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Stepwise reduction of electron-precise, six-electron, triangular, $[Mo_3^{IV}S_4(CN)_9]^{5-}$ to electron-rich seven, eight and unstable nine-electron species resulting in core expansion to electron-precise, twelve-electron, tetrahedral, $[Mo_4^{III}S_4(CN)_{12}]^{8-}$

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Abstract. Facile reduction of the triangular $\{Mo_3^{IV}\}^6$-core containing $[Mo_3S_4(CN)_9]^{5-}$ derivative is achieved in aqueous medium, containing the KOH-KCN-$K_2[Zn(CN)_4]$ ternary system as supporting electrolyte, in a two-step one-electron reduction reaction followed by an irreversible one. The diamagnetic species containing the $\{Mo_3\}^8$ core, obtained by chemical reduction of $[Mo_3S_4(CN)_9]^{5-}$ with zinc in aqueous medium containing KOH–KCN, is oxidized by air in two steps. The partially oxidized species with $\{Mo_3\}^7$ core in the first step exhibits characteristic ESR signals which on further oxidation quantitatively reverts to the original compound with $\{Mo_3\}^6$ core displaying distinctly separate isosbestic points in the stepwise conversion of $\{Mo_3\}^8$ to $\{Mo_3\}^7$ and $\{Mo_3\}^7$ to $\{Mo_3\}^6$ cores. Under drastic reduction conditions with aluminium in 40% aqueous KOH solution the $\{Mo_3\}^6$ core is reduced to unstable trinuclear $\{Mo_3^{III}\}^9$ core which expands to tetrahedral $\{Mo_4^{III}\}^{12}$-core containing $[Mo_4S_4(CN)_{12}]^{8-}$ derivative according to electron-precise cluster rule.

Keywords. Trinuclear; tetranuclear; molybdenum-sulphur clusters; cluster core expansion.

1. Introduction

Triangular $Mo_3O_4^{4+}$ ion containing species have electron-precise six cluster electrons for the set of three Mo–Mo bonds in the $\{Mo_3^{IV}\}^6$ core (Cotton 1964; Muller *et al* 1980; Bursten *et al* 1982; Cotton and Feng 1991). Proton coupled reductions of compounds containing this ion involve two sequential electron transfer steps to yield $\{Mo_3\}^8$ and $\{Mo_3\}^9$ with the absence of $\{Mo_3\}^7$ core (Richens and Sykes 1982; Paffett and Anson 1983). Complexes of eight or nine cluster electrons containing Mo_3OCl_3 moiety have been reported (Cotton *et al* 1991). For the related $Mo_3S_4^{4+}$ ion containing complexes, redox reactions are extremely varied. Thus for $[Mo_3^{IV}S_4(HN(CH_2\ Co_2)_2\}_3]^{2-}$, three sequential electron transfer steps in its reduction has been reported relatively at very low negative potential in water (Shibahara and Kuroya 1986) compared to the one-step reduction of $[Mo_3^{IV}S_4(CN)_9]^{5-}$ at very high negative potential in dimethylsulphoxide (Howlader *et al* 1983; Weighardt *et al* 1984). This large difference in reduction potentials may not solely be due to the effects of peripheral ligands in these complexes. Moreover, the cuboidal $Mo_4S_4^{4+}$ ion with the set of six Mo–Mo bonds in the

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tetrahedral $\{Mo_4^{III}\}^{12}$ core, when not properly stabilized by peripheral ligands, gets oxidized with core contraction to yield $\{Mo_3^{IV}\}^6$ core (Cotton *et al* 1985; Shibahara *et al* 1986; Martinez *et al* 1987). We report here the tuning of the reduction potential of $[Mo_3^{IV}S_4(CN)_9]^{5-}$ (1) in aqueous medium to demonstrate media-dependent three sequential electron transfer steps wherein the ultimate reduced $\{Mo_3\}^9$ core is rearranged to yield the electron-precise, twelve-electron containing $[Mo_3^{III}S_4(CN)_{12}]^{8-}$ ion (Muller *et al* 1985).

2. Experimental

All reactions were carried out in an atmosphere of pure nitrogen. Elemental analyses were performed by EA 1108 elemental analyzer and sulphur by conventional gravimetric methods after oxidizing the compound by peroxide fusion. Reagents such as aluminium powder (99·7%), KOH, KCN, ammonium heptamolybdate were used as purchased. IR spectra were recorded on a Perkin–Elmer instrument (Model 577) using CsI pellets. Electronic spectra were measured by a Shimadzu 160 spectrophotomer. EPR spectra were obtained with a Varian E-109 spectrometer using DPPH as calibrant. Cyclic voltammograms were recorded in 0·5 M KCl, 0·4 M KOH + 0·1 M KCN or 0·35 M KOH + 0·1 M KCN + 0·05 M $K_2[Zn(CN)_4]$ aqueous solution on a Bas CV 27 instrument connected to a Houston Instruments Omnigraphic X-Y recorder under nitrogen using glassy carbon electrode as working electrode and Ag/AgCl as reference electrode which was separated from the test solution by a glass jacket with a porous Vycor tip and a platinum wire as an auxilliary electrode. Potential values were quoted vs Ag/AgCl (3M NaCl) and checked with $[Fe(CN)_6]^{3-}//Fe(CN)_6]^{4-}$ couple. X-ray powder diffraction patterns were measured using a Rich Seifert Isodebyeflex 2002 diffractometer.

$K_5[Mo_3S_4(CN)_9]\cdot 2H_2O$ (1) and $K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$ (2) were prepared by the literature procedure (Muller *et al* 1985).

$K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$ (2) from $K_5[Mo_3S_4(CN)_9]\cdot 2H_2O$ (1) by core expansion. Complex (1) (0·449 g, 0·51 mmol) was taken in 40 ml of 40% aqueous KOH solution. Aluminium powder (0·549 g, 20·40 mmol) was slowly added into this solution with stirring. This exothermic reaction was controlled by the addition of Al powder portion-wise to keep the temperature around 70°C wherein the green colour changed to reddish brown. The mixture was kept further at 70°C for an hour and filtered hot. The solution on cooling precipitated 2 as needle-shaped red crystals. These were filtered, washed with 40% aqueous KOH and finally with MeOH and recrystallized from aqueous KOH–KCN medium: yield 0·52 g (84%).

Analysis – calcd. for $K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$; C, 11·9; H, 0·7; N, 13·9; S, 10·6%. Found: C, 11·6; H, 0·9; N, 13·7; S, 10·5%. Its X-ray powder data and other physiochemical properties were identical to those of the authentic complex (Muller *et al* 1985). The mother liquor of complex (2), on acidification with hydrochloric acid in the presence of $HgCl_2$ produced HgS confirming the release of sulphide ion as shown in (1) (*vide infra*).

3. Results and discussion

Cyclic voltammograms of 1 in water with different supporting electrolyte compositions (KCl; KOH–KCN; KOH–KCN–$K_2[Zn(CN)_4]$) are shown in figure 1 (A–C). The

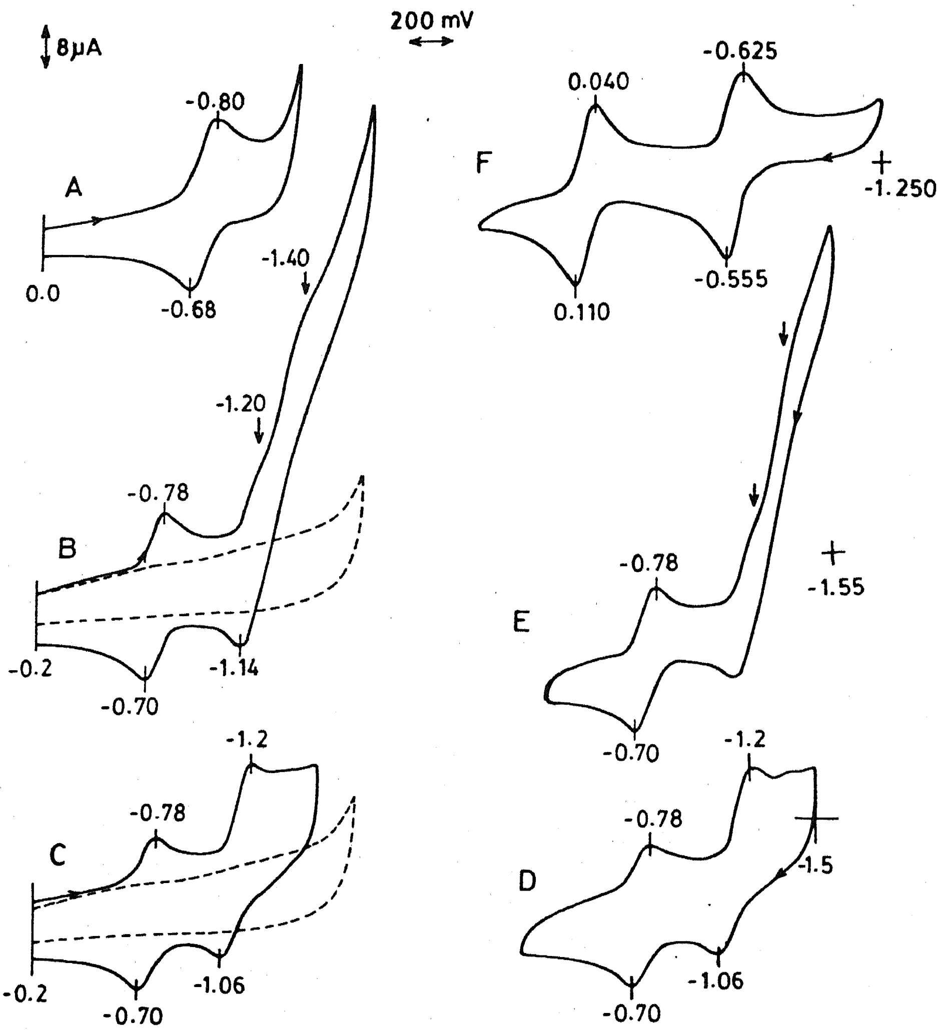

Figure 1. Cyclic voltammograms of 0·98 mM $K_5[Mo_3S_4(CN)_9]$ in different supporting electrolyte compositions: (**A**), KCl; (**B**), KOH–KCN; (**C**), KOH–KCN–$K_2[Zn(CN)_4]$. Broken lines in B and C were blank scans. Voltammograms of chemically generated 0·98 mM $[Mo_3S_4(CN)_9]^{7-}$ by zinc (**D**) and aluminium (**E**) (see text for electrolyte compositions). Voltammogram of 1 mM solution of $[Mo_4S_4(CN)_{12}]^{8-}$ in 0·5 M KCl (**F**). All scan rates, 100 mV s^{-1} at 25 ± 1°C.

reported $E_{1/2} = -1{\cdot}49$ V vs NHE, for one-electron reduction of (1) in dimethylsulphoxide (Weighardt *et al* 1984), is drastically shifted to $-0{\cdot}74$ V using KCl ($\Delta E = 100$ mV) and KOH–KCN ($\Delta E = 80$ mV) as supporting electrolyte respectively. In the latter case, two more successive reduction peak potentials appeared around $-1{\cdot}20$ and $-1{\cdot}40$ V respectively. When KOH–KCN–$K_2[Zn(CN)_4]$ combined supporting electrolyte was used the appearance of the second reduction process became quasireversible ($-1{\cdot}13$ V, $\Delta E = 140$ mV) in addition to the reversible first reduction process ($-0{\cdot}74$ V, $\Delta E = 80$ mV) followed by the third irreversible reduction which is well separated from the voltage limit of the solvent. The quasireversible nature of the first reduction step in KCl changed to fully reversible form in KOH–KCN or in KOH–KCN–$K_2[Zn(CN)_4]$ supporting electrolyte whereas in the latter case the second reduction step appeared as quasireversible. All the reduction steps are diffusion controlled in nature (Bard and Faulkner 1980). Anaerobic chemical reduction of 1 in KOH–KCN medium by zinc powder led to the change of colour from bright green to yellow *via* olive green. Oxodative (reverse) scan of this species (resting potential at − 1·50 V) showed an identical voltammogram to that observed in the reductive scan (resting potential at 0·00 V) for 1 with KOH–KCN–$K_2[Zn(CN)_4]$ as supporting electrolyte (figure 1, D, C). When reduction of 1 was accomplished by using aluminium powder instead of zinc, the reverse scan (oxidative, resting potential at − 1·55 V) of the yellow solution was identical to what was observed in the reductive scan of 1 with KOH–KCN as supporting electrolyte (figure 1 E, B). The electronic spectrum of the fully reduced yellow solution (obtained chemically either by zinc or aluminium) changed back to that of 1 on intermittent exposure of the yellow solution to air. This quantitative conversion occurs *via* two distinct stages of oxidation displaying two different sets of isosbestic points (733 nm in the first stage followed by 620 nm and 576 nm in the second stage). Electronic spectra of these species are shown in figure 2. For fully reduced species (curve A, figure 2), appearance of a band beyond 1100 nm could not be located because of the limitation of the spectrophotometer used. The feature of this spectrum is fairly comparable to that of the $\{Mo_3\}^8$ core of reduced Mo_3O_4 species (Richens and Sykes 1982; Paffett and Anson 1983). The partially oxidized species in solution with λ_{max} 660 nm (curve B, figure 2) when vacuum-dried and diluted with potassium salt of 1 exhibited room temperature ESR spectrum ($g_{\parallel} = 2{\cdot}073$, $g_{\perp} = 1{\cdot}985$) as shown in figure 3. The fully reduced species under similar treatment did not show any ESR signal. The reversal of the axial line shape of this ESR signal compared to that of $\{Mo_3\}^9$ core (Paffett and Anson 1983) may indicate the presence of $\{Mo_3\}^7$ core in this half oxidized species. The electron-accepting property of water from the N-atoms in the ligated cyano groups in these species and stabilization of the reduced species by outer sphere complex formation with water may be responsible for the shift of half wave reduction potential to a less negative value compared to that in dimethylsulphoxide. A regular shift of half-wave potential to a less negative value for $\{Mo_3\}^6$ to $\{Mo_3\}^7$ and to a more positive one for $\{Mo_3\}^6$ to $\{Mo_3\}^5$ steps due to increase of the percentage of water in dimethylsulphoxide has been observed, demonstrating the role of a protic solvent in cyano-ligated species (Mascharak 1986). However, the role of KOH–KCN over KCl or KOH–KCN–$K_2[Zn(CN)_4]$ over KOH–KCN for improving successive reduction steps are difficult to explain. Appropriate outer

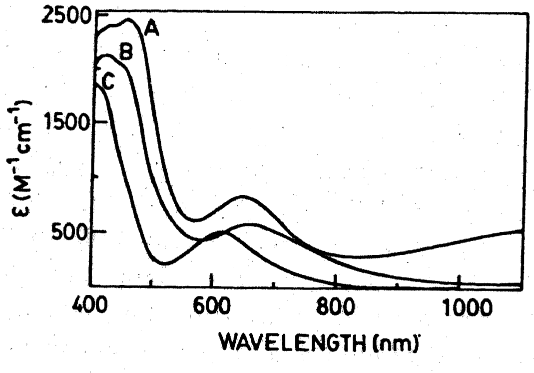

Figure 2. Electronic absorption spectra of (A) $[Mo_3S_4(CN)_9]^{7-}$, (B) $[Mo_3S_4(CN)_9]^{6-}$ and (C) $[Mo_3S_4(CN)_9]^{5-}$ in aqueous 0·35 M KOH + 0·1 M KCN + 0·05 M $K_2[Zn(CN)_4]$.

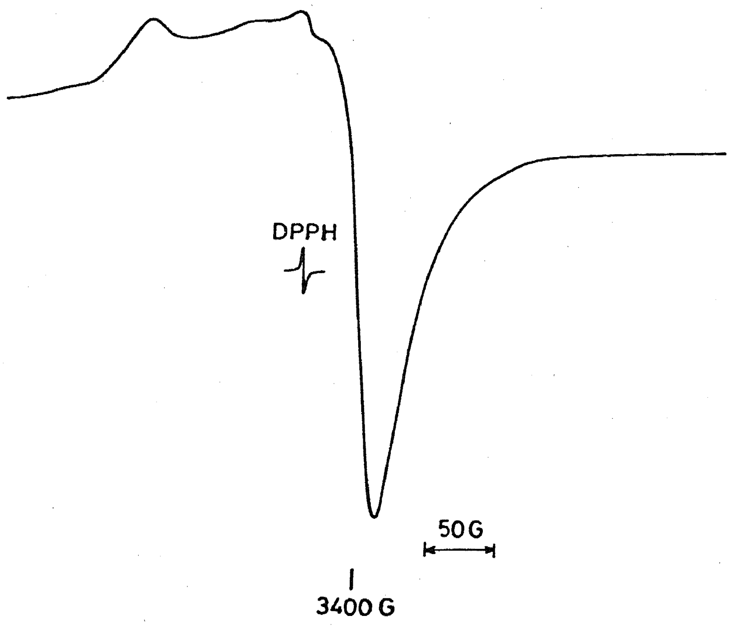

Figure 3. Room temperature *X*-band ESR spectrum (modulation amplitude 5G, microwave power 10 mW) of $[Mo_3S_4(CN)_9]^{6-}$ diluted with KCN–KOH–$K_2[Zn(CN)_4]$ and $K_5[Mo_3S_4(CN)_9]\cdot 2H_2O$.

sphere complexation with favorable hydrogen bonded solvent structure may be important contributions to stabilize these species.

For the expansion of the core of Mo_3S_4 to Mo_4S_4, it is necessary for the ninth electron to occupy the Mo–Mo antibonding orbital (Muller *et al* 1985) of $\underline{1}$. This reduction has been identified with an ill-defined cathodic peak potential around −1·40 V (figure 1, B, C). To achieve this step chemically, a drastic reducing condition with aluminium rather than zinc powder in 40% aqueous KOH solution followed by warming is required. Warming is necessary for the core conversion with the irreversible change of colour from yellow to reddish brown as shown below,

$$4K_5[Mo_3^{IV}S_4(CN)_9] + 4Al + 16KOH \xrightarrow{H_2O} 3K_8[Mo_4^{III}S_4(CN)_{12}] + 4K_2S + 4K[Al(OH)_4]. \qquad (1)$$

The cyclic voltammogram of the isolated compound by this process as shown in figure 1F is identical to that of $\underline{2}$ obtained by the authentic method (Weighardt *et al* 1984).

4. Conclusions

Tuning of reduction potential of $K_5[Mo_3S_4(CN)_9]$, with $\{Mo_3\}^6$ core, in aqueous medium led to media-dependent electron transfer steps using KOH–KCN–$K_2[Zn(CN)_4]$ ternary system as supporting electrolyte. We have identified the species containing $\{Mo_3\}^7$ and $\{Mo_3\}^8$ cores by electrochemical and spectroscopic techniques. It is important to note that the unstable reduced $\{Mo_3^{III}\}^9$ core is rearranged to yield an electron-precise tetrahedral $\{Mo_4^{III}\}^{12}$ core containing $[Mo_4^{III}S_4(CN)_{12}]^{8-}$ ion by core expansion: $4\{Mo_3^{III}\}^9 \rightarrow 3\{Mo_4^{III}\}^{12}$ according to the electron-precise cluster rule.

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