Inorganica Chimica Acta, *171* (1990) 135–137

Inorganica Chimica Acta
LETTER

Preparation of Dodecamolybdovanadate(V)

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(Received December 15, 1989)

Among several types of heteropolymolybdates, most voltammetric studies have been carried out on Keggin- and Dawson-type complexes, which undergo reversible multi-step reductions to heteropoly blues [1]. The Keggin- and Dawson-type complexes prepared so far contain voltammetrically inactive oxoanions such as silicate(IV), germanate(IV), phosphate(V) and arsenate(V). Recently we have prepared a Dawson-type complex containing sulfate(VI) from a Mo(VI)–H_2SO_4–CH_3CN system [2–4]. As for these heteropoly complexes, it is generally accepted that the electrochemical properties depend little on the kind of heteroatoms, but depend on the configuration of the molybdenum atoms around the heteroatoms.

In the hope of gaining more insight into the role of central heteroatoms in the electrochemical properties of heteropolyanions, we have prepared heteropoly complexes containing voltammetrically active hetero species such as vanadate(V) as a central tetrahedron. Vanadium(V) is voltammetrically reduced at relatively positive potentials [5]. As far as molybdovanadate(V) is concerned, vanadium(V) replaces in some cases some of the molybdenum atoms in the structure [6, 7]. Bjornberg and Hedman have obtained a mixed-valence reduced crystal, $K_6V(V_2^{IV,V}Mo_{10})O_{40}\cdot 13H_2O$ which has a Keggin-type structure with a central VO_4 tetrahedron [8]. The existence of the mixed molybdovanadovanadate(V) shows strong promise of the formation of a Keggin-type 12-molybdovanadate(V) complex.

In the present study, a heteropoly complex with a composition of Mo/V = 12/1 was prepared from a Mo(VI)–V(V)–HCl–CH_3CN system at ambient temperature. The yellow heteropolyanion underwent four-step voltammetric reduction to mixed-valence heteropoly blues at a glassy carbon (GC) electrode. Both oxidized (yellow) and reduced (blue) forms of the 12-molybdovanadate(V) complex were characterized by IR spectroscopy.

Experimental

Voltammetric measurements were carried out with a PARC Model 174-A polarographic analyzer equipped with a Yokogawa Model 3023 X–Y recorder. Tokai glassy carbon (GC-30S) with a surface area of 0.071 cm^2 was used as the working electrode. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. Controlled potential electrolysis (CPE) was carried out with a Hokuto Denko Model HA-501 potentiostat. Coulometric analysis was made with a Hokuto Denko Model HF-202D coulometer. A Hitachi Model 220-A spectrophotometer was used to record UV–Vis absorption spectra. IR spectra were recorded on a Hitachi Model 270-30 spectrophotometer using KBr pellets. The TG–DTA measurements were made with a Rigaku Denki 8002-SD thermal analyzer. All reagents were of analytical grade and were used as received.

The $n\text{-}(C_4H_9)_4N^+$ salt of the yellow 12-molybdovanadate was prepared by the following procedure. A 6.1 g quantity of $Na_2MoO_4\cdot 2H_2O$ was dissolved in *c.* 170 ml of water and 0.3 g of NH_4VO_3 dissolved in 26 ml of conc. HCl was added. Upon the addition of 300 ml of acetonitrile, the solution turned from pale yellow due to vanadate(V) to orange–yellow. The solution was stirred for *c.* 30 min at room temperature. The addition of 5 g of solid $n\text{-}Bu_4NBr$ induced a yellow precipitate, which was filtered, washed with water and ethanol, and air dried. The yield was *c.* 3.7 g. The $n\text{-}Bu_4N^+$ salt was further purified by recrystallization from acetonitrile. *Anal.* Calc. for $(n\text{-}Bu_4N)_3VMo_{12}O_{40}$: Mo, 44.80; V, 1.98; C, 22.44; H, 4.24; N, 1.64. Found: Mo, 44.87; V, 2.12; C, 22.49; H, 4.24; N, 1.63%. The Et_4N^+ salt of 12-molybdovanadate(V) was obtained in a similar manner. Vanadium was determined spectrophotometrically at 545 nm as the complex with PAR (4-(2-pyridylazo)resorcinol) [9]. Molybdenum was determined by the SCN^- method [10]. The TG–DTA results show that the yellow salts contain no water of hydration.

The $n\text{-}Bu_4N^+$ and Et_4N^+ salts of the Keggin-type 12-molybdoarsenate(V) anion were prepared according to the method of Rocchiccioli-Deltcheff *et al.* [11].

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0020-1693/90/$3.50

Results and Discussion

UV–Vis Spectroscopic Measurements

The n-Bu_4N^+ salt of 12-molybdovanadate(V) is soluble in acetonitrile, acetone and 1,4-dioxane, giving rise to yellow solutions, but insoluble in water or ethanol. Figure 1 shows a UV–Vis spectrum of 6.46×10^{-5} M 12-molybdovanadate(V) in neat acetonitrile. The spectrum shows an absorption maximum around 310 nm. The yellow solution obeys Beer's law in the spectral region studied (molar absorption coefficient = 1.92×10^4 cm^{-1} M^{-1} at 310 nm).

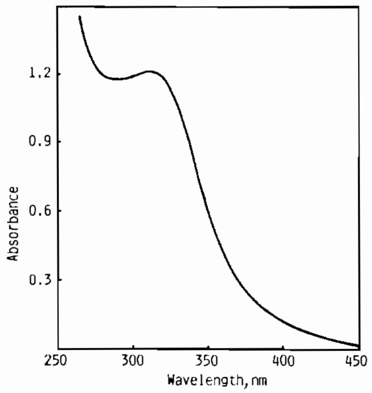

Fig. 1. UV–Vis spectrum of 6.46×10^{-5} M 12-molybdovanadate(V) in neat acetonitrile (path length, 1 cm).

Voltammetric Measurements

Figure 2 shows a cyclic voltammogram of 3.9×10^{-4} M 12-molybdovanadate(V) in 95% (vol./vol.) CH_3CN–water containing 0.1 M $HClO_4$. Two well-defined reduction waves are observed with peak potentials (E_p) of +0.402 and +0.330 V, followed by ill-defined waves with E_p values of *c.* +0.06 and −0.05 V. Each wave height depends on the square root of the voltage scan rate (20–200 mV s^{-1}), indicating that the electrode processes are diffusion controlled. Coulometric analysis showed that each of the first two waves corresponds to a two-electron transfer. The cathodic and anodic peak potentials (E_{pc} and E_{pa}) were independent of the scan rate, and the ($E_{pc} - E_{pa}$) values for the 1st and 2nd waves averaged 28 ± 2 mV, indicating the reversible nature of the waves. On the other hand, the 3rd wave was broad, and the 3rd and 4th waves were estimated to be due to reduction of 2.5–3 electrons. The voltammetric behavior is very interesting because a series of 12-molybdo complexes with Si(IV), Ge(IV), P(V) and As(V) as central heteroatoms are known to undergo multi-step two-electron reductions [1]. There is a possibility that vanadium(V), which is assumed to be a central heteroatom, is electroreduced simultaneously with molybdenum at the potentials of the 3rd and 4th waves. Further studies are being carried out to elucidate the reduction mechanism responsible for this anomalous voltammetric behavior. Blue solutions were obtained by the electrochemical reduction at each of the four reduction steps.

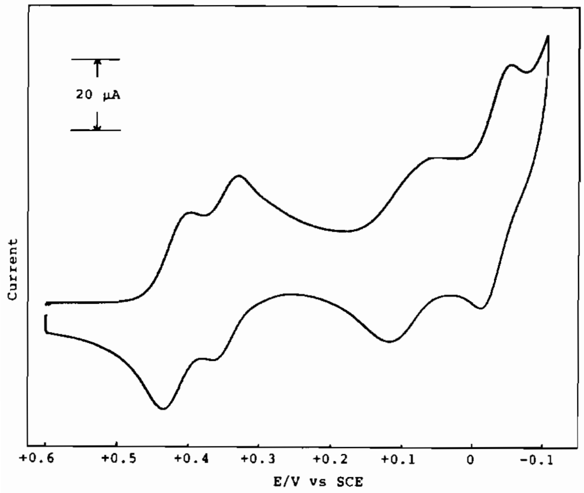

Fig. 2. Cyclic voltammogram of 3.9×10^{-4} M 12-molybdovanadate(V) in 95% (vol./vol.) CH_3CN–water containing 0.1 M $HClO_4$ (scan rate, 100 mV s^{-1}).

In solutions of <90% (vol./vol.) CH_3CN, the 12-molybdovanadate(V) anion decomposed gradually, as judged by the decrease of the reduction currents with time.

IR Spectroscopic Measurements

Curve (a) in Fig. 3 shows an IR spectrum of the Et_4N^+ salt of 12-molybdovanadate(V) in a KBr pellet. The spectrum shows strong bands at 958, 887 and 776 cm^{-1} and a weak band at 840 cm^{-1}. In general, Keggin anions exhibit the same pattern of four bands [11]. As an example, curve (a) in

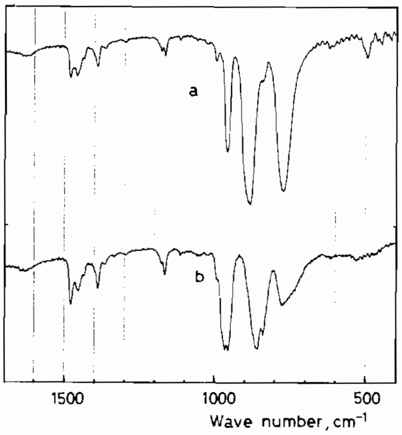

Fig. 3. IR spectra of the Et_4N^+ salt of 12-molybdovanadate(V): (a) the oxidized (yellow) species; (b) the four-electron reduction (blue) species.

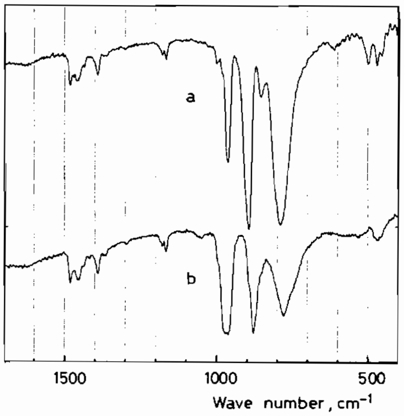

Fig. 4. IR spectra of the Et_4N^+ salt of 12-molybdoarsenate-(V): (a) the oxidized (yellow) species; (b) the four-electron reduction (blue) species.

Fig. 4 shows an IR spectrum of the Et_4N^+ salt of 12-molybdoarsenate(V). The spectra are very similar. Therefore, the four bands in the former spectrum can be assigned by comparison with those in the latter one [11]. On this basis we can tentatively assign the 958 cm^{-1} band to the Mo=O terminal bond, the 840 and 776 cm^{-1} bands to the Mo–O–Mo bridges between corner-sharing octahedra and between edge-sharing octahedra, respectively, and the 887 cm^{-1} band to the VO_4 group. It is known that ν_1 and ν_3 bands of $[VO_4]^{3-}$ occur at 826 and 804 cm^{-1} [12]. The bands in the 1500–1300 and 1160 cm^{-1} regions correspond to the Et_4N^+ group. In addition, the spectrum contains weak bands at 620, 496, 452 and 419 cm^{-1} to which no assignments can be made.

Curve (b) in Fig. 3 shows an IR spectrum of the Et_4N^+ salt of the four-electron reduction (blue) species, which was isolated from a blue solution obtained by CPE of a 0.4 mM $(n\text{-}Bu_4N)_3VMo_{12}O_{40}$–95% (vol./vol.) CH_3CN–0.1 M $HClO_4$ solution at +0.25 V. The original yellow species was isolated from a yellow solution obtained by re-oxidation of the blue solution at +0.70 V, which indicates that the conformation of the heteropoly-anion is retained in both the oxidized and four-electron reduction species. The band assigned to the V–O bond decreased in intensity with a shift to shorter wave numbers. Simultaneously, the intensities of the bands assigned to the Mo–O–Mo bridges were weakened. For comparison, curve (b) in Fig. 4 shows the IR spectrum of the Et_4N^+ salt of the four-electron reduction species of 12-molybdoarsenate(V). The blue species of 12-molybdoarsenate-(V) was obtained by CPE of a 0.5 mM $(n\text{-}Bu_4N)_3AsMo_{12}O_{40}$–95% (vol./vol.) CH_3CN–0.1 M $HClO_4$ solution at the potential of the 2nd reduction wave (+0.25 V). It was found that similar behavior was observed for both heteropoly complexes. Similar results have already been reported for the salt of 12-molybdophosphate(V) with a Keggin structure [13, 14].

The results reported in this paper strongly suggest that the 12-molybdovanadate(V) ion is structurally related to the Keggin anions, although the crystallographic structure has not been determined.

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