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Effect of the Central Oxoanion Size on the Voltammetric Properties of Keggin-Type $[XW_{12}O_{40}]^{n-}$ (n = 2−6) Complexes

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An α-Keggin-type $[ZnW_{12}O_{40}]^{6-}$ complex was prepared and structurally characterized. Unlike $[XW_{12}O_{40}]^{n-}$ (n = 3−5) complexes that undergo one- and two-electron reductions in neutral and acidic media, respectively, $[ZnW_{12}O_{40}]^{6-}$ showed a four-electron redox wave in acidified CH_3CN. The present study demonstrated that the voltammetric properties of the Keggin anions were governed by the bond valence of the μ_4-O−W bond as well as the ionic charge, and the four-electron behavior was ascribed to the increase of the bond valence (the decrease of the μ_4-O−W distance), owing to the greater X−μ_4-O distances. For the Keggin anions with identical ionic charge, the first one-electron redox wave was situated at more positive potentials with an increase of the bond valence. It turned out that the electron density on the W atom was decreased with an increase of the bond valence, because the positive shift of the one-electron wave parallels the downfield shift of the ^{183}W NMR chemical shift value.

Introduction

The voltammetric properties of Keggin-type $[XW_{12}O_{40}]^{n-}$ (n = 2−5) complexes have been extensively investigated so far.[1] It is known that they exhibit successive one-electron redox waves in neutral media, and the first redox potential depends linearly on their ionic charge. With the exception of $[SW_{12}O_{40}]^{2-}$,[2] the Keggin complexes undergo two-electron reductions in acidified organic solvents, owing to the protonation of the reduced form at the electrode surface.[3] In addition, the Keggin anion with a greater negative charge possesses a greater basicity, and the potential difference between the first one- and two-electron waves can be used as a measure of the basicity.[3h]

Although Gao et al. recently reported that $[XMo_{12}O_{40}]^{6-}$ (X = Co^{II}, Ni^{II}) underwent four-electron reductions in acidic aqueous media,[4] the voltammetric properties of the corresponding W^{VI} complexes, $[XW_{12}O_{40}]^{6-}$, have not been fully elucidated. As far as α-Keggin-type $[XW_{12}O_{40}]^{6-}$ complexes are concerned, $[Co^{II}W_{12}O_{40}]^{6-}$ was prepared and structurally characterized.[5] For the preparation of $[CuW_{12}O_{40}]^{6-}$ from aqueous media, on the other hand, the difficulty arises from the coexistence of $[(H_2)W_{12}O_{40}]^{6-}$, which produces a mixed salt such as α-$[(CH_3)_4N]_6[CuW_{12}O_{40}]_{0.4}\cdot[(H_2)W_{12}O_{40}]_{0.6}\cdot 9H_2O$.[6a] Thus, no structural analysis has been made on the $[CuW_{12}O_{40}]^{6-}$ complex in the pure form, and the knowledge of synthesis of $[ZnW_{12}O_{40}]^{6-}$ is also insufficient, although some inorganic−organic hybrid compounds consisting of $[ZnW_{12}O_{40}]^{6-}$ have already been synthesized by hydrothermal techniques.[7]

In the present study, $[ZnW_{12}O_{40}]^{6-}$ was prepared with improved synthetic procedures, and the single-crystal X-ray structural analysis identified it as an α-Keggin structure (Figure S1, Tables S1 and S2, Supporting Information). The voltammetric behaviors of all the α-Keggin-type $[XW_{12}O_{40}]^{n-}$ complexes (n = 2−6) were fully investigated in the absence

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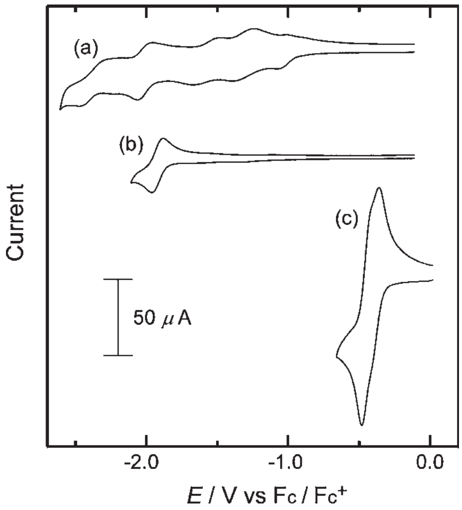

Figure 1. Cyclic voltammograms for (a) 0.50 mM $(Bu_4N)_4H_2[ZnW_{12}O_{40}]$ dissolved in CH_3CN (0.10 M Bu_4NClO_4); (b) (a) + 1.0 mM Bu_4NOH; (c) (a) + 10 mM CF_3SO_3H.

and presence of protons, and we came to the conclusion that their voltammetric properties were governed by the bond valence of the μ_4-O−W bond trans-positioned to the terminal oxygen as well as the ionic charge.

Results and Discussion

Electrochemistry in CH_3CN. Figure 1a shows a cyclic voltammogram for 0.50 mM $(Bu_4N)_4H_2[ZnW_{12}O_{40}]$ in dry CH_3CN (water content < 50 ppm). Like some protonated polyoxometalates (POMs),[8] $H_2[ZnW_{12}O_{40}]^{4-}$ exhibited ill-defined redox waves, owing to the presence of acidic protons. On the addition of 1.0 mM Bu_4NOH, we obtained a well-defined one-electron redox wave with midpoint potentials (E_{mid}) of −1.92 V (Figure 1b), where $E_{mid} = (E_{pc} - E_{pa})/2$; E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. Similarly, $[Co^{II}W_{12}O_{40}]^{6-}$ also exhibited a one-electron redox wave with E_{mid} of −1.90 V, except for an additional redox wave (E_{mid} −0.26 V) due to the central Co^{II}/Co^{III} couple. For highly charged POMs like $[\alpha\text{-}SiW_{11}O_{39}]^{8-}$ and $[\alpha\text{-}PW_{11}O_{39}]^{7-}$,[9] Bond and coworkers recommend the use of carefully dried CH_3CN, because the reduced forms of such POMs may abstract protons from water to produce protonated species being reduced at potentials more positive than those for the corresponding unprotonated species. For the Keggin POMs concerned, however, the E_{mid} values were independent of the presence of traces of water. There is agreement that the E_{mid} values of the first one-electron waves, denoted as $E_1(1)$, show a linear dependence on the ionic charge of Keggin anions, which is ascribed to the electron affinity variations.[1c] In accordance with the previous observations, the $E_1(1)$ values for $[XW_{12}O_{40}]^{6-}$ (X = Zn^{II}, Co^{II}) also lie on the linear line extended to $n = -6$ (Figure S2, Supporting Information).

Table 1. $E_1(1)$ Values, ^{183}W NMR Chemical Shifts (δ), Average Atomic Distances ($d_{\mu4\text{-O-W}}$), and Bond Valences (s) of μ_4-O−W Bonds

$[XW_{12}O_{40}]^{n-}$	$E_1(1)$/V	δ/ppm	$d_{\mu4\text{-O-W}}$/Å	s
$n = 2$				
(1) X = S	−0.26		2.55	0.18
$n = 3$				
(2) X = P	−0.67	−88	2.43	0.25
(3) X = As	−0.64	−68	2.36	0.30
$n = 4$				
(4) X = Si	−1.13	−93	2.33	0.33
(5) X = Ge	−1.09	−70	2.29	0.36
$n = 5$				
(6) X = B	−1.65	−120	2.34	0.32
(7) X = Al	−1.56	−96	2.27	0.39
(8) X = Ga	−1.54	−74	2.21	0.45
$n = 6$				
(9) X = H_2	−2.02		2.22	0.44
(10) X = Zn	−1.92		2.17	0.50
(11) X = Co	−1.90		2.15	0.53

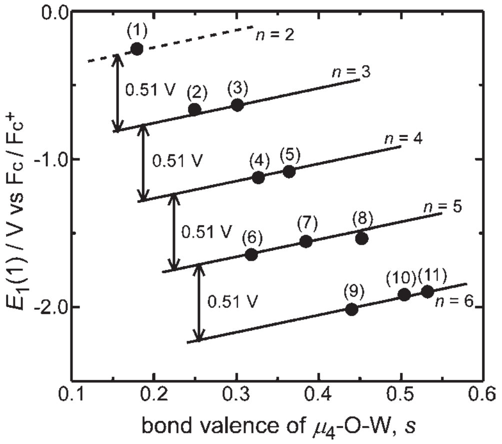

Figure 2. Plots of $E_1(1)$ against the bond valence for $[XW_{12}O_{40}]^{n-}$ (n = 2−6). The respective Keggin anions are indicated by the numbers in parentheses (Table 1).

Whereas the $E_1(1)$ values have been regarded so far as almost the same for the Keggin anions with identical ionic charge, we found a significant difference of $E_1(1)$ with the variation of the XO_4 tetrahedron size for $[XW_{12}O_{40}]^{5-}$ (X = B^{III}, Al^{III}, Ga^{III}). It is known that the size of the $W_{12}O_{36}$ cage is independent of the kind of tetrahedral heteroatom, X, and the sum of the X−μ_4-O and μ_4-O−W distances averages ca. 4.0 Å,[10] where $d(\mu_4\text{-O-W})$ is the bond length of μ_4-O−W trans-positioned to the terminal oxygen. As the XO_4-tetrahedron size is increased in the order X = B^{III} < Al^{III} < Ga^{III}, the $d(\mu_4\text{-O-W})$ value is accordingly decreased, leading to a positive shift of the $E_1(1)$ values (Table 1). This trend was also found for $[XW_{12}O_{40}]^{3-}$ (X = P, As), $[XW_{12}O_{40}]^{4-}$ (X = Si, Ge), and $[XW_{12}O_{40}]^{6-}$ (X = H_2, Zn, Co). These findings can be accounted for in terms of the lowering of the electron density on the W (2.36) atom, owing to the greater electronegativity of oxygen (3.44); the numerals in parentheses denote Pauling electronegativities.[11] Table 1 also shows that the chemical shift (δ) values of ^{183}W NMR also vary with the $d(\mu_4\text{-O-W})$ value. As the $d(\mu_4\text{-O-W})$ value was decreased for Keggin anions with identical ionic charge, the δ values in CH_3CN underwent a downfield shift in that order, suggesting the decrease of the

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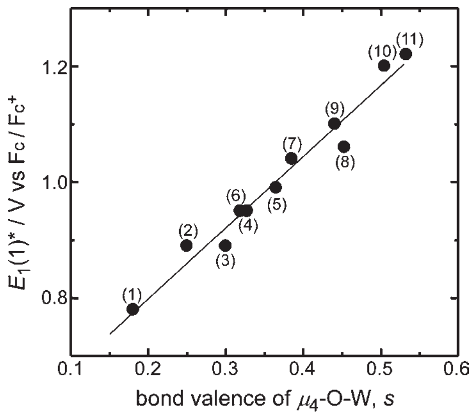

Figure 3. Plots of $E_1(1)^*$ against the bond valence for $[XW_{12}O_{40}]^{n-}$ (n = 2−6). The respective Keggin anions are indicated by the numbers in parentheses (Table 1).

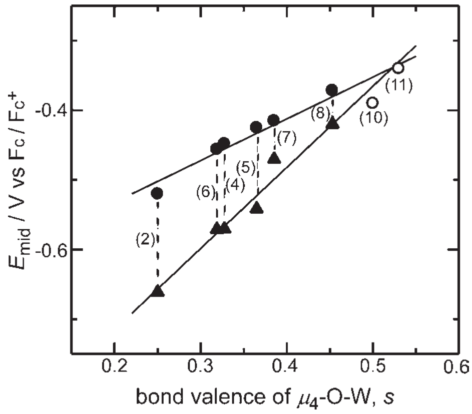

Figure 4. Plots of $E_2(1)$ and $E_2(2)$ against the bond valence for $[XW_{12}O_{40}]^{n-}$ (n = 3−5). Solid circles and triangles denote $E_2(1)$ and $E_2(2)$ values, respectively, and open circles show the E_{mid} values for the four-electron redox wave. The respective Keggin anions are indicated by the numbers in parentheses (Table 1).

electron density on the W atom. These ^{183}W NMR results seems consistent with the positive shift of $E_1(1)$.

In the following, the bond valence, s, of the μ_4-O−W bond was calculated for each Keggin complex, using the relationship $s = \exp[(r_o - r)/B]$, where $r_o = 1.917$, r = the μ_4-O−W bond length, and $B = 0.37$.[12] We found that plots of the $E_1(1)$ value against the s value gave parallel straight lines, and the respective separations averaged 0.51 V (Figure 2). In order to discuss the effect of s on the $E_1(1)$ values without the effect of ionic charge, we estimated the corresponding E_{mid} values for hypothetical Keggin complexes with null charge, $E_1(1)^*$, using the equation $E_1(1)^* = E_1(1) + 0.51n$. As shown in Figure 3, a linear correlation was obtained between the $E_1(1)^*$ and s values for $[XW_{12}O_{40}]^{n-}$ (n = 2−6), indicating that the voltammetric properties are governed by the bond valence as well as the ionic charge.

For $[XW_{12}O_{40}]^{n-}$ (n = 3−5), the presence of H$^+$ causes one-electron waves to be converted into two-electron waves.[3] As shown in Figure 1c, on the other hand, the addition of 10 mM H$^+$ to the $[ZnW_{12}O_{40}]^{6-}$ solution produced a big redox wave at a potential more positive than the one-electron wave (E_{mid} = −0.39 V). The reduction current was 5.6 times the one-electron reduction current, and the normal pulse voltammetric and coulometric measurements indicated a four-electron transfer of the wave. A Keggin-type $[Co^{II}W_{12}O_{40}]^{6-}$ complex exhibited a similar four-electron redox wave (E_{mid} = −0.34 V).

In order to correlate the ionic charge with the four-electron behavior, the $E_2(1)$ and $E_2(2)$ values were measured for $[XW_{12}O_{40}]^{n-}$ (n = 3−5), where $E_2(1)$ and $E_2(2)$ denote the E_{mid} values for the first and second two-electron waves, respectively. In contrast to the linear $E_1(1)$−ionic charge dependence shown in Figure S2, Supporting Information, no correlation was found between the $E_2(1)$ or $E_2(2)$ value and the ionic charge (Figure S3, Supporting Information). Instead, we found that the respective $E_2(1)$ and $E_2(2)$ values depended linearly on the s values (Figure 4), and both linear lines became closer as the s value was increased, leading to the merging of the first and second two-electron waves into an apparent four-electron wave for $[XW_{12}O_{40}]^{6-}$ (X = Zn^{II}, Co^{II}).

Conclusions

In the present paper, $[ZnW_{12}O_{40}]^{6-}$ was prepared from aqueous solution, and the α-Keggin structures were confirmed by the single-crystal X-ray structural analysis. The voltammetric behaviors of all the α-$[XW_{12}O_{40}]^{n-}$ (n = 2−6) complexes were investigated in CH_3CN with and without H$^+$. When one-electron reduction proceeds with an increase of the negative charge in neutral media, the $E_1(1)$ value is mainly dependent on the ionic charge. For Keggin anions with identical charge, the $E_1(1)$ value is situated at more positive potentials as the bond valence, s, of the μ_4-O−W bond is increased (Figure 2). These behaviors can be accounted for in terms of the lowering of the electron density on the W atom, because the positive shift of $E_1(1)$ parallels the downfield shift of the ^{183}W NMR line (Table 1).

It is known that α-$[XW_{12}O_{40}]^{n-}$ (n = 3−5) undergoes two-electron reduction accompanied by consumption of two protons in acidified media.[3] When the electrochemical reduction proceeds without the change of the ionic charge, no correlation was found between the $E_2(1)$ or $E_2(2)$ values and their ionic charges (Figure S3, Supporting Information). Instead, the respective $E_2(1)$ and $E_2(2)$ values showed linear dependences on the s values (Figure 4). The separation of the $E_2(1)$ and $E_2(2)$ lines became closer as the s value was increased, and ultimately, the two two-electron waves were merged into a four-electron wave for $[XW_{12}O_{40}]^{6-}$ (X = Co^{II}, Zn^{II}) with the bigger bond valence, s, of the μ_4-O−W bond.

The present findings give a clue to the design and preparation of novel Keggin complexes being electrochemically reduced by multielectrons.

Experimental Section

Instrumentation. The X-ray intensity data were collected at 193 K on a Bruker-AXS SMART 1000 diffractometer equipped with a CCD detector using graphite-monochromated Mo Kα radiation (0.71073 Å). The crystal structure was solved by a direct method and refined by full-matrix least-squares calculations based on F_o^2 using the program package SHELX97.[13] A Bruker model AVANCE 500 spectrometer was used to record

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^{183}W NMR spectra in a 10 mm diameter NMR tube with a concentric capillary containing D_2O for instrumental lock. The chemical shifts were referenced to 1 M $Na_2WO_4 \cdot 2H_2O$ in D_2O. Voltammetric measurements were made with a Hokuto Denko model HA-101 potentiostat interfaced to a microcomputer-controlled system. The working electrode was a Tokai glassy carbon rod (GC-30S) with a surface area of 0.20 cm^2, and a platinum wire served as the counter electrode. The GC electrode was polished manually with 0.25 μm diamond slurry before each measurement. The reference electrode was an Ag/Ag$^+$ (0.010 M; CH_3CN) electrode: the potentials were referred to the redox potential of ferrocene(Fc)/ferrocenium ion (Fc$^+$) as an internal standard. The voltammetric measurements were made at 25 ± 0.1 °C.

Syntheses. $(Me_4N)_6[ZnW_{12}O_{40}] \cdot 9H_2O$. A 500 mL solution of 8.3 g of $Na_2WO_4 \cdot 2H_2O$ (25 mmol) and 0.74 g of $Zn(NO_3)_2 \cdot 6H_2O$ (2.5 mmol) in 0.1 M acetate buffer (pH 5.5) was prepared. The resultant colorless solution was refluxed for 6 h. After cooling to room temperature, 10 g of Me_4NCl was added to precipitate a white salt. The salt was collected by filtration, washed with water and ethanol, and air-dried (yield 2.9 g). The salt was further purified by recrystallization from water at ambient temperature. Anal. Found: C, 8.13; H, 2.72; N, 2.42; Zn, 1.9; W, 62.7; H_2O, 4.8. Calcd for $(Me_4N)_6[ZnW_{12}O_{40}] \cdot 9H_2O$: C, 8.19; H, 2.58; N, 2.39; Zn, 1.9; W, 62.7; H_2O, 4.6.

$(Bu_4N)_4H_2[ZnW_{12}O_{40}]$. A 0.54 g quantity of $(Me_4N)_6[ZnW_{12}O_{40}] \cdot 9H_2O$ was dissolved in 100 mL of water. With the addition of 10 g of Bu_4NBr, no precipitates appeared, but the subsequent addition of 10 mL of 10 M HNO_3 produced spontaneously a white salt, which was filtered off, washed with water and ethanol, and air-dried. The salt was recrystallized from a 1:1 (v/v) $CH_3CN-C_2H_5OH$ solution. Anal. Found: C, 19.6; H, 3.91; N, 1.48. Calcd for $(Bu_4N)_4H_2[ZnW_{12}O_{40}]$: C, 19.8; H, 3.79; N, 1.44.

The Me_4N^+ salt was used for the X-ray crystallographic structural determination, and the Bu_4N^+ salt was used for CV studies. For comparative studies, the Bu_4N^+ salts of Keggin anions $[XW_{12}O_{40}]^{n-}$ (X = S^{VI}, P^{V}, As^{V}, Si^{IV}, Ge^{IV}, B^{III}, Al^{III}, Ga^{III}, Co^{II}, H_2; n = 2−6) were prepared and purified according to slight modifications of the literature method.[2,14] Their IR, CV, and ^{183}W NMR measurements confirmed that they possessed Keggin structures.

Supporting Information Available: X-ray crystallographic data, Table S1 (crystal data of $(Me_4N)_6[ZnW_{12}O_{40}] \cdot 9H_2O$), Table S2 (interatomic distances concerning possible hydrogen bonding), Figure S1 (structure of $[ZnW_{12}O_{40}]^{6-}$), Figure S2 (plots of $E_1(1)$ against the ionic charge for $[XW_{12}O_{40}]^{n-}$), Figure S3 (plots of $E_2(1)$ and $E_2(2)$ against the ionic charge). This material is available free of charge via the Internet at http://pubs.acs.org.

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