Pergamon

PII: S0277-5387(97)00182-4

Polyhedron Vol. 16, No. 23, pp. 3985–3989, 1997

0277-5387/97 $17.00+0.00

Synthesis, structure and properties of undecatungstozincate containing 3A elements

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(Received 23 October 1996; accepted 7 May 1997)

Abstract—New compounds $K_aH_b[ZnW_{11}O_{39}M(H_2O)]\cdot xH_2O$ (M = Al, Ga or In) were prepared and characterized by elemental analysis, IR and UV and ^{27}Al NMR spectroscopy, electrochemistry and X-ray crystallography. In the crystals of $K_6H_3[ZnW_{11}AlO_{40}]\cdot 9.5H_2O$, the anion is of the α-type Keggin structure with C_s symmetry. The Al and W atoms are statistically distributed in the crystal. © 1997 Elsevier Science Ltd

Keywords: Keggin structure; heteropolyanion; synthesis; 3A elements; undecatungstozincate.

The remarkable properties and structures of polyoxoanions of molybdenum, tungsten, and vanadium continue to stimulate investigation with respect to their widespread applications [1]. Recent studies have shown that heteropolytungstates containing 3A elements are efficient catalysts [2]. After the first example of a heteropoly complex containing 3A elements was reported by Tourne [3], other heteropoly complexes containing 3A elements have been prepared and discussed [4,5,6]. However, there have been few reports on the structure of 3A element monosubstituted heteropolyanions. Here we report the synthesis, structure and properties of undecatungstozincates containing 3A elements.

EXPERIMENTAL

Reagents and apparatus

All reagents were of analytical or guaranteed quality. ^{27}Al NMR was recorded at 16.6 MHz on a Unity-400 spectrometer using a 10 mm diameter NMR tube at 20°C. Chemical shifts was referenced to $Al(NO_3)_3\cdot 6H_2O$ in D_2O. IR spectra were recorded on an Alpha Centauri FTIR spectrometer (4000–200 cm^{-1} range) as KBr pellets. UV spectra were recorded on a Beckman DU-8B spectrometer (solvent H_2O). Electrochemical measurements were made using a BAS-100A electrochemical analyser. Cyclic voltammetry measurements were performed using a hanging drop mercury working electrode and a SCE reference electrode. Crystal data were collected at 20°C on a Siemens P4 diffractometer with graphite-mono-chromated Mo Kα radiation ($\lambda = 0.7103$ Å). The structure was solved using SHELXTL-PLUS (Siemens) direct methods.

Preparation and analysis of complexes

$K_6H_3[ZnW_{11}AlO_{40}]\cdot 9.5H_2O$: Na_2WO_4 (36.3 g, 0.11 mol) was dissolved in H_2O (100 cm^3), and the pH of the solution was adjusted to 6.3 with glacial HOAc. $Zn(AC)_2\cdot 2H_2O$ (2.2 g, 0.01 mol) in H_2O (20 cm^3) was added at 80°C. After 30 min, the pH of the solution was readjusted to 4.8 and then $Al(NO_3)_3\cdot 6H_2O$ (3.8 g, 0.01 mol) in H_2O (20 cm^3) was added dropwise. the mixture was stirred at 80°C for an hour. After cooling, KCl (20 g) was added and the resulting white precipitate filtered off. Crystallization from warm water giving colorless rectangular crystals. Found: K, 7.6; Zn, 1.9; Al, 0.8; W, 64.8; H_2O, 5.6, Calc.: K, 7.4; Zn: 2.0; Al, 0.8; W, 64.0; H_2O 5.4%.

$K_6H[ZnW_{11}Ga(H_2O)O_{39}]\cdot 6H_2O$ was prepared using a similar procedure. Found: K, 7.3; Zn, 2.0; Ga, 2.3;

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W, 64.7; H_2O, 3.2, Calc: K, 7.5; Zn, 2.1; Ga, 2.2; W, 64.8; H_2O, 3.1%.

$K_5H_2[ZnW_{11}In(H_2O)O_{39}] \cdot 10H_2O$ was prepared as above. Found: K, 5.9; Zn, 2.2; In, 3.6; W, 61.7; H_2O, 6.2, Calc.: K, 6.1; Zn, 2.0; In, 3.6; W, 62.8; H_2O, 6.1%.

Chemical analyses for Zn, W, Al, Ga, and In were determined by ICP-AES spectroscopy. K was determined by atomic absorption spectroscopy. The water content was determined by thermogravimetry.

RESULTS AND DISCUSSION

The comparison of the IR absorption frequencies between $ZnW_{11}M$ and ZnW_{12} are listed in Table 1. The IR spectra of undecatungstozincates exhibit the following characteristics: (1) the IR spectra of all the complexes exhibit the four characteristic W—O(d), W—O(b)—W, W—O(c)—W and Zn—O(a) asymmetric stretching vibrational peaks for heteropolyanions with the Keggin structure, suggesting that the title heteropolyanion has the Keggin structure; (2) the replacement of 3A elements in the polyanions causes the vibrational peaks assigned to the W—O(c)—W to split compared with the peak of ZnW_{12}, this result is consistent with that of other mixed-type polyanions [8]; (3) the vibrational frequencies of W—O(d) bonds of the complexes decreased, this is due to an increase in negative charge on the polyanion.

As with all heteropolyanions exhibiting the Keggin structure, the characteristic O—W C.T. peaks of the title anion occur at about 255 nm in the UV spectra. In order to determine the structure of $ZnW_{11}M$ anions, the ^{27}Al NMR spectrum of $ZnW_{11}Al$ was obtained and the spectrum of the potassium salt of $ZnW_{11}Al$ anion is shown in Fig. 1. The ^{27}Al NMR shows one peak at 8.41 ppm and this indicates the Al atom in the heteropolyanion has the same coordination environment as that of $Al(H_2O)_6^{3+}$ [9,10]. so the Al atom must occupy the empty octahedral site of the ZnW_{11} anion.

Electrochemistry

The redox properties of $ZnW_{11}M$ anions were investigated by cyclic voltammographic and differential pulse voltammographic methods. Cyclic data and differential pulse potentials are listed in Tables 2 and 3, respectively. Figure 2 shows the diagram of cyclic voltammograms of $ZnW_{11}Ga$.

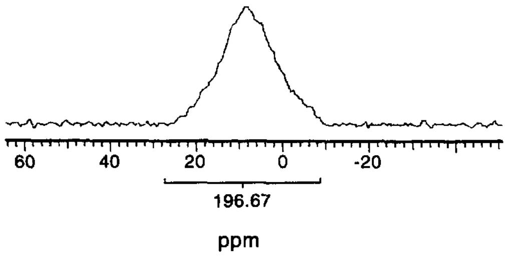

Fig. 1. ^{27}Al NMR spectrum of $ZnW_{11}Al$-K in D_2O, pH = 6.0.

It can be seen from these data (1) the redox processes involved the reduction of indium and tungsten; (2) electrochemical data show that all heteropolyanions underwent a two-step tungsten reduction process. A straight line is obtained by logarithm analysis in each of the two polarographic waves. The number of electrons involved in the reduction can be calculated to be two from the slope of the straight lines, showing that the title heteropolyanions all underwent a two-step, two-electron tungsten reduction process; (3) it is known that $\Delta Ep = 57\text{–}63/n$ (*n* stands for electron number) for a reversible process of electrode reaction and does not change obviously with scan rate. The ΔEp values of $ZnW_{11}Al$ and $ZnW_{11}Ga$ are close to the theoretical

Table 1. IR data for $ZnW_{11}M$

Assignment	$(TBA)_6ZnW_{12}O_{40}$ [7]	$ZnW_{11}Al$	$ZnW_{11}Ga$	$ZnW_{11}In$
ν as (W—O_d)	940s	935s	933s	931s
ν as (W—O_b—W)	874s	879s	877s	876s
ν as (W—O_c—W)	766vs	775vs	769vs	769vs
ν as (Zn—O_a)	550w	579w	580w	580w
ν as (O—Zn—O)	441m	443m	446m	445m

Table 2. Peak potentials of cyclic voltammograms at different scan rates for $ZnW_{11}M^a$

		I			II			III		
Complex	Scan rate	Epc	Epa	ΔEp(mv)	Epc	Epa	ΔEp(mv)	Epc	Epa	ΔEp(mv)
$ZnW_{11}Al$	100	−0.674	−0.637	37	−0.814	−0.770	44			
	200	−0.676	−0.639	37	−0.816	−0.776	40			
$ZnW_{11}Ga$	100	−0.648	−0.611	37	−0.793	−0.756	37			
	200	−0.651	−0.614	37	−0.795	−0.758	37			
$ZnW_{11}In$	100	−0.518	−0.491	20	−0.655	−0.603	52	−0.788	−0.743	45
	200	−0.522	−0.497	25	−0.657	−0.604	53	−0.790	−0.744	46

[a] All voltammograms in 1.0 mol dm^{-3} acetate buffer at pH = 4.7; 5×10^{-4} mol dm^{-3} heteropolyanion.

Table 3. Peak potentials of different pulse voltammograms for $ZnW_{11}M$ anions[a]

		Peak potentials (v)			
Complex	Peak pH	3.7	4.2	4.7	5.2
$ZnW_{11}Al$	1	−0.616	−0.672	−0.710	−0.748
	2	−0.808	−0.869	−0.901	−0.944
$ZnW_{11}Ga$	1	−0.504	−0.564	−0.600	−0.644
	2	−0.644	−0.700	−0.744	−0.800
$ZnW_{11}In$	1	−0.472	−0.474	−0.475	−0.478
	2	−0.604	−0.659	−0.690	−0.721
	3	−0.744	−0.752	−0.792	−0.833

[a] In 1.0 mol dm^{-3} acetate buffer and 5×10^{-4} mol dm^{-3} heteropolyanion.

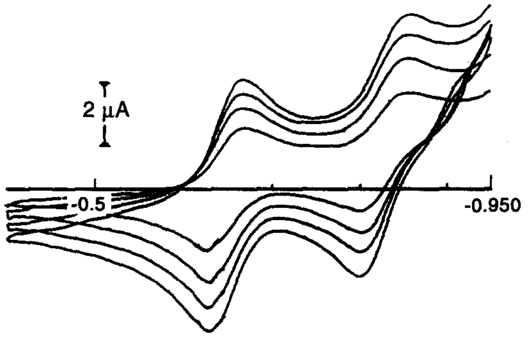

Fig. 2. Cyclic voltammograms of $ZnW_{11}Ga$.

value, so the tungsten reduction of $ZnW_{11}Al$ and $ZnW_{11}Ga$ can be considered to be reversible. Influenced by In, the first tungsten reduction of $ZnW_{11}In$ is a quasi-reversible reduction, the second is reversible; (4) the cathode peak potentials of two peaks shift to negative values with increase in the pH of the solution, implying that the reduction of heteropoly anions is accompanied by protonation. Plots of the peak potentials *vs* pH are linear, from the slope of E *vs* pH plots, it can be calculated that $m = 2$ (m stands for proton number) when $n = 2$, showing that two protons must be added to gain two electrons while the heteropolyanions are reduced. This prevents a charge build-up in the anion, that would otherwise be destabilized. Thus, the reduction process of tungsten in $[ZnW_{11}O_{39}M(H_2O)]^{7-}$ anions (Fig. 2) may be written as follows:

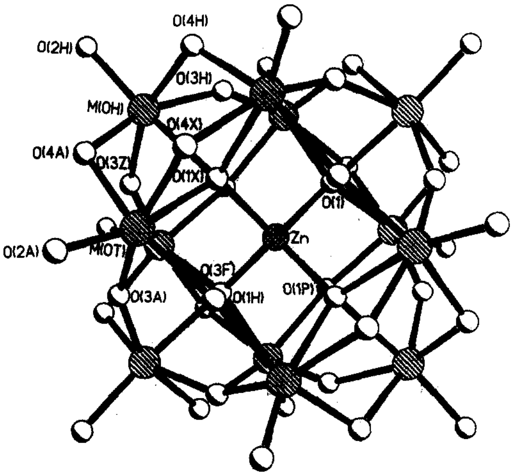

Fig. 3. Octahedron structure of $ZnW_{11}Al$. Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, y, -z+1/2$ #2 $x, -y+1/2, -z+1/2$ #3 $-x+1/2, -y+1/2, z$ #4 z, y, x #5 z, x, y #6 $z, -x+1/2, -y+1/2$ #7 $x, -z+1/2, -y+1/2$ #8 y, z, x, #9 $-z, x, y$ #10 $-z-x+1/2, -y+1/2$ #11 $-x, y, -z$, #12 $-x, y, z$ #13 $x, y, -z$ #14 $-z-x+1/2, y-1/2$ #15 $-y+1/2, -x+1/2, z$ #16 $-y+1/2, -z+1/2, x$ #17 y, x, z #18 $-y+1/2, -z, -x$).

$$[ZnW_{11}O_{39}M(H_2O)]^{7-} + 2e + 2H^+ \rightarrow [H_2ZnW_9W_2^VO_{39}M(H_2O)]^{7-}$$

$$[H_2ZnW_9W_2^VO_{39}M(H_2O)]^{7-} + 2e + 2H^+ \rightarrow [H_4ZnW_7W_4^VO_{39}M(H_2O)]^{7-}.$$

(5) the redox properties of $ZnW_{11}In$ are different from the complexes of Al and Ga. Compared with the polarographic behavior of $In(NO_3)_3 \cdot 4.5H_2O$, the first peak at -0.472 V can be assigned to the reduction of In^{3+} to In^+.

Crystallography

The crystallographic data and selected bond lengths and angles are given in Tables 4 and 5, respectively.

The structure of $ZnW_{11}Al$ in Fig. 3 shows the compound has the ideal Td($\bar{4}$3m) α-Keggin $XM_{12}O_{40}^{n-}$ anion structure, in which four M_3O_{13} groups constructed from three edge-shared MO_6 octahedra are linked together by sharing vertices of MO_6 around the central ZnO_4 tetrahedron ($M = 11/12W + 1/12Al$). There are four types of oxygen atoms in the anion: the internal oxygen O(a) atoms shared by the Zn atom and the M atoms (O(IX) in Fig. 3), the edge-shared oxygen O(c) atoms belong to two M atoms of the same M_3O_{13} group [O(4A) in Fig. 3], the corner-shared O(b) atoms bridging two M atoms of two M_3O_{13} group [O(3Z) in Fig. 3] and terminal O(d) atoms [O(2H) in Fig. 3]. The monosubstituted $ZnW_{11}Al$ anion has a Cs symmetry and Al atom may be sited in any one of the twelve positions. In the crystal, the orientation of the substituted atom is random, just like that of $SiW_{11}Ni$ [11] and the occupancy of the Al atom is 1/12.

Table 4. Crystallographic data

Formula	$K_6H_3[ZnW_{11}O_{40}Al] \cdot 9.5H_2O$
Crystal size, mm	0.44 × 0.40 × 0.20
Crystal system	cubic
Space group	*F*m-3m
a, *b*, *c* (A[faaN])	21.448(2)
V (Å^3)	9866(2)
Z	8
T (°C)	20
ρcalc.g/cm^3	4.225
U (cm^{-1})	266.45
F(000)	11088
θ (°)	1.64–25.01
Index ranges	$-1 \leqslant h \leqslant 25$ $-1 \leqslant k \leqslant 25$ $-1 \leqslant l \leqslant 25$
Refl collected	2903
Independent refl	497
Refinement method	Full-matrix least-squares on F
Data/restrain/para	497/042
Goodness of fit on F^2	1.091
R(1), [$I > 2\delta(I)$]	0.0578
Wr^2, [$I > 2\delta(I)$]	0.1738
R(1), (all data)	0.0625
Wr^2, (all data)	0.1795
Lgst diff. peak & hole (Å^3)	3.60 & 3.010

Table 5. Selected bond lengths (Å) and angles (°)^a

M(OH)—O(1X)	2.168(9)	M(OT)—O(4A)	1.901(7)	O(1H)—Zn—O(1X)	109.371(1)
M(OT)—O(2A)	1.71(2)	M(OT)—O(4X)	2.002(7)	O(1X)—Zn—O(1)	109.521(1)
M(OH)—O(4A)	1.901(7)	M(OT)—O(3A)	1.862(4)	O(2H)—M(OH)—O(4A)	98.5(5)
M(OH)—O(4H)	2.001(7)	M(OT)—O(3F)	1.959(4)	O(2H)—M(OH)—O(4H)	95.1(5)
M(OH)—O(3H)	1.863(4)			O(4H)—M(OH)—O(3H)	160.3(5)
M(OH)—O(3Z)	1.958(4)			O(3H)—M(OH)—O(1X)	85.8(5)
Zn—O(1)	1.88(2)			O(3Z)—M(OH)—O(4A)	159.6(5)

^{a} Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, y, -z+1/2$ #2 $x, -y+1/2, -z+1/2$ #3 $-x+1/2, -y+1/2, z$ #4 z, y, x #5 z, x, y #6 $z, -x+1/2, -y+1/2$ #7 $x, -z+1/2, -y+1/2$ #8 y, z, x, #9 $-z, x, y$ #10 $-z-x+1/2, -y+1/2$ #11 $-x, y, -z$, #12 $-x, y, z$ #13 $x, y, -z$ #14 $-z-x+1/2, y-1/2$ #15 $-y+1/2, -x+1/2, z$ #16 $-y+1/2, -z+1/2, x$ #17 y, x, z #18 $-y+1/2, -z, +1/2 -x$

The ZnO_4 tetrahedron in $ZnW_{11}Al$ anion is ideal. The bond lengths are equal by symmetry and the two independent bond angles are almost the same. The MO_6 octahedra of $ZnW_{11}Al$ anion are distorted, for the bonds and angles of MO_6 are different. For example, in the same MO_6, the angle of O(2Z)—M(OH)—O(4A) and O(2H)—M(OH)—O(4H) are 98.5 and 95.1°, respectively.

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