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Synthesis and Characterization of Bis(undeca tungstogallate) Lanthanates of Potassium

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Abstract

The complexes of $K_{11}(Ln(GaW_{11}O_{39}H_2)_2)\cdot xH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb) have been prepared from their lacunary precursor $K_8GaW_{11}O_{39}$, and characterized by elemental analysis, IR, UV, emission spectra, XPS and magnetic susceptibility. The emission spectrum of $K_{11}[Eu(GaW_{11}O_{39}H_2)_2]$ is very similar to those of $[Eu(XW_{11}O_{39})_2]^{n-}$ (X = P, As, Si, Ge), indicating they all have the same structure. XPS determination reveals that the Ln–O bond has coordination character. Magnetic measurement confirms that the lanthanide elements are +3 valent in these complexes.

Introduction

A heteropolyanion with Keggin or Dawson structure becomes an unsaturated heteropolyanion with a lacuna after losing one heavy atom and its terminal oxygen. These unsaturated anions can form mixed-type polyanions with transition metals and lanthanides as five or four-dentate ligands respectively [1]. Recently Wu *et al.* reported that some triheteropolytungstate acids containing lanthanide elements displayed catalytic activity for some organic synthesis reactions [2]. In order to make use of the rich resources of rare earth elements in China and develop new rare earth catalysts, we have prepared a number of new heteropolytungstates and heteropolymolybdates of lanthanide elements and studied their properties [3]. This paper gives the results of the preparation and characterization of $K_{11}[Ln(GaW_{11}O_{39}H_2)_2]\cdot xH_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb).

Experimental

Starting materials

Lanthanide nitrates were prepared from lanthanide oxides which contain over 99.9% Ln_2O_3. Gallium nitrate solution was made by dissolving the metal gallium (99.99%) in nitric acid. $K_8GaW_{11}O_{39}\cdot xH_2O$ was prepared according to the published method [4] and was identified by infrared spectroscopy.

Syntheses of $K_{11}[Ln(GaW_{11}O_{39}H_2)_2]\cdot xH_2O$

A total of 16.24 g (0.005 mol) of $K_8GaW_{11}O_{39}\cdot xH_2O$ was dissolved in 100 ml of water. To this solution *c.* 1.1 g (0.0025 mol) of $Ln(NO_3)_3$ dissolved in 5 ml of water was added dropwise with vigorous stirring at 80 °C. After cooling the solution to room temperature, 2.5 g of KCl was added. At 0 °C an oil formed at the bottom of the beaker, which then changed to crystal. The crystals of the complexes were recrystallized from warm water three times and kept in a desiccator over P_2O_5. The yields were about 50%.

Spectral studies made during the addition reaction show clearly the formation of the complexes in the ratio $Ln/GaW_{11} = 0.5$ (Fig. 1).

Chemical Analyses

Tungsten was determined gravimetrically by the classical cinchonine method. The lanthanides were determined volumetrically (back-titration of an excess of EDTA with $MnSO_4$). Potassium was de-

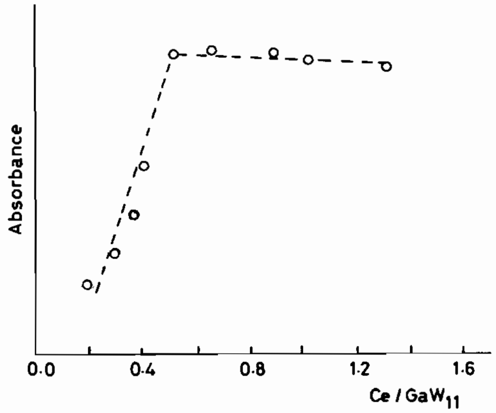

Fig. 1. Spectrophotometric study of the formation of the complex $Ce(GaW_{11})_2$, λ = 259 nm.

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TABLE 1. The results of elemental analyses

Complex	Found(calc.) (%)				
	Ln	W	K	Ga	H_2O
$K_{11}[La(GaW_{11}O_{39}H_2)_2]\cdot 29H_2O$	2.06(2.18)	61.62(62.01)	6.71(6.59)	2.18(2.13)	8.46(8.55)
$K_{11}[Ce(GaW_{11}O_{39}H_2)_2]\cdot 24H_2O$	2.15(2.17)	62.72(62.88)	6.70(6.66)	2.20(2.16)	9.32(9.37)
$K_{11}[Pr(GaW_{11}O_{39}H_2)_2]\cdot 31H_2O$	2.12(2.14)	60.98(61.61)	6.64(6.53)	2.20(2.12)	9.00(9.05)
$K_{11}[Nd(GaW_{11}O_{39}H_2)_2]\cdot 32H_2O$	2.18(2.18)	60.98(61.46)	6.49(6.51)	2.11(2.11)	9.29(9.29)
$K_{11}[Sm(GaW_{11}O_{39}H_2)_2]\cdot 25H_2O$	2.28(2.32)	62.44(62.57)	6.69(6.63)	2.18(2.15)	9.60(9.52)
$K_{11}[Eu(GaW_{11}O_{39}H_2)_2]\cdot 28H_2O$	2.33(2.32)	62.09(62.01)	6.71(6.58)	2.12(2.13)	8.30(8.28)
$K_{11}[Gd(GaW_{11}O_{39}H_2)_2]\cdot 23H_2O$	2.38(2.44)	62.33(62.85)	6.67(6.63)	2.09(2.16)	7.05(6.99)
$K_{11}[Tb(GaW_{11}O_{39}H_2)_2]\cdot 21H_2O$	2.39(2.49)	63.12(63.20)	6.65(6.70)	2.17(2.17)	6.57(6.46)
$K_{11}[Dy(GaW_{11}O_{39}H_2)_2]\cdot 28H_2O$	2.43(2.43)	61.38(61.73)	6.68(6.57)	2.12(2.13)	8.30(8.27)
$K_{11}[Tm(GaW_{11}O_{39}H_2)_2]\cdot 24H_2O$	2.50(2.60)	62.09(62.33)	6.55(6.61)	1.98(2.14)	7.33(7.21)
$K_{11}[Yb(GaW_{11}O_{39}H_2)_2]\cdot 19H_2O$	2.57(2.69)	63.60(63.04)	6.62(6.69)	2.03(2.17)	6.00(5.89)

termined gravimetrically as the tetraphenylborate. Gallium was determined gravimetrically utilizing camphoric acid as a precipitating agent. The water content was determined by thermogravimetry. The analytical results are presented in Table 1.

Physical Measurements

UV–Vis spectra were recorded on a DU-8 B spectrophotometer. IR spectra were obtained on a Nicolet 5DX FT infrared spectrometer as KCl pellets at 4000–400 cm^{-1}. X-ray powder diffraction patterns were made with a D/max-3A X-ray spectrometer. XPS data were obtained on a Shimadzu ESCA-650B spectrometer under 10 torr and were calibrated against carbon. Magnetic susceptibility measurements were carried out by the Faraday method with an MB-2 magnetic balance at room temperature. Emission and excitation spectra were recorded with a Perkin-Elmer MPE-66 spectrofluorometer.

Results and Discussion

Stability

The stability of the $[Ln(GaW_{11}O_{39}H_2)_2]^{11-}$ (abbreviated $Ln(GaW_{11})_2$) anions is studied in terms of the pH by spectrophotometry. Figure 2 shows the result for $K_{11}[Ce(GaW_{11}O_{39}H_2)_2]$. The results for other samples were similar to this one. It can be seen from Fig. 2 that the pH limits of stability of $Ln(GaW_{11})_2$ anions are 3.2–7.5, over the limit they will be decomposed.

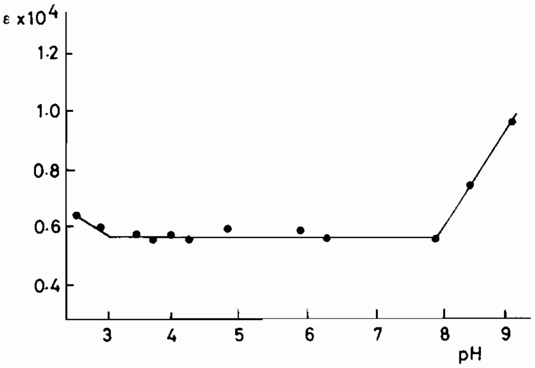

Fig. 2. Study of the stability of $K_{11}[Ce(GaW_{11}O_{39}H_2)_2]$, absorbance in terms of pH; $C = 10^{-5}$ M, $\lambda = 259$ nm.

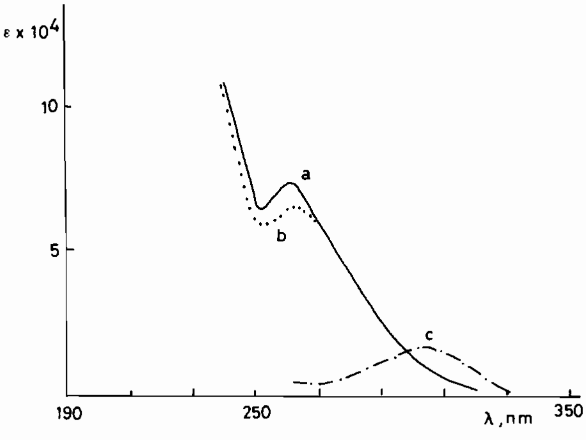

Fig. 3. UV absorption spectra of (a) GaW_{11}, (b) $Ce(GaW_{11})_2$, (c) $Ga(NO_3)_3$ in aqueous solution.

UV Absorption Spectra

Most of these new complexes are colorless, so the spectral region of interest is to be found in the near UV from 200 to 300 nm. In this range all samples reported reveal a peak at about 260 nm, and their peak positions are almost identical with that of the parent lacunary compound (Fig. 3) and do not change for different lanthanide elements. These facts indicate that this transfer is a O → W charge transfer band. The O → Eu CT bands are expected to lie in the 240–250 nm region [5] but they have small extinction coefficients and thus they are covered by the intense O → W CT bands.

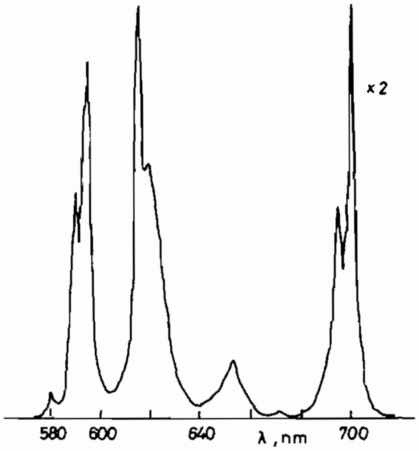

Fig. 4. Emission spectrum of solid $Eu(GaW_{11})_2$ at room temperature.

Emission Spectra

Figure 4 shows the emission spectrum of solid $K_{11}[Eu(GaW_{11}O_{39}H_2)_2]$ at 295 K. The spectrum of the complex in aqueous form is exactly the same. The emission spectrum consists of $^5D_0 \rightarrow {}^9F_J$ bands split by the local crystal field, whose transition frequencies are listed in Table 2. It can be seen that in the $^5D_0 \rightarrow {}^7F_0$ region there is a single line, in the $^5D_0 \rightarrow {}^9F_2$ region there are at least two bands at room temperature. The number of peaks and transition frequency of $Eu(GaW_{11})_2$ are very similar to those of $Eu(SiW_{11})_2$, $Eu(PW_{11})_2$, $Eu(GeW_{11})_2$ and $Eu(AsW_{11})_2$ [6], indicating that they all have the same structure. According to Blase *et al.* [7], the structure of $K_{13}[Eu(SiW_{11}O_{39})_2]$ is similar to that of $Cs_{12}[U(GeW_{11}O_{39})_2]$ described by Tourne *et al.* [8]. In the later complex U is coordinated by eight oxygen atoms forming a distorted archimedean antiprism.

The luminescence intensity of $Eu(GaW_{11})_2$ is lower than those of $Eu(XW_{11})_2$ (X = P, As, Si, Ge), which is caused by the OH radical contained in the heteropolyanion. The bands shown in the emission spectrum of $Eu(GaW_{11})$ correspond to radiative transitions from the $^5D_0$ excited level to the ^7F_J ground state manifold within the Eu^{3+} ion. The emitting $^5D_0$ level can be reached by exciting both the various f → f bands of Eu^{3+} and the O → W CT band of the ligand. The radiationless deactivation of the $^5D_0$ emitting level, however is strongly enhanced by coupling with the high frequency of O–H oscillators. The luminescence intensity is strongly affected by the presence of water molecules in the first coordination sphere.

IR Spectra

The observed frequencies of the complexes and the tentative assignments of the main absorption

TABLE 2. Transition frequencies of some $Eu(XW_{11})_2$ complexes in the emission spectra in the solid state at room temperature (nm)

Complex	$^5D_0 \rightarrow {}^7F_0$	$^5D_0 \rightarrow {}^7F_1$	$^5D_0 \rightarrow {}^7F_2$	$^5D_0 \rightarrow {}^7F_3$	$^5D_0 \rightarrow {}^7F_4$
$K_{11}[Eu(GaW_{11}O_{39}H_2)_2]$	580(vw)	590(s) 597(vs)	613(vs) 617(s)	653(w)	694(w) 700(ms)
$K_{13}[Eu(Ge_2W_{11}O_{39})_2]$	579(vw)	588(s) 594(vs)	613(vs) 617(s)	652(w)	693(ms) 698(vs)
$K_{11}[Eu(AsW_{11}O_{39})_2]$	580(vw)	590(s) 594(vs)	614(vs) 617(s)	650(w)	693(ms) 699(s)
$K_{11}[Eu(PW_{11}O_{39})_2]$	579(vw)	588(s) 598(vs)	612(vs) 617(s)	651(w)	692(ms) 698(s)
$K_{13}[Eu(SiW_{11}O_{39})_2]$	579(vw)	589(s) 594(vs)	614(vs) 619(s)	652(w)	694(ms) 700(s)

TABLE 3. IR data (cm^{-1})

	$H_5GaW_{12}O_{40}$	$K_{11}[Ln(GaW_{11}O_{39}H_2)_2]$										
		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Tm	Yb
ν_{as}(W–Od)	970	935(s)	935(s)	935(s)	932(s)	935(s)	937(s)	935(s)	937(s)	935(s)	936(s)	937(s)
ν_{as}(W–Ob–W)	890	875(s)	875(s)	875(s)	875(s)	875(s)	879(s)	875(s)	876(s)	870(s)	876(s)	879(s)
		810(s)	815(s)	790(s)	815(s)	805(s)	786(s)	810(s)	791(s)	800(s)	786(s)	786(s)
ν_{as}(W–Oc–W)	780	760(s)	755(s)	760(s)	760(s)	760(s)	749(s)	765(s)	754(s)	760(s)	757(s)	750(s)
		690(s)	690(s)	690(s)	690(s)	690(s)	711(s)	690(s)	711(s)	690(s)	706(s)	710(s)
ν_{as}(Ga–O)	560	535(m)	535(m)	535(m)	530(m)	535(m)	545(m)	540(m)	540(m)	540(m)	547(m)	545(m)
δ(O–Ga–O)	450	440(m)	440(m)	440(m)	440(m)	440(m)	448(m)	440(m)	446(m)	445(m)	448(m)	448(m)

TABLE 4. The electronic bound energy of Ln, W, Ga and O elements in $Ln(GaW_{11})_2$ complexes

	Ln3d(5/2)	Ln4d(5/2)	Ga2p(3/2)	W4f(7/2)	W4f(5/2)	O1s(1/2)
$La(GaW_{11})_2$	835.1(836.5)[a]		1118.1	35.7	37.8	530.9
$Ce(GaW_{11})_2$	885.6(887.0)		1118.0	35.8	37.8	530.9
$Pr(GaW_{11})_2$	934.0(934.8)		1118.0	35.8	37.8	531.0
$Nd(GaW_{11})_2$	(983.8)		1118.0	35.7	37.7	530.7
$Sm(GaW_{11})_2$	1081.3(1084.8)		1118.0	35.8	37.8	531.0
$Eu(GaW_{11})_2$	1134.4(1135.7)		1117.8	35.6	37.6	530.8
$Gd(GaW_{11})_2$		143.7(144.1)	1117.7	35.8	37.9	530.7
$Tb(GaW_{11})_2$		151.0(152.3)	1118.0	35.7	37.6	530.7
$Dy(GaW_{11})_2$		155.3(158.0)	1118.0	35.7	37.7	530.8
$Tm(GaW_{11})_2$		181.3	1118.0	35.5	37.7	530.5
$Tb(GaW_{11})_2$		191.0	1118.1	35.6	37.6	530.9

[a] The values of lanthanide nitrate.

bands are listed in Table 3. Because of the change of structural symmetry and charge on the anions the infrared spectra of $Ln(GaW_{11})_2$ anions have the following characteristics as compared with α-GaW_{12} with Keggin structure.

(i) The ν_{as}(W–Od), which is at 970 cm^{-1} in α-GaW_{12}, decreases to 936 ± 1 cm^{-1}. The asymmetric stretching frequency of the (W–Od) bond vibration of heteropolyanions is a individual stretching mode, which is not affected by the change of the anions symmetry [9]. Obviously, this decrease of ν_{as}(W–Od) is due to the increase of negative charge on the polyanions, strengthening the anion cohesion.

(ii) The decrease of the asymmetric bridge stretching frequency and splitting of W–Ob–W and W–Oc–W bridge bond vibrations. ν_{as}(W–Ob–W), which is at 890 cm^{-1} in α-GaW_{12}, is separated into 875 ± 5 and 805 ± 10 cm^{-1} in $Ln(GaW_{11})_2$. This is the same as the case of ν_{as}(W–Oc–W) which is at 780 cm^{-1} and changes into 755 ± 5 and 690 ± 10 cm^{-1}. It is known that the asymmetric bridge stretching frequency of heteropolyanions is related to the M–O–M angle, which is more open the higher the stretching frequency is [10]. This fact results from the change of anion symmetry and corresponding M–Oc–M angle.

(iii) The asymmetric stretching frequency of the GaO_4 tetrahedron in GaW_{12} decreases from 560 to 540 ± 5 cm^{-1}. This decrease is due to the change of anion symmetry. It is noticeable that δ(O–Ga–O) does not vary much with an increase in the atomic number of Ln. This is possibly due to the fact that the ionic radii of Ln^{3+} are too large to occupy the position of the tungsten atom left after GaW_{11} is formed. Therefore, Ln^{3+} ion is not expected to form a bond with one of the four oxygen atoms in the GaO_4 tetrahedron.

XPS

The XPS data of Ln, W and O elements in $K_{11}[Ln(GaW_{11}O_{39}H_2)_2]$ are listed in Table 4. Ln3d(5/2) or Ln4d(5/2) in $Ln(GaW_{11})_2$ is lower than that in the lanthanide nitrates. The decrease of the inner shell electron bound energy means an increase of negative charge density on the nucleus. This fact indicates that there is more elctron density around the Ln nuclei, arising from the transfer of part of the electron pairs from the oxygen in α-GaW_{11} to Ln^{3+}. This shows the Ln–O bond has a coordination character in the $Ln(GaW_{11})_2$ anion.

Magnetic Susceptibility

The magnetic susceptibility of the lanthanides in the complexes was determined by the Faraday method at room temperature and from this the efficient magnetic moment was calculated ($K_{11}[La(GaW_{11}O_{39}H_2)_2]$ acted as the diamagnetic correction material), see Table 5. The observed values of magnetic moments are very close to those given by Van Vleck, showing that the lanthanides in the complexes remain in the +3 oxidation state and the 4f electrons are little influenced by the ligand of the two GaW_{11} groups.

TABLE 5. Magnetic measurements data

	$\chi_g \times 10^{-6}$	μ_{eff} (BM)
$K_{11}[La(GaW_{11}O_{39}H_2)_2]\cdot 31H_2O$	−0.1465	0
$K_{11}[Ce(GaW_{11}O_{39}H_2)_2]\cdot 24H_2O$	0.2542	2.477(2.56)[a]
$K_{11}[Pr(GaW_{11}O_{39}H_2)_2]\cdot 31H_2O$	0.7877	3.805(3.62)
$K_{11}[Nd(GaW_{11}O_{39}H_2)_2]\cdot 26H_2O$	0.6179	3.424(3.68)
$K_{11}[Sm(GaW_{11}O_{39}H_2)_2]\cdot 25H_2O$	0.0200	1.402(1.55)
$K_{11}[Eu(GaW_{11}O_{39}H_2)_2]\cdot 28H_2O$	0.4866	3.125(3.40)
$K_{11}[Gd(GaW_{11}O_{39}H_2)_2]\cdot 25H_2O$	4.1606	8.116(7.94)
$K_{11}[Tb(GaW_{11}O_{39}H_2)_2]21H_2O$	5.3264	9.100(9.70)
$K_{11}[Dy(GaW_{11}O_{39}H_2)_2]\cdot 28H_2O$	7.0550	10.54(10.66)
$K_{11}[Tm(GaW_{11}O_{39}H_2O_2]\cdot 24H_2O$	1.1369	4.431(7.60)
$K_{11}[Yb(GaW_{11}O_{39}H_2)_2]\cdot 15H_2O$	0.6057	3.361(4.50)

[a] Values from Van Vleck.

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