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Bis(undecatungstogermanate) Lanthanates of Potassium

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Abstract

The $K_{13}[Ln(GeW_{11}O_{39})_2]\cdot nH_2O$ (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb) have been prepared. Some properties of these compounds have been studied. The change of main bands in their IR spectra with reference to α-$GeW_{12}O_{40}{}^{4-}$ is discussed. ν_{as}(W–O_d) is shifted toward low wavenumber and ν_{as}(W–O_b–W), δ(O–Ge–O) each appear as two distinct bands. X-ray powder diffraction shows that the molecular symmetry of $K_{13}[Ln(GeW_{11}O_{39})_2]$ is lower than that of α-$K_8(GeW_{11}O_{39})$. XPS determination reveals that the Ln–O bond has coordination character and that the shifts of W_{4f} and O_{1s} are between $K_{13}Ln(GeW_{11}O_{39})_2$ and α-$H_4(GeW_{12}O_{40})$. Magnetic measurement confirms that the lanthanide elements are +3 valent in these complexes and the magnetic moments are very close to the values found by Van Vleck.

Introduction

Study of the heteropolyanion complexes of lanthanides has been continued since the 1970s. After Peacock and Weakley's work [1], Zubairi *et al.* [2] prepared $La(XW_{11}O_{39})_2{}^{n-}$ (X = B, Si, Ge, P, As) complexes. Study of the heteropolytungstates $(XW_{11}O_{39})^{n-}$ was conducted by Tégé and Herre [3, 4]. The 'unsaturated' Keggin anions have not only strong ability of coordination, but can also stabilize Pr(IV) and Tb(IV) which have an extremely strong oxidizing power in neutral or weak acidic solutions [5, 6]. Recently it has been reported that heteropolytungstosilicate complexes of the lanthanides have catalytic properties and may be prospective catalysts [17].

In this paper we report the preparation of $K_{13}[Ln(GeW_{11}O_{39})_2]$ (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb) and some of their physical and chemical properties.

Experimental

Preparation

Tungstogermanic acid was isolated as the etherate [8] and was gently heated with 100 ml water to remove ether. $Ln(NO_3)_3$ solution was added to the above solution in the proportion $H_4GeW_{12}O_{40}$:Ln = 2:1 (Ln = 0.006 mol). Concentrated potassium acetate solution (40 g KAc in 40 ml H_2O, pH adjusted to 7) was added dropwise with stirring at 70 °C. After 20 min the reaction solution was filtered. When the filtrate was cooled to room temperature, an oil formed at the bottom of the beaker. At 0 °C the oil could be crystallized. The crystals of the complexes were recrystallized in warm water three times and kept in a desiccator over P_2O_5.

Analysis

Potassium was precipitated as the tetraphenylborate complex [9]. The lanthanides were determined volumetrically (back-titration of an excess of EDTA with $MnSO_4$ [1]). Germanium was analysed as GeO_2 [8]. Tungsten was precipitated as the 8-hydroxyquinoline complexes and weighed as WO_3 after ignition at 700 °C. The hydration water was determined by the loss of weight after 30 min at 300 °C. The results are reported in Table I.

Physical Measurements

IR spectra were obtained on a Nicolet 5DX FT infrared spectrometer as KBr 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^{-8} 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.

Results and Discussion

IR spectra

The formation of bis(tungstogermano)lanthanide was from α-$(GeW_{12}O_{40})^{4-}$ to α-$(GeW_{11}O_{39})^{8-}$ to $[Ln(GeW_{11}O_{39})_2]^{13-}$. The observed frequencies of their IR spectra and the tentative assignments of the main absorption bands are listed in Table II.

The IR and Raman study on heteropolyanions of Keggin structure has been well investigated [10], and also on 'unsaturated' polyanions [11–13]. We find that after Keggin anions become 'unsaturated' in the

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TABLE I. The Results of Elemental Analyses[a] (%)

Complex	K	Ln	Ge	W	H_2O
$K_{13}Ce(GeW_{11}O_{39})_2\cdot 11H_2O$	8.12 (8.09)	2.30 (2.23)	2.38 (2.30)	64.50 (64.36)	3.12 (3.15)
$K_{13}Pr(GeW_{11}O_{39})_2\cdot 10H_2O$	8.14 (8.11)	2.42 (2.25)	2.47 (2.32)	64.61 (64.53)	3.00 (2.87)
$K_{13}Nd(GeW_{11}O_{39})_2\cdot 11H_2O$	8.03 (8.08)	2.25 (2.29)	2.42 (2.31)	64.45 (64.32)	3.08 (3.15)
$K_{13}Sm(GeW_{11}O_{39})_2\cdot 18H_2O$	7.82 (7.92)	2.38 (2.34)	2.30 (2.26)	62.80 (62.99)	5.15 (5.05)
$K_{13}Eu(GeW_{11}O_{39})_2\cdot 28H_2O$	7.59 (7.70)	2.28 (2.30)	2.23 (2.20)	62.05 (61.26)	7.59 (7.63)
$K_{13}Gd(GeW_{11}O_{39})_2\cdot 25H_2O$	7.67 (7.76)	2.38 (2.40)	2.19 (2.22)	61.10 (61.70)	6.80 (6.87)
$K_{13}Tb(GeW_{11}O_{39})_2\cdot 6H_2O$	8.25 (8.18)	2.56 (2.56)	2.38 (2.34)	64.98 (65.10)	1.68 (1.74)
$K_{13}Dy(GeW_{11}O_{39})_2\cdot 21H_2O$	7.97 (7.84)	2.55 (2.50)	2.50 (2.24)	63.50 (62.35)	5.04 (5.83)
$K_{13}Tm(GeW_{11}O_{39})_2\cdot 29H_2O$	7.67 (7.66)	2.53 (2.54)	2.20 (2.29)	61.21 (60.94)	7.87 (7.86)
$K_{13}Yb(GeW_{11}O_{39})_2\cdot 41H_2O$	7.46 (7.41)	2.41 (2.52)	2.09 (2.12)	59.76 (58.90)	10.74 (10.76)

[a] Calculated values in parenthesis.

TABLE II. IR Data (cm^{-1})

			$K_{13}Ln(GeW_{11}O_{39})_2$				
	α-GeW_{12}[a]	α-GeW_{11}[b]	La	Ce	Pr	Nd	Sm
$\nu_{as}(W-O_d)$	979(s)	958(s)	945(s)	944(s)	944(s)	949(s)	950(s)
$\nu_{as}(W-O_b-W)$	880(s)	882(s)	871(s)	874(s)	873(s)	880(s)	878(s)
		850(s)	816(s)	818(s)	819(s)	818(s)	819(s)
$\nu_{as}(Ge-O)$	823(sh)						
	527(m)	525(m)	525(m)	528(m)	526(m)	524(m)	525(m)
$\nu_{as}(W-O_c-W)$	769(vs)	796(s)	784(m)	785(m)	788(m)	788(m)	787(m)
		720(s)	756(s)	758(s)	757(s)	757(s)	755(s)
			712(s)	714(s)	708(s)	710(s)	698(s)
$\delta(O-Ge-O)$	462(m)	470(m)	463(m)	465(m)	464(m)	470(m)	465(m)
		446(m)	445(m)	446(m)	445(m)	446(m)	445(m)

	$K_{13}Ln(GeW_{11}O_{39})_2$					
	Eu	Gd	Tb	Dy	Tm	Yb
$\nu_{as}(W-O_d)$	950(s)	497(s)	948(s)	944(s)	945(s)	944(s)
$\nu_{as}(W-O_b-W)$	884(s)	879(s)	885(s)	876(s)	881(s)	876(s)
	818(s)	819(s)	821(s)	822(s)	824(s)	823(s)
$\nu_{as}(Ge-O)$						
	524(m)	521(m)	533(m)	533(m)	532(m)	530(m)
$\nu_{as}(W-O_c-W)$	794(m)	788(m)	792(m)	791(m)	793(m)	786(m)
	758(s)	762(s)	765(s)	758(s)	758(s)	757(s)
	716(s)	716(s)	718(s)	710(s)	712(s)	717(s)
$\delta(O-Ge-O)$	459(m)	465(m)	463(m)	461(m)	469(m)	457(m)
	443(m)	448(m)	442(m)	443(m)	447(m)	440(m)

[a] The data are from ref. 10. [b] α-$K_8(GeW_{11}O_{39})\cdot 12H_2O$ was prepared according to ref. 3.

11-series anions the change of structural symmetry and of charge on the anions are reflected in their IR spectra, see Table II.

Decrease of stretching vibration frequencies

It can be seen that the wavenumber of the main bands of α-$GeW_{12}O_{40}{}^{4-}$ decreases to some extent in α-$GeW_{11}O_{39}{}^{8-}$ and $[Ln(GeW_{11}O_{39})_2]^{13-}$, particularly for the individual stretching mode of $\nu_{as}(W-O_d)$, which is not affected by the anion symmetry. The frequency also decreases, that is, from 979 to 958 and 947 ± 3 cm^{-1}. This shows that the structural change of heteropolyanion leads to more negative charge on the changed anion and some of this charge might well fill certain antibonding molecular orbitals of the α-$GeW_{11}O_{39}{}^{8-}$ and $[Ln(GeW_{11}O_{39})_2]^{13-}$ anions. Thus some bond force constants become smaller and vibration frequencies decrease.

Splitting of W–O$_b$–W, W–O$_c$–W bridge bond vibrations

The ν_{as}(W–O$_b$–W), which is at 880 cm^{-1} in α-GeW$_{12}$O$_{40}$$^{4-}$, is separated into 875 ± 5 and 810 ± 5 cm^{-1} in [Ln(GeW$_{11}$O$_{39}$)$_2$]$^{13-}$. This is the same as the case of ν_{as}(W–O$_c$–W) which is at 796 cm^{-1} and changes into 784, 756 and 712 cm^{-1}. This fact most probably results from the change of α-GeW$_{12}$O$_{40}$$^{4-}$ anion symmetry. We do not think that Ln atoms can make the α-GeW$_{11}$O$_{39}$$^{8-}$ anion recover the Td symmetry of α-GeW$_{12}$O$_{40}$.

Another result is that the absorptions at 815 and 784 cm^{-1} show a tendency to increasing frequencies going from La to Yb, see Fig. 1. This confirms that Ln^{3+} in [Ln(GeW$_{11}$O$_{39}$)]$^{13-}$ has an influence on the W–O$_b$–W and W–O$_c$–W bonds through the Ln–O bond.

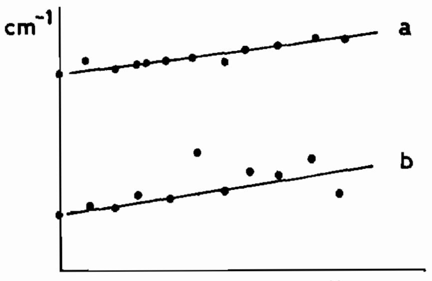

Fig. 1. The variation of wavenumber with lanthanide atomic number in the IR spectra of the compounds; (a) ν_{as}(W–O$_b$–W) at 815 cm^{-1} to 823 cm^{-1}, (b) ν_{as}(W–O$_c$–W) at 784 cm^{-1} to 786 cm^{-1}.

Splitting of the bending vibration of the GeO$_4$ tetrahedron in α-GeW$_{12}$O$_{40}$$^{4-}$

In the case of δ(O–Ge–O), this lies at 462 cm^{-1} in α-GeW$_{12}$O$_{40}$$^{4-}$. However it appears as two distinct bonds, see Table II. Contrary to the bridge bonds of W–O$_b$–W and W–O$_c$–W, δ(O–Ge–O) does not vary with an increase in the atomic number of Ln. This is possibly due to the fact that the ionic radia of Ln^{3+} (1.06–0.848 Å) are larger than that of W^{6+} (0.62 Å), thus Ln^{3+} cannot occupy the position of the tungsten atom which has been removed from the Keggin structure of α-GeW$_{12}$O$_{40}$$^{4-}$ after α-GeW$_{11}$O$_{39}$$^{8-}$ is formed. Therefore Ln^{3+} is not expected to form a bond with one of the four oxygen atoms in the GeO$_4$ tetrahedron. So the lanthanides in Ln(GeW$_{11}$O$_{39}$)$_2$$^{13-}$ only cause the change of the δ(O–Ge–O) bending vibration mode, not the 'purple shift' of the IR band.

As for ν_{as}(Ge–O), we think it could be hidden by the ν_{as}(W–O$_b$–W) band near 815 cm^{-1}.

X-ray Powder Diffraction

K$_{13}$[Ln(GeW$_{11}$O$_{39}$)$_2$]·nH$_2$O show basically identical diffraction patterns. The single crystal determination for the compounds is in process.

Figure 2 illustrates the difference between the pattern of α-K$_8$(GeW$_{11}$O$_{39}$)·12H$_2$O and K$_{13}$[Ce(GeW$_{11}$O$_{39}$)$_2$]·11H$_2$O. We calculated the observed powder diffraction data of K$_8$(GeW$_{11}$O$_{39}$)·12H$_2$O. The result is that the α-K$_8$(GeW$_{11}$O$_{39}$)·12H$_2$O belongs to the cubic system and the parameter a equals 10.70 Å which does not agree with the result of 21.32 Å [14]. However, it is very close to the result for α-K$_8$(SiW$_{11}$O$_{39}$)·12H$_2$O which has a parameter a = 10.55 Å [15].

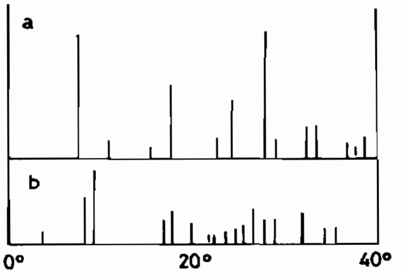

Fig. 2. The X-ray powder diffraction patterns of GeW$_{11}$ (a) and Ce(GeW$_{11}$)$_2$ (b).

The extent of the difference between K$_8$(GeW$_{11}$O$_{39}$)·12H$_2$O and K$_{13}$[Ce(GeW$_{11}$O$_{39}$)$_2$]·11H$_2$O is beyond that between K$_8$(SiW$_{11}$O$_{39}$)·12H$_2$O and KnSiZW$_{11}$O$_{39}$ (n = 5, 6; Z = Mn, Fe, Co, Ni, Zn) [16]. It can be predicated from Fig. 2 that the crystal symmetry of the [Ln(GeW$_{11}$O$_{39}$)$_2$]$^{13-}$ anion would be very low. From the fact that the composition of [Ln(GeW$_{11}$O$_{39}$)$_2$]$^{13-}$ and [U(GeW$_{11}$O$_{39}$)$_2$]$^{12-}$ and the ionic radii of Ln^{3+} and U^{4+} (0.97 Å) are very close to each other, it can be inferred that [Ln(GeW$_{11}$O$_{39}$)$_2$]$^{13-}$ anion structure would be similar to that of [U(GeW$_{11}$O$_{39}$)$_2$]$^{12-}$ which is triclinic, $P\bar{1}$ space group [17], and the coordination number of Ln^{3+} in the anions would be eight.

XPS

The XPS data of Ln, W and O elements in H$_4$GeW$_{12}$O$_{40}$, K$_8$GeW$_{11}$O$_{39}$ and K$_{13}$[Ln(GeW$_{11}$O$_{39}$)$_2$] are listed in Table III.

The inner shell electron bound energy of W$_{4f(5/2)}$, W$_{4f(7/2)}$ and O$_{1s(1/2)}$ in α-K$_8$GeW$_{11}$O$_{39}$·12H$_2$O is lower than that in α-H$_4$GeW$_{12}$O$_{40}$·nH$_2$O(W$_{4f(5/2)}$; 38.5 → 37.8; W$_{4f(7/2)}$: 36.5 → 35.7; O$_{1s}$: 531.6 → 531.0). This result shows that the structural change of anion α-GeW$_{12}$O$_{40}$$^{4-}$ to α-GeW$_{11}$O$_{39}$$^{8-}$ leads to an increase in negative charge (from −4 to −8), and these negative charges are added to the tungsten and oxygen atoms, therefore the energy of W$_{4f(5/2)}$, W$_{4f(7/2)}$ and O$_{1s(1/2)}$ decreases.

Ln$_{3d(5/2)}$ or Ln$_{4d(5/2)}$ in [Ln(GeW$_{11}$O$_{39}$)$_2$]$^{13-}$ is lower than that in the lanthanide nitrates, from 0.1 to 3.6 eV. This fact indicates that there is more electron

TABLE III. The Electronic Bound Energy of Ln, W and O Elements

	$Ln_{3d(5/2)}$	$Ln_{4d(5/2)}$	$W_{4f(5/2)}$	$W_{4f(7/2)}$	$O_{1s(1/2)}$
$K_{13}[La(GeW_{11}O_{39})_2]\cdot 14H_2O$	835.6 (836.5)[a]		37.8	35.7	530.9
$K_{13}[Ce(GeW_{11}O_{39})_2]\cdot 11H_2O$	885.5 (887.0)		37.9	35.8	531.0
$K_{13}[Pr(GeW_{11}O_{39})_2]\cdot 10H_2O$	934.7 (934.8)		37.9	35.8	530.9
$K_{13}[Nd(GeW_{11}O_{39})_2]\cdot 11H_2O$	982.6 (983.8)		37.9	35.8	530.8
$K_{13}[Sm(GeW_{11}O_{39})_2]\cdot 18H_2O$	1082.3 (1084.8)		37.8	35.7	530.9
$K_{13}[Eu(GeW_{11}O_{39})_2]\cdot 28H_2O$	1134.4 (1135.7)		38.0	36.0	531.0
$K_{13}[Gd(GeW_{11}O_{39})_2]\cdot 25H_2O$		141.7 (144.1)	37.9	35.9	531.0
$K_{13}[Dy(GeW_{11}O_{39})_2]\cdot 21H_2O$		154.4 (158.8)	37.8	36.0	531.0
$K_{13}[Tm(GeW_{11}O_{39})_2]\cdot 29H_2O$		184.8	37.9	35.9	531.1
$K_{13}[Yb(GeW_{11}O_{39})_2]\cdot 41H_2O$		185.4	37.8	36.0	531.1
$K_8GeW_{11}O_{39}\cdot 12H_2O$			37.8	35.7	531.0
$K_4GeW_{12}O_{40}\cdot xH_2O$			38.5	36.5	531.6

[a]The values of lanthanide nitrates.

TABLE IV. Magnetic Measurements Data

	χ_g	μ_{eff} (BM)
$K_{13}[Ce(GeW_{11}O_{39})_2]\cdot 11H_2O$	0.2603×10^{-6}	2.48 (2.56)[a]
$K_{13}[Pr(GeW_{11}O_{39})_2]\cdot 10H_2O$	0.7315×10^{-6}	3.62 (3.62)
$K_{13}[Nd(GeW_{11}O_{39})_2]\cdot 11H_2O$	0.5999×10^{-6}	3.36 (3.68)
$K_{13}[Sm(GeW_{11}O_{39})_2]\cdot 18H_2O$	0.0015×10^{-6}	1.52 (1.55)
$K_{13}[Eu(GeW_{11}O_{39})_2]\cdot 28H_2O$	0.6068×10^{-6}	3.29 (3.40)
$K_{13}[Gd(GeW_{11}O_{39})_2]\cdot 25H_2O$	4.0189×10^{-6}	7.97 (7.94)
$K_{13}[Tb(GeW_{11}O_{39})_2]\cdot 6H_2O$	6.047×10^{-6}	9.49 (9.70)
$K_{13}[Dy(GeW_{11}O_{39})_2]\cdot 21H_2O$	6.858×10^{-6}	10.3 (10.66)
$K_{13}[Tm(GeW_{11}O_{39})_2]\cdot 29H_2O$	3.463×10^{-6}	7.46 (7.60)
$K_{13}[Yb(GeW_{11}O_{39})_2]\cdot 41H_2O$	0.961×10^{-6}	4.11 (4.50)

[a]Values from Van Vleck.

density around the Ln nuclei, arising from the transfer of part of the electron pairs from the oxygen in $\alpha\text{-}GeW_{11}O_{39}{}^{8-}$ to Ln^{3+}. This shows the Ln–O bond is characteristic of coordination in the $[Ln(GeW_{11}O_{39})_2]^{13-}$ anion. In the case when the coordination number of Ln is less than nine, thus the bonding of 4f electrons can be neglected [18], it can be assumed that the lanthanides would form a covalent coordinate bond with oxygen by their vacant 5d orbital.

Magnetic Measurements

The magnetic susceptibility of the lanthanides in the complexes was determined by the Faraday method at room temperature and the effective magnetic moment calculated, see Table IV.

The observed values of magnetic moments are very close to ones by Van Vleck, showing that the lanthanides in the compounds remain in the +3 oxidation state and the 4f electrons are little influenced by the ligand field of the two $[GeW_{11}O_{39}]^{8-}$ groups.

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