thus suggesting that the uranium coordination to the lacunary fragments takes place so that the symmetry of the complete structure is regained.

The W–O$_a$ bond presents a broad band with a shoulder in the FT-IR spectrum of the complex and only one shifted toward lower frequencies for the complex. This is due to the active pair of electrons of the Ge^{IV} ion, which leads to an active character of the lacunary region of the Keggin units and so to some distortions of the GeO_3 pyramid [14].

The stretching and deformation bands of the water molecules (Table 1) are very broad and present some shoulders. The ligand presents two water deformation vibrations up to 1650 cm^{-1} and six stretching vibrations up to 3000 cm^{-1}, while the complex has two deformations and four stretching vibrations (Fig. 3). There are two bands in the FT-IR spectrum of the complex at lower frequencies than the others (at 1559 and 2746 cm^{-1}) which correspond to water molecules coordinated to the uranium atoms. Different bands obtained are due to different water molecules of crystallization and coordination types, respectively [15].

3.2. UV Spectra

The UV electronic spectra of the uranium(IV)–polyoxometalate complex in aqueous solution and of the ligand has two charge transfer bands (Fig. 4). The absorption bands centered at ≈46 000 cm^{-1} in the free ligand and at ≈45 760 cm^{-1} in the complex spectra are assigned to p_π–d_π electronic transitions into the W=O bonds [16]. The transitions d_π–p_π–d_π between the energetic levels of the W–O–W tricentric bonds lead to a shoulder at ≈41 600 cm^{-1} for the ligand and to a distinct and very broad band at ≈38 800 cm^{-1} for the uranium complex [17]. The shifts of these electronic transitions can be attributed to geometrical changes (lengths and angles) of the polyanion after the uranium coordination. This coordination intensifies the charge transfer into the heteropolyoxometalate framework more than into the terminal bonds.

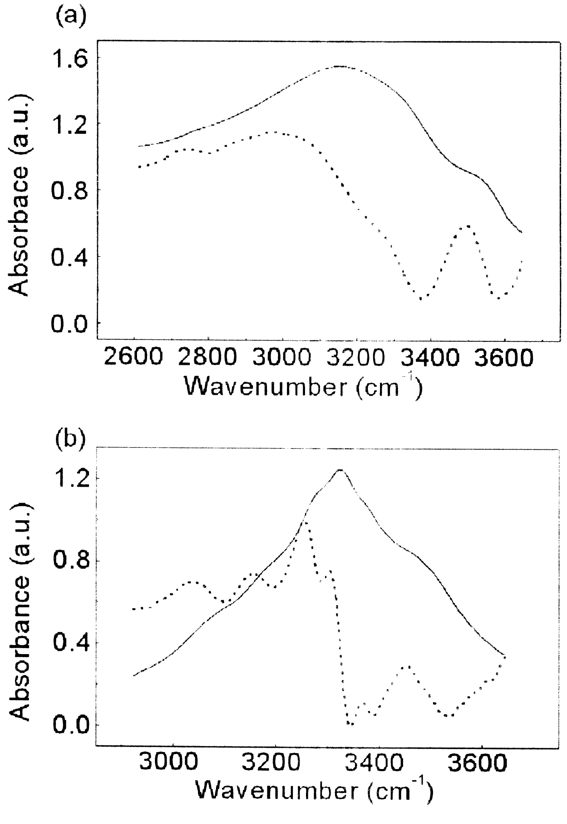

Fig. 3. Bands of water molecule vibrations. (a) U^{IV}–POM complex; (b) polyoxometalate ligand.

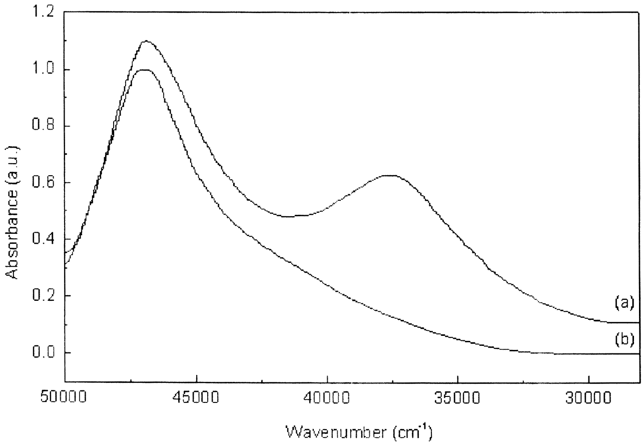

Fig. 4. UV spectra. (a) U^{IV}–POM complex; (b) polyoxometalate ligand obtained in a 5×10^{-5} mol l^{-1} aqueous solution.

3.3. Visible spectra

The visible electronic spectra of the U^{IV}–POM complex, made in aqueous solutions at different concentrations (Fig. 5) indicate that the local symmetry around the uranium ions is quasicubic, with $^3H_4$ ground level [18]. The L band is typical for eight-coordinated U^{IV} ions. The observed bands correspond to f→f transitions (Table 2). In addition, the R, V and W bands are superposed to $U^{IV}\rightarrow W^{VI}$ charge transfer bands.

3.4. Magnetic susceptibility measurements

The magnetic susceptibility data were corrected by the diamagnetic contribution χ_0, by means of Pascal constants. Fig. 6 shows the dependence of the inverse of the measured (χ_m) and corrected (χ_m–χ_0) susceptibility by the temperature. In the temperature range 125–280 K, the reciprocal molar magnetic susceptibility follows a Curie–Weiss behavior [19]:

$$\chi_m = \frac{N\mu_B^2\mu_{eff}^2}{3k(T-\theta)} + \chi_0$$

The obtained effective magnetic moment is $\mu_{eff}=$

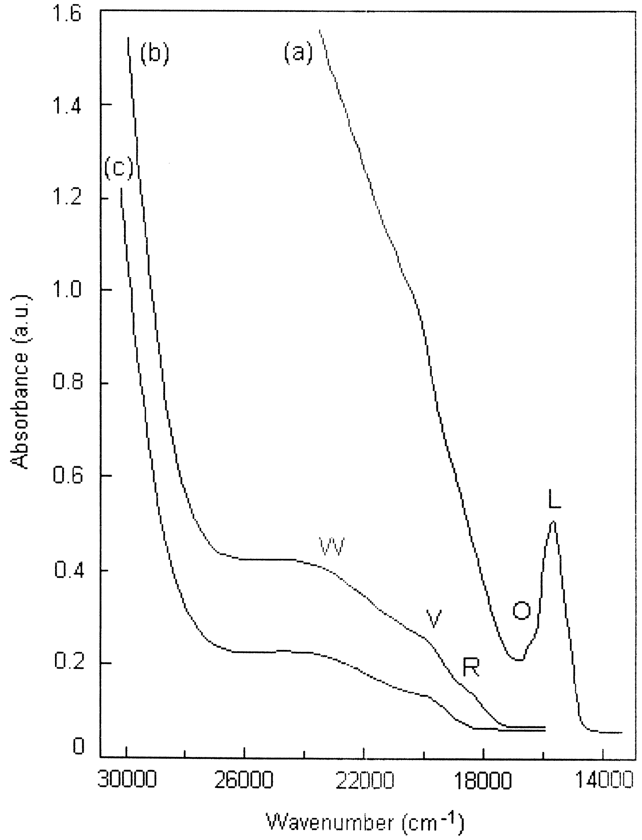

Fig. 5. Visible electronic spectra of the U^{IV}–POM complex in aqueous solutions with different concentrations ((a) 5×10^{-3} mol l^{-1}, (b) 2.5×10^{-3} mol l^{-1}, (c) 10^{-3} mol l^{-1}).

$4.40\mu_B$ and the Curie temperature is $\theta=-73$ K. The magnetic moment value and the negative θ correspond to a system with $S=1$ ground state [20], obtained through antiferromagnetic exchange between the uranium(IV) spins.

4. Conclusions

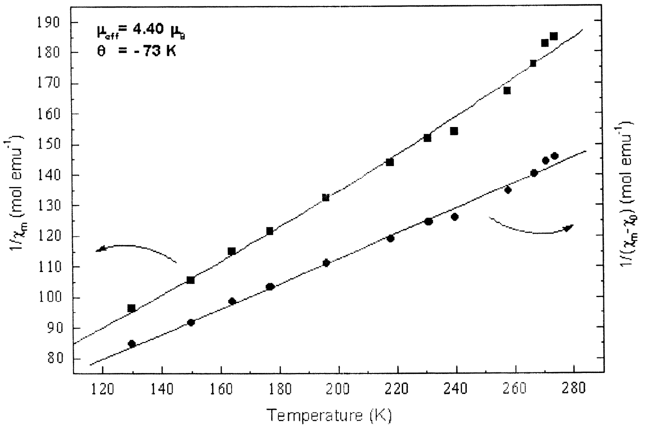

Fig. 6. Temperature dependence of the reciprocal molar magnetic susceptibility of the U^{IV}–POM complex. Lines are the best fit of the temperature dependence of the measured (■) data and diamagnetic corrected (●) values, respectively.

The FT-IR spectrum of the U^{IV}–POM contains the additional bands for ν_{as}(U–O) vibrations compared to the ligand spectrum, a proof of the coordination of the uranium ions to the oxygen atoms. The uranium coordination increases the strength of the bridges between the cap and belt regions of the trilacunary Keggin units and weakens those between edge-sharing octahedra from their cap regions. As the 2700–3600 cm^{-1} region of the FT-IR spectrum indicates, the complex contains different types of water molecules: the coordinated water to the polyoxometalate frame, that coordinated to the uranium(IV) ions and the crystallization water. UV spectra show that the uranium coordination to the ligand intensifies the charge transfer into the heteropolyoxometalate framework. The appearance of the L-band in the Vis spectrum of the complex, specific for quasicubic environment around the actinide ion, indicates that the electronic ground state is $^3H_4$. The spins of the three uranium ions are antiferromagnetically coupled leading to an effective $S=1$ ground state.

Table 2
Electronic transitions of the U^{IV}–POM complex from the visible absorption spectra[a]

Band	ν (cm^{-1})	Assignment
L	15 000 m,sp	$^3H_4\rightarrow{}^3P_0$
O	16 000 w,sh	$^3H_4\rightarrow{}^1D_2$ ($^1G_4$)
R	18 480 s,sh	$^3H_4\rightarrow{}^3P_1$
V	19 600 vs,sh	$^3H_4\rightarrow{}^1I_6$
W	23 920 vs,sh	$^3H_4\rightarrow{}^3P_2$

[a] s, strong; b, broad; m, medium; vs, very strong; sh, shoulder; sp, sharp; w, weak.

References

[1] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983.
[2] D.E. Katsoulis, Chem. Rev. 98 (1998) 359.
[3] J.T. Rhule, C.L. Hill, D.A. Judd, Chem. Rev. 98 (1998) 327.
[4] M.H. Dickman, G.J. Gama, K.-C. Kim, M.T. Pope, J. Cluster Sci. 7 (1996) 567.
[5] N. Mizuno, M. Misono, Chem. Rev. 98 (1998) 199.
[6] A. Müller, F. Peters, M.T. Pope, D. Gatteschi, Chem. Rev. 98 (1998) 239.
[7] M.T. Pope, in: R.B. King (Ed.), Encyclopedia of Inorganic Chemistry, Wiley, Chichester, UK, 1994, p. 3361.
[8] G. Hervé, A. Tézé, Inorg. Chem. 16 (1977) 2115.
[9] C. Rocchiccioli-Deltcheff, R. Thouvenot, R. Franck, Spectrochim. Acta A 32 (1976) 587.
[10] R.A. Gazarov, G.A. Gardeeva, I.D. Koli, V.I. Spitsyn, Dokl. Nauk. SSSR 255 (2) (1980) 373.
[11] C. Rocchiccioli-Deltcheff, R. Thouvenot, Spectrosc. Lett. 12 (2) (1979) 127.
[12] C. Rocchiccioli-Deltcheff, R. Thouvenot, C.R. Acad. Sci. Paris C 278 (1974) 857.

[13] M.H. Alizadeh, S.P. Harmalker, Y. Jeannin, J. Martin-Frère, M.T. Pope, J. Am. Chem. Soc. 107 (1985) 2662.

[14] F. Robert, M. Leyrie, G. Hervé, Acta Crystallogr. Sect. B 38 (1982) 358.

[15] R. Massart, R. Contant, J.M. Fruchart, J.F. Ciabrini, M. Fournier, Inorg. Chem. 16 (1977) 2916.

[16] T. Yamase, Chem. Rev. 98 (1998) 307.

[17] H. So, M.T. Pope, Inorg. Chem. 11 (1972) 1441.

[18] I. Creaser, M.C. Heckel, R.J. Neitz, M.T. Pope, Inorg. Chem. 32 (1993) 1573.

[19] O. Vogt, K. Mattenberger, J. Löhle, J. Rebizant, J. Alloys Comp. 271 (1998) 508.

[20] T.H. Siddall, in: E.A. Boudreaux, L.N. Mulay (Eds.), Theory and Applications of Molecular Paramagnetism, Wiley, New York, 1976, p. 317.