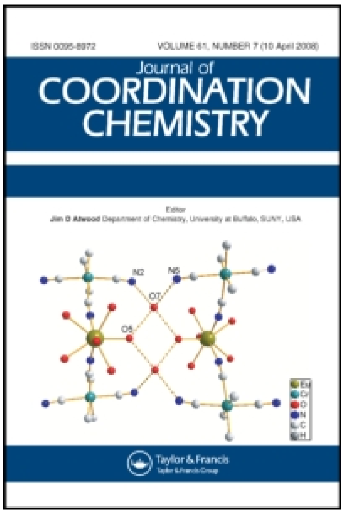

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Synthesis and Crystal Structure of $K_{6.5}H_{4.5}[CeK_2(SiW_{11}O_{39})_2]\cdot 26H_2O$

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SYNTHESIS AND CRYSTAL STRUCTURE OF $K_{6.5}H_{4.5}[CeK_2(SiW_{11}O_{39})_2] \cdot 26H_2O$

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The title compound, $K_{6.5}H_{4.5}[CeK_2(SiW_{11}O_{39})_2] \cdot 26H_2O$ was prepared and its structure characterized by IR and single crystal X-ray structural analysis. It belongs to triclinic, space group $P1$ with $a = 12.719(3)$ Å, $b = 16.658(4)$ Å, $c = 23.075(6)$ Å, $\alpha = 94.41(2)°$, $\beta = 98.90(2)°$, $\gamma = 92.40(2)°$; $V = 4809(2)$ Å^{-3}, $Z = 2$, $Dc = 4.344\,g\,cm^{-3}$, $\mu = 27.170\,mm^{-1}$, $F(000) = 5519$. The results show that the cerium and two potassium atoms link the two anionic units $SiW_{11}O_{39}^{8-}$ through O–Ce–O and O–K–O bridges and construct the double 1 : 11 series heteropolytungstate. Furthermore, cerium is coordinated to eight oxygen atoms (four O_c and four O_b) from two tetradentate $SiW_{11}O_{39}^{8-}$ ligands forming a square anti-prism. The coordination numbers for K1 and K2 are 8 and 7, respectively.

Keywords: Tungstosilic heteropoly complex; Cerium; Synthesis; Crystal structure

INTRODUCTION

Polyoxotungstates with the Keggin structure have attracted considerable attention because of their potential applications in catalysis, medicine and other areas [1,2]. This class of compounds includes the parent Keggin anions, $[XW_{12}O_{40}]^{n-}$ ($X = P$, As, B, Si, Ge, or other metals), their lacunar derivatives $[XW_{11}O_{39}]^{(n+4)-}$, and metal complexes of the latter $[XW_{11}O_{39}M^{m+}(H_2O)]^{(n+4-m)-}$ [3]. Thus design and synthesis of new heteropoly complexes is important. The monovacant heteropoly complex [L] of the Keggin structure is an inorganic ligand. It has strong coordination ability and can form a 1 : 1 complex [ML] with transition metal ions and some main group elements [M] having small radii. It can also form 1 : 2 complexes [ML_2] with lanthanides or actinides of large radius. Because such compounds have special structures, large formula weights and good catalytic activity [4–6], they have received considerable attention. Though the double 1 : 11 series heteropoly complexes have been widely studied, single crystal structures have been rarely reported to date.

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Since the compounds $K_{13}[Ln(SiW_{11}O_{39})_2] \cdot nH_2O$ and $K_{11}[Ln(PW_{11}O_{39})_2] \cdot nH_2O$ were first synthesized by Peacock and Weakly [4] in 1971, complexes, $K_m[Ln(XW_{11}O_{39})_2] \cdot nH_2O$ (X = Ge, As, B), have been reported frequently [7] and their syntheses, physico-chemical properties and structural characterizations [8–11] have been widely studied. However, their single crystal structures have rarely been reported except for $K_{11}H_2[Dy(SiW_{11}O_{39})_2] \cdot 29H_2O$ [12] and $K_{4.5}Na_4(H_3O)_{3.5}[Ce(SiW_{11}O_{39})_2] \cdot 23H_2O$ [13]. In this paper, we report the single crystal structure of $K_{6.5}H_{4.5}[CeK_2(SiW_{11}O_{39})_2] \cdot 26H_2O$.

EXPERIMENTAL

Materials

All chemicals used for synthesis were reagent grade. $Ce(NO_3)_3 \cdot 6H_2O$ and AcOK were used as received from commercial sources. $H_4SiW_{12}O_{40} \cdot nH_2O$ was prepared by the literature method [14]. IR spectra of samples were obtained as KBr pellets on a Nicolet 170 SXFT-IR spectrometer.

Preparation of the Title Complex

Following a literature procedure [4]; $H_4SiW_{12}O_{40}$ (50 g) in water (100 mL; 90 °C) was treated successively, dropwise, with warm concentrated solutions of $Ce(NO_3) \cdot 6H_2O$ (3.2 g) and AcOK (40 g, pH = 7). The brown solution was stirred at 90°C until the suspension of $K_8SiW_{11}O_{39}$ dissolved (2–3 min). On cooling to 5°C a brown oil separated and crystallized when set aside at 5°C. The compound was recrystallized three times from hot water, and good quality brown single crystals were obtained.

X-ray Structure Determination of the Title Compound

The structure determination for the title compound (0.44 mm × 0.30 mm × 0.24 mm) was performed on a P4 four-circle diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature 293(2) K. A total of 16953 independent reflections ($R_{int} = 0.0582$) were collected in the range of $3.16° \leq 2\theta \leq 50.02°$ with $0 \leq h \leq 15$, $-19 \leq k \leq 19$, $-27 \leq l \leq 27$ by ω–2θ scan type; all these independent reflections were used for refinement. The intensities were corrected by Lorentz–polarization factors and empirical absorption. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXTL-97 program [15]. All non-hydrogen atoms were refined anistropically. Hydrogen atoms were added according to theoretical models. The maximum and minimum peaks on the final difference Fourier map are +7.147 and $-7.137\,e\,Å^{-3}$. Relevant crystallographic data and structure determination parameters are listed in Table I. Selected bond distances and angles are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

X-ray Crystal Structure of the Title Compound

The title compound consists of a $[CeK_2(SiW_{11}O_{39})_2]^{11-}$ heteropolyanion. There are also 26 free water molecules and several K^+ and H^+ cations present in the complex.

TABLE I Summary of crystallographic data of the title compound.

Molecular formula	$H_{56.5}CeK_{8.5}O_{104}Si_2W_{22}$
Molecular weight	6294.27
Crystal system	Triclinic
Space group	$P1$
a (Å)	12.719(3)
b (Å)	16.658(4)
c (Å)	23.075(6)
α (°)	94.41(2)
β (°)	98.90(2)
γ (°)	92.40 (2)
Z	2
V (Å^3)	4809(2)
Wavelength (Å)	$\lambda = 0.71073$
D_{calcd} (g cm^{-3})	4.344
R_{int}	0.0582
Absorption coefficient (mm^{-1})	27.170
Goodness-of-fit on	0.979
Final R indices ($I > 2.0\,\sigma(I)$)	$R = 0.0777$, $Rw = 0.1885$
R indices (all data)	$R = 0.1118$, $Rw = 0.2025$

As shown in Fig. 1, the structure of $[CeK_2(SiW_{11}O_{39})_2]^{11-}$ is composed of one cerium atom, two potassium atoms (K1 and K2) and two symmetric units of $SiW_{11}O_{39}^{8-}$ [$Si(1)W_{11}O_{39}^{8-}$ and $Si(2)W_{11}O_{39}^{8-}$]. The two potassium and cerium atoms link the two ligands $Si(1)W_{11}O_{39}^{8-}$ and $Si(2)W_{11}O_{39}^{8-}$ by O–K–O and O–Ce–O bridges and the coordination numbers of K1 and K2 are 8 and 7, respectively. The different coordination environments can be described as follows: the oxygen atoms coordinated to K1 can be divided into three groups: terminal oxygen atoms (K–O = 3.28(5) Å), doubly bridging atoms (K–O = 2.82(3) Å) and triply bridging oxygen atoms (K–O = 2.83(2)–3.03(2) Å). However, the oxygen atoms coordinated to K2 can only be grouped into two sets: terminal oxygen atoms (K–O = 2.82(4) Å) and triply bridging oxygen atoms (K–O = 2.85(3)–3.39(3) Å). Cerium is coordinated to eight oxygen atoms (four O_b [16] and four O_c [16]), which are from the two tetradentate $SiW_{11}O_{39}^{8-}$ ligands and form a square antiprism. The Ce–O bond lengths range from 2.43(3) to 2.50(2) Å (average 2.46 Å). The Ce–O_b and Ce–O_c bond lengths are in the range of 2.43(3)–2.48(2) Å and 2.45(2)–2.50(2) Å and their mean bond lengths are 2.45 and 2.47 Å, respectively. The results show that Ce^{3+} has a stronger interaction with corner-shared oxygen than that with edge-shared oxygen. In the anionic unit $Si(1)W_{11}O_{39}^{8-}$, the W–O bond distances are in the range of 1.66(3)–1.77(2) Å for the terminal oxygen, 1.72(2)–2.13(2) Å for the bridging oxygen, and 2.24(2)–2.41(2) Å for the oxygen of the SiO_4 tetrahedron. The shortest W–O_t [16] bond length is W(5)–O(24), 1.65(2) Å and the longest W–O bond is W(7)–O(11), 2.41(2) Å. In the $Si(1)O_4$ tetrahedron, the Si(1)–O bond lengths of Si(1)–O(5), Si(1)–O(11), Si(1)–O(15), Si(1)–O(38) are 1.59(2), 1.60(2), 1.64(2) and 1.65(2) Å, respectively. Their mean distance, 1.62(2) Å, is 0.01 Å shorter than that of previous studies [17]. The O–Si(1)–O angles vary from 106.3(12)° to 111.3(12)° with an average value of 109.45°, which is 0.25° larger than in the literature [17]. The results indicate that WO_6 octahedra and $Si(1)O_4$ tetrahedra are distorted greatly in the anion. Similarly, in another anionic unit of $Si(2)W_{11}O_{39}^{8-}$, the bond lengths of W–O_t, W–$O_{b,c}$, W–O_a [16] are in the range of 1.65(2)–1.74(2) Å, 1.73(2)–2.34(2) Å, and 2.208(19)–2.44(2) Å, respectively. The W(13)–O(50) (1.65(2) Å) and W(18)–O(49) (2.41(2) Å) bonds are the shortest and longest, respectively.

TABLE II Selected bond lengths (Å) of the title compound.

W(1)–O(3)	2.06(3)	W(1)–O(2)	1.95(2)
W(1)–O(4)	1.87(3)	W(1)–O(1)	1.72(2)
W(2)–O(7)	1.78(2)	W(2)–O(9)	2.09(2)
W(2)–O(8)	1.89(2)	W(2)–O(10)	1.96(2)
W(3)–O(8)	1.93(2)	W(3)–O(14)	1.94(2)
W(3)–O(13)	1.77(2)	W(3)–O(17)	2.13(2)
W(4)–O(19)	1.95(2)	W(4)–O(2)	1.90(2)
W(4)–O(20)	2.08(2)	W(4)–O(18)	1.76(2)
W(5)–O(19)	1.89(2)	W(5)–O(14)	1.94(2)
W(5)–O(23)	1.91(2)	W(5)–O(22)	1.92(3)
W(6)–O(25)	1.88(2)	W(6)–O(17)	1.79(2)
W(6)–O(26)	1.96(2)	W(6)–O(22)	1.95(3)
W(7)–O(29)	1.91(2)	W(7)–O(9)	1.80(2)
W(7)–O(25)	1.93(2)	W(7)–O(28)	1.86(3)
W(8)–O(4)	1.92(3)	W(8)–O(10)	1.919(19)
W(8)–O(31)	1.92(2)	W(8)–O(28)	1.90(3)
W(9)–O(3)	1.85(3)	W(9)–O(33)	1.98(3)
W(9)–O(31)	1.89(2)	W(9)–O(34)	1.94(2)
W(10)–O(20)	1.82(2)	W(10)–O(34)	1.92(2)
W(10)–O(23)	1.96(2)	W(10)–O(36)	1.98(3)
W(11)–O(26)	1.90(2)	W(11)–O(33)	1.89(2)
W(11)–O(29)	1.95(2)	W(11)–O(36)	1.91(3)
W(12)–O(41)	1.89(2)	W(12)–O(42)	2.07(2)
W(12)–O(40)	1.78(2)	W(12)–O(43)	2.02(2)
W(13)–O(46)	1.75(2)	W(13)–O(47)	1.95(2)
W(13)–O(41)	1.93(2)	W(13)–O(48)	2.10(2)
W(14)–O(53)	2.16(2)	W(14)–O(51)	1.78(2)
W(14)–O(54)	1.96(2)	W(14)–O(52)	1.95(2)
W(15)–O(58)	1.92(2)	W(15)–O(52)	1.91(3)
W(15)–O(59)	2.13(2)	W(15)–O(57)	1.80(2)
W(16)–O(58)	1.92(2)	W(16)–O(43)	1.88(2)
W(16)–O(62)	1.97(2)	W(16)–O(61)	1.957(19)
W(17)–O(64)	1.89(3)	W(17)–O(42)	1.81(2)
W(17)–O(65)	1.94(3)	W(17)–O(61)	1.95(2)
W(18)–O(64)	1.91(3)	W(18)–O(48)	1.80(2)
W(18)–O(68)	1.96(3)	W(18)–O(67)	1.90(2)
W(19)–O(54)	1.86(2)	W(19)–O(47)	1.90(2)
W(19)–O(70)	1.91(3)	W(19)–O(67)	1.94(2)
W(20)–O(70)	1.91(3)	W(20)–O(72)	1.89(2)
W(20)–O(53)	1.73(2)	W(20)–O(73)	1.89(2)
W(21)–O(59)	1.78(2)	W(21)–O(72)	1.97(2)
W(21)–O(62)	1.85(2)	W(21)–O(76)	1.999(18)
W(22)–O(68)	1.92(3)	W(22)–O(73)	1.97(3)
W(22)–O(65)	1.88(3)	W(22)–O(76)	1.90(2)
Si(1)–O(5)	1.59(2)	Si(1)–O(11)	1.60(2)
Si(1)–O(15)	1.64(2)	Si(1)–O(38)	1.65(2)
Si(2)–O(44)	1.60(2)	Si(2)–O(49)	1.59(2)
Si(2)–O(55)	1.63(2)	Si(2)–O(74)	1.630(19)
Ce–O(7)	2.43(3)	Ce–O(40)	2.442(2)
Ce–O(57)	2.45(2)	Ce–O(13)	2.45(2)
Ce–O(51)	2.46(2)	Ce–O(1)	2.47(2)
Ce–O(46)	2.48(2)	Ce–O(18)	2.50(2)
Ce–K(1)	4.148(9)	Ce–K(2)	4.183(12)
K(1)–O(45)	2.82(3)	K(1)–O(87)	2.82(4)
K(1)–O(24)#4	2.79(3)	K(1)–O(14)	2.90(2)
K(1)–O(19)	2.83(3)	K(1)–O(40)	3.00(2)
K(1)–O(18)	2.96(2)	K(1)–O(93)	3.28(5)
K(1)–O(13)	3.03(2)	K(2)–O(1)	3.37(3)
K(2)–O(99)	2.83(3)	K(2)–O(10)	3.09(2)
K(2)–O(51)	2.85(3)	K(2)–O(4)	3.39(3)
K(2)–O(81)	2.81(3)	K(2)–O(71)#2	2.84(3)
K(2)–O(7)	3.06(3)	K(2)–O(99)#2	2.96(4)
K(2)–W(19) #2	3.932(11)		

Symmetry transformation used to generate equivalent atom: #2 $-x$-1, $-y$, $-z-1$ #4 $-x-1$, $-y$, $-z$.

TABLE III Selected bond angles (°) of the title compound.

O(13)–Ce–O(1)	112.7(7)	O(7)–Ce–O(13)	70.8(7)
O(7)–Ce–O(1)	73.2(7)	O(7)–Ce–O(18)	113.7(8)
O(18)–Ce–O(1)	72.8(7)	O(13)–Ce–O(7)	70.8(7)
O(40)–Ce–O(51)	115.1(7)	O(46)–Ce–O(51)	70.3(7)
O(57)–Ce–O(46)	113.5(7)	O(40)–Ce–O(57)	74.9(7)
O(40)–Ce–O(46)	72.2(8)	O(57)–Ce–O(51)	74.4(8)
O(5)–Si(1)–O(15)	113.4(12)	O(15)–Si(1)–O(11)	106.3(12)
O(15)–Si(1)–O(38)	107.9(12)	O(5)–Si(1)–O(11)	111.3(12)
O(5)–Si(1)–O(38)	109.5(12)	O(38)–Si(1)–O(11)	108.3(12)
O(49)–Si(2)–O(44)	108.3(12)	O(49)–Si(2)O(74)	108.0(12)
O(49)–Si(2)–O(55)	110.3(12)	O(44)–Si(2)–O(74)	108.8(12)
O(44)–Si(2)–O(55)	112.2(12)	O(74)–Si(2)–O(55)	109.2(11)

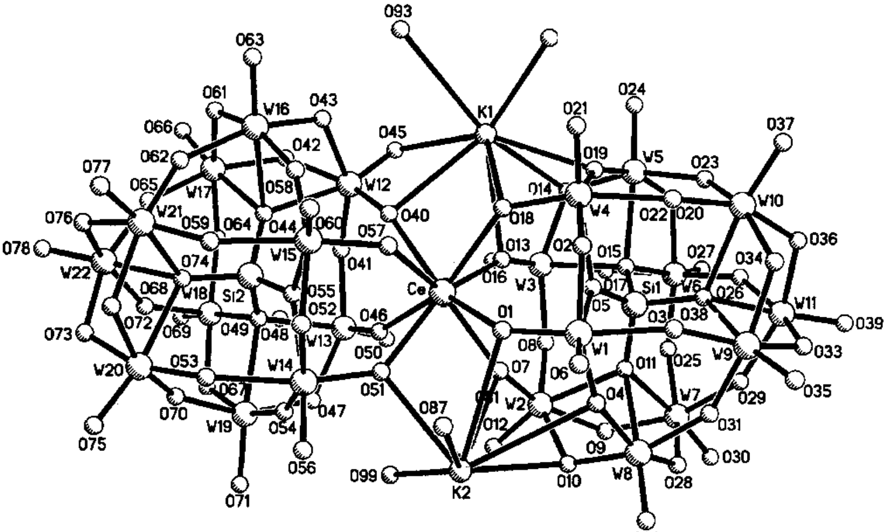

FIGURE 1 Anionic structure of the title compound.

The Si(2)–O_a bond lengths range from 1.59(2) to 1.630(19) Å and its average bond length is 1.63 Å, while the O–Si(2)–O bond angle is in the range of 108.0(12)–112.2(11)° with a mean bond angle of 109.46°, 0.26° larger than previously reported [17]. These data show that WO_6 octahedra and $Si(2)O_4$ tetrahedra are distorted severely in $Si(2)W_{11}O_{39}^{8-}$, indicating a strong interaction between the cerium atom and the heteropolyanion $SiW_{11}O_{39}^{8-}$. Furthermore, the distortion relates to the position of WO_6 octahedra in the anion. For WO_6 octahedra joined directly with the cerium atom, the W–O bonds distances (O: coordinated to Ce atom) are less than the average bond length. For example, in the compound $K_{6.5}H_{4.5}[CeK_2(SiW_{11}O_{39})_2]\cdot 26H_2O$, the mean value for W–$O_c$ and W–O_b are 1.92 and 2.00 Å, respectively. However, in the $Si(1)W_{11}O_{39}^{8-}$ ligand, the W–O_c bond lengths for W(4)–O(18) and W(1)–O(1) are 1.76(2) and 1.72(2) Å and the W–O_b bond distances for W(3)–O(13) and W(2)–O(7) are 1.77(2) and 1.78(2) Å, less than the average bond length. Those WO_6 octahedra joined indirectly with the cerium atom are less affected with increasing distance between the WO_6 octahedron and cerium. The anionic structure of the title compound is similar to that of $K_{4.5}Na_4(H_3O)_{3.5}[Ce(SiW_{11}O_{39})_2] \cdot 23H_2O$ [13]. Both complexes include two $SiW_{11}O_{39}^{8-}$ units, which are located on two sides of Ce. Although the two cerium atoms are coordinated to eight oxygen atoms and form a square antiprism, they have obvious differences. First, in the anion $[Ce(SiW_{11}O_{39})_2]^{12-}$, the charge of Ce is +4 due to its starting material $(NH_4)_2Ce(NO_3)_6$. Second, although the two complexes are prepared at room temperature, their syntheses are different. The complex, $K_{4.5}Na_4(H_3O)_{3.5}[Ce(SiW_{11}O_{39})_2] \cdot 23H_2O$ [13], is obtained from reaction of the isolated $SiW_{11}O_{39}^{8-}$ compound, $(NH_4)_2Ce(NO_3)_6$ and KCl, while the title compound is prepared from the "template" reaction of $H_4SiW_{12}O_{40}$, $CeCl_3 \cdot 6H_2O$ and AcOK. Third, the bond distance ranges of W–O_t, W–$O_{b,c}$, W–O_a are narrower than for the title compound. In addition, the Ce–O bond distances are shorter than for $K_{6.5}H_{4.5}[CeK_2(SiW_{11}O_{39})_2] \cdot 26H_2O$. Unexpectedly, two K atoms are found in the heteropolyanion $[CeK_2(SiW_{11}O_{39})_2]^{11-}$, different from the literature [4]. This indicates that the experiment is affected by reaction conditions, such as temperature, reaction time, pH and so on.

IR Spectrum

Comparing the IR spectrum of the title compound with that of $H_4SiW_{12}O_{40} \cdot nH_2O$ [17], the vibrational bands of both Si–O_a, and W=O_t of the title compound have a red shift from 926 to 905 cm^{-1} and from 980 to 950 cm^{-1}, respectively. The vibrational band of W=O_t has a red shift because the structural change of the anion places negative charge on the anionic surface and the additional negative charge occupies the antibonding orbital of the anion, $SiW_{11}O_{39}^{8-}$, reducing the force constant and the vibrational frequency. The vibrational band of the W–O_b bond is split from 881 cm^{-1} to 887 and 830 cm^{-1}. The W–O_c band is split from 785 cm^{-1} to 767 and 722 cm^{-1}. The results show that the Si–O_a, W=O_t and W–O_c bonds are all weakened in the title compound and the anion has a large distortion due to the interaction between the Ce atom and heteropolyanion, $SiW_{11}O_{39}^{8-}$.

Acknowledgments

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[16] O_a refer to oxygen atoms connecting the Si (Ge, P) and Mo (W) atoms; O_b refers to atoms located in the shared corners between two W_3O_{13} unit; O_c refers to oxygen atoms connecting edge-sharing MoO_6 octahedra in the Mo_3O_{13} units; O_t are the terminal oxygen atoms.

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