



$K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$: A New Alternative Synthetic Route for its Formation by Core Conversion from Trimer to Tetramer

RAMJEE SAH* and BALRAMJEE SAH

University Department of Chemistry, B.R.A. Bihar University, Muzaffarpur-842 001, India

*Corresponding author: E-mail: ramjeebrabu@yahoo.co.in

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For the first time the conversion of trimeric (M_3S_4)⁴⁺ to tetrameric (M_4S_4)⁴⁺ core has been made for molybdenum complex. The complex, $K_5[Mo_3S_4(CN)_9]$ (**1**) on using with strong reducing agent transform into $K_8[Mo_4S_4(CN)_{12}]$ (**2**) in near quantitative yield. The diamagnetic complex (**1**) containing (Mo_3)₆ core can accommodate two electrons in its non bonding molecular orbital $2a_1$ under reducing environment to give a complex ion $[Mo_3S_4(CN)_9]^{7-}$ with $[Mo_3]_8$ electronic configuration. This reduced species undergoes re-oxidation by atmospheric air to give back the original compound with $[Mo_3]_6$ core via a partially oxidized an intermediate species $[Mo_3S_4(CN)_9]^{6-}$ with $[Mo_3]_7$ core shows a characteristic EPR signal. However, under drastic reducing condition, the two electrons reduced species $[Mo_3S_4(CN)_9]^{7-}$ with $[Mo_3]_8$ core accommodate the next coming electron to its anti-bonding two electron orbital and thus achieve an unstable trinuclear $[Mo_3^{III}]_9$ core, where each metal centre has been reduced by one electron. The highly unstable and super reduced species $[Mo_3S_4(CN)_9]^{8-}$ with $[Mo_3^{III}]_9$ configuration undergoes core transformation from cuboidal trinuclear $[Mo_3^{IV}S_4]^{4+}$ to the cubane type tetranuclear core $[Mo_4^{III}S_4]^{4+}$ of $[Mo_4S_4(CN)_{12}]^{8-}$ complex ion. The corresponding tungsten-analogue though responses this reduction, but quickly oxidizes back to the starting material during work-up procedure.

Key Words: Core conversion, Trinuclear-cuboidal, Tetra-nuclear cubane type, Molybdenum-sulfur cluster.

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 $\{Mo_3^{IV}\}_6$ core¹⁻⁴. Proton coupled reductions for compounds containing this ion involve two sequential electron transfer steps to yield $\{Mo_3\}^8$ and $\{Mo_3\}^9$ with the absence of $\{Mo_3\}^7$ core⁴⁻⁶. Complex of eight or nine cluster electrons containing Mo_3OCl_3 moiety have been reported³. For the related $Mo_3S_4^{4+}$ ion containing complex, the redox reaction are extremely varied. Thus for $[Mo_3^{IV}S_4HN(CH_2CO_2)_2]_3^{2-}$, three sequential electron transfer steps in its reduction has been reported relatively at very low negative potential in water^{6,7} compared to the our step. Reduction of $[Mo_3^{IV}S_4(CN)_9]^{5-}$ at high negative potential in dimethyl sulphoxide⁷⁻⁹. This large difference in reduction potential may not solely be due to the effect of peripheral ligands in these complex.

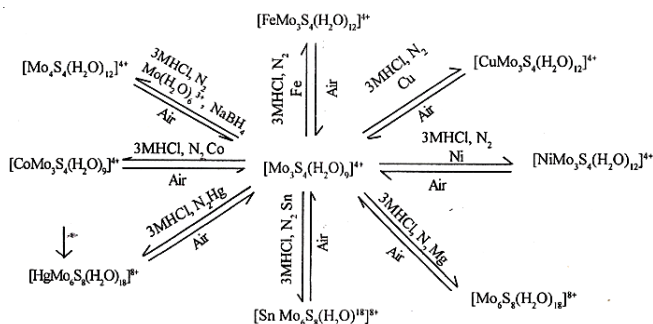
Formation of heterometal cubane $\{M'Mo_3S_4\}^{n+}$ core has been made by reacting $[Mo_3S_4(H_2O)_9]^{4+}$ ion with metal in acidic medium under the inert atmosphere of nitrogen¹⁰⁻¹². Interestingly by following magnesium, tin, or mercury, as reducing agent, double cubane $[Mo_6S_8(H_2O)_{18}]^{8+}$, $[Sn.Mo_6S_8(H_2O)_{18}]^{8+}$ and $[Hg.Mo_6S_8(H_2O)_{18}]^{8+}$, have also been synthesized¹³⁻¹⁵. These are similar to the hetero double cubane of Fe-Mo-S system

made as model for nitrogenase enzyme¹⁶⁻¹⁸ and using this strategy for the first time ammonia coordinated cubane, has also been synthesized¹⁹.

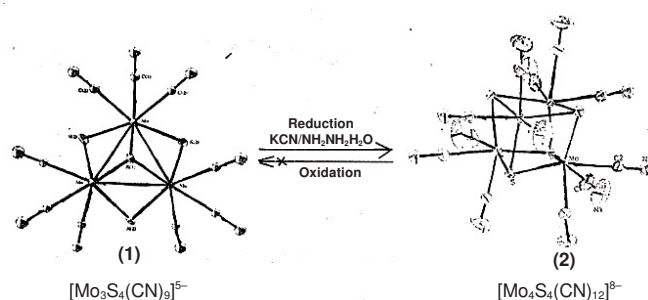
Regeneration of complete homo metal cubane $[Mo_4S_4(H_2O)_{12}]^{5+}$ achieved by the reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo(H_2O)_6]^{3+}$ with $NaBH_4$ in 0.3 M HCl under nitrogen atmosphere. However, this cubane cluster containing $\{Mo_4S_4\}^{n+}$ core gets slowly revert back to the starting material $[Mo_3S_4(H_2O)_9]^{4+}$ on keeping in air for 3 days. The entire inter conversion of $\{Mo_3S_4\}^{4+}$ core to $\{Mo_4S_4\}^{4+}$ core under drastic reducing atmosphere have been shown in **Schemes I** and **II** where sometimes it gets also inter convert to the heterometallic or homometallic double cubane core like $[M'Mo_6S_8(H_2O)_{18}]^{8+}$ or $[Mo_6S_8(H_2O)_{18}]^{8+}$ complex respectively.

Though the complex $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$ (**2**) has been isolated in poor yield (2.5 %) long back as by-product of $K_5[Mo_3S_4(CN)_9] \cdot 5H_2O$ (**1**) by Muller and co-worker²⁰. It is a time taking long process and require 7 days for its complete synthesis. Here, authors wish to describe an easy procedure for the synthesis of (**2**) in near quantitative yield by the reduction of (**1**) obtained as a product after cyanolysis of $(NH_4)_2[Mo_3S_{13}]$ with strong reducing agents like Na/Hg or $NH_2NH_2 \cdot H_2O$ in presence of KCN. Here $\{Mo_4S_4\}^{4+}$ core is

stabilized by strong π -bonding of CN^- ligand which has already been shown in **Scheme-II**.



Scheme-I: Inter conversion of $[\text{Mo}_3\text{S}_4]^{4+}$ cuboidal core to the complete cubane $[\text{Mo}_4\text{S}_4]^{4+}$ core and vice-versa



Scheme-II

EXPERIMENTAL

IR spectra of these complexes were recorded on Perkin-Elmer model 580 infrared spectrophotometer. Samples were prepared as CsI pellets and referenced to polystyrene bands. The electronic spectra of complexes were recorded on Shimadzu UV-VIS 190 and Perkin-Elmer λ_2 double beam spectrophotometers using matched quartz cell. EPR spectra were obtained from varian-E-109 using DPPH.

The cyclic voltammograms were recorded on a Bioanalytical system CV-27 voltammogram, in the connection with a C1B-Cell stand. All the experiments were performed in a standard three electrode configuration using an auxiliary Pt-electrode, a glassy carbon working electrode and a saturated calomel electrode under dry nitrogen atmosphere. All results were collected at 298 K and referenced to saturated calomel electrode (SCE). Distilled and dry DMSO was used as a solvent. $[(\text{C}_2\text{H}_5)_4\text{NClO}_4]$ and KCl, KOH-KCN, KOH-KCN- $\text{K}_2[\text{Zn}(\text{CN})_4]$ were used as supporting electrolyte for non-aqueous and aqueous medium respectively. The reported values were uncorrected for junction potential where voltammograms were recorded in different scan speeds but with the scan speed at 100 mV/s was used for discussion. The X-ray powder patterns were recorded on a Siefert-isodebyflex-2002 diffractometer using $\text{CuK}\alpha$ radiation with Ni-filter. The powdered sample was packed on a perspex sample holder.

All reagents and solvents were of A.R. grade and were used without further purification. Water was distilled in quick-fit apparatus over alkaline KMnO_4 and H_2SO_4 . The electric conductance of distilled water varied between 7×10^{-7} to $9 \times 10^{-9} \text{ W}^{-1} \text{ cm}^{-1}$. The compound $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ was prepared

from $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ by the reported methods¹⁹. All experiments were carried out under nitrogen atmosphere with degassed distilled water. Chemicals like KCN, $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ and Al-powder were used as purchased. Elemental analyses were performed by EA-1108 elemental analyzer. Sulfur and molybdenum were analyzed by oxidizing the compound under peroxide fusion as BaSO_4 and molybdenum oxinate respectively.

Synthesis of $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}] \cdot 4\text{H}_2\text{O}$

Method-A: Conversion of trimer $\{\text{Mo}_3\text{S}_4\}^{4+}$ core to a tetramer $\{\text{Mo}_4\text{S}_4\}^{4+}$ core in solution.

Method-I: $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ (0.5 mmol; 370 mg) and KCN (30 mmol; 2.0 g) were taken in 30 mL water and warmed up to $60^\circ\text{--}70^\circ\text{C}$ for 30 min. A bright green solution of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 2\text{H}_2\text{O}$ identified by UV-visible spectra was obtained. To this KOH (2 g); KCN (10 mmol; 650 mg) and $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ (1 mL) were added. The resultant solution was allowed to warm slowly. The colour of solution changed from green to red in the period of 15 min. The solution was kept warm (70°C) for 1 h and then allowed to cool at room temperature. On slow evaporation the red solution produced needle shaped red crystalline product which was isolated in (ca: 65.5 %) yields good based on the starting materials.

Method-II: $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 2\text{H}_2\text{O}$ (1 mmol; 880 mg); obtained by the cyanolysis of $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ [19b] (1 mmol; 740 mg) was dissolved in the minimum amount of water (20 mL) KCN (20 mmol; 1.30 g) and KOH (2 g) were added to it and then this was reduced by the addition of a total amount of 5 g (20 mmol) Na/Hg (2 %) slowly where by the colour of the solution changed from green to red in the period of 15 min. The red solution was kept at 70°C for 1 h and then was allowed to cool at room temperature. The red solution was filtered and the clear filtrate on slow evaporation gave needle shaped red crystalline product which was isolated in 85 % yield based on the starting material and the isolated product was characterized as $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}] \cdot 4\text{H}_2\text{O}$ ²¹.

Method-III: The process exactly similar to method-II was performed using aluminum powder (1 g) with a mixture of KOH (4 g) and KCN (30 mmol; 2 g) in 20 mL of water. Addition of aluminium powder was done in portion wise at room temperature to avoid the exothermic reaction. After the complete consumption of aluminium powder the reaction mixture was warmed at 70°C for 1 h and after that it was hot filtered. On cooling down the solution at room temperature, the reaction mixture gave red needle-shaped crystals which were filtered, washed with 40 % KOH to make it free from Al-impurity and then with any MeOH. Finally the crystals were re-crystallized from aqueous KOH-KCN medium. Yield: 84 % based on the starting material. Anal. calcd. for $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}] \cdot 4\text{H}_2\text{O}$; calcd. (found): C: 12.16 (12.06); H: 0.675 (0.708); N: 14.19 (14.24); O: 5.4 (5.8); S: 10.81 (10.50); Mo: 32.43 (32.12)

Method-B: Conversion of a trimer $\{\text{Mo}_3\text{S}_4\}^{4+}$ core to a tetramer $\{\text{Mo}_4\text{S}_4\}^{4+}$ core using a solid state reaction.

A thoroughly mixed powder mixture containing $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 2\text{H}_2\text{O}$; (1 mmol; 880 mg); KCN (30 mmol; 2 g) and KSCN (10 g) was heated up to 250°C in a closed

vessel under dry nitrogen atmosphere on an oil bath. The green colour of starting material started changing to brown and finally stopped to red. The temperature at 250 °C was maintained for 1 h. After cooling down the red product at room temperature, it was washed thoroughly with excess of MeOH-H₂O mixture to remove excess of potassium salt as impurity. Then the product was dissolved in the minimum amount of water and finally allowed to slow evaporation. A red needle-shaped crystalline product was isolated in 70 % yield based on the starting material K₅[Mo₃S₄(CN)₉].2H₂O and characterized as K₈[Mo₄S₄(CN)₁₂].4H₂O.

Reaction attempted for the synthesis of K₄[Mo₃S₄(CN)₉]: An oxidized species of (1): K₅[Mo₃S₄(CN)₉].2H₂O (1 mmol; 880 mg) was dissolved in the minimum amount of water (20 mL) followed by addition of KOH (2 g) to it. The reaction mixture was placed in a ice-bath to maintain the temperature at 0 °C. Addition of H₂O₂ (17 %; 1 mL) was added drop wise to the constantly stirred solution. The temperature of the reaction mixture was maintained at 0 °C throughout the progress of reaction. The colour of starting material changed from green to light-green within 4 min. The product was precipitated by adding an excess of methanol to the solution. The isolated precipitated product was filtered, washed thoroughly by methanol to remove un-reacted KOH. The compound was re-dissolved in minimum amount of water (10 mL) and re-crystallized by adding a mixture of MeOH /i-PrOH (20:10). Light green block shaped crystals were obtained (yield: ca. 70 %) and where characterized as K₅[Mo₃(μ₃-S)(μ₂-S)₂(μ₂-O)(CN)₉].2H₂O (3), in spite of expected K₄[Mo₃S₄(CN)₉]. The identity of product was confirmed by electronic spectral and ESR spectral studies.

RESULTS AND DISCUSSION

IR-spectrum of product obtained as K₈[Mo₄S₄(CN)₁₂].4H₂O shows vibration at 2123 cm⁻¹ for ν(CN), 1620 (m) for H₂O, 3490 (s) and 3570 (s) for H₂O, 370, 340, 310 and at 228 cm⁻¹ for ν(Mo-S) and ν(Mo-Mo). The various physico-chemical characterization of synthesized complex suggest that it is identical to that reported earlier as K₈[Mo₄S₄(CN)₁₂].2H₂O which has already been well characterized by Muller and co-workers using several physical measurements^{11,20}.

IR spectral data: IR-spectrum of product obtained shows vibration at 2123 cm⁻¹ for ν(CN⁻¹), 1620 (m) for δ(H₂O), 3490 (S) and 3570 (S) for ν(H₂O), 370, 340, 310 and 228 cm⁻¹ for ν(Mo-S) and ν(Mo-Mo).

According to the X-ray structure analysis [Mo₄S₄(CN)₁₂]⁸⁻ has practically T_d symmetry. In spite of the high symmetry of this complex, the assignment of IR and Raman spectra is not so easy according to the large number of vibrational degree of freedom (3N-6 = 90). The analysis was extended to the complete species [Mo₄S₄(CN)₁₂]⁸⁻ by including the M-C-N linear bending and C-N stretching. The normal modes of vibrations are distributed among the symmetry species of the T_d group according to:

$$\Gamma_{\text{vib}} = 6A_1(\text{R}) + 2A_2 + 8E(\text{R}) + 9 T_1 13T_2(\text{R, IR})$$

The designations are explained in the following manner, where the multiplicity of each type is shown in parenthesis: d = MC stretching (12), γ = CMC bending (12); r = M-S stretching

(12) α = MSM bending (12); δ = SMC bending (24); t = CN stretching (12); κ = MCN linear bending in a plane through the model centre (12); λ = MCN linear bending in a plane perpendicular to the one through the model centre (12) where the given designations d, γ, r, α, δ, t, κ, λ are various types of valance coordinates used for the construction of a set of independent symmetry coordinates for the [Mo₄S₄(CN)₁₂]⁸⁻ with T_d symmetry.

The bands in the region of the ν(CN) vibrations (2100 cm⁻¹) are easy to locate. It seems to be possible to distinguish between the Mo-S stretching vibrations less than 370 cm⁻¹ (< 370 cm⁻¹) on the one hand and the vibrations of the Mo-C-N linkage on the other hand (Mo-C stretching and δ(Mo-CN) bending those lying at more than 370 cm⁻¹ (> 370 cm⁻¹), which are strongly coupled. A₁ fundamentals are the strongest bands in the Raman and T₂ bands the strongest bands in the IR.

There are 24 δ-type bending but only 12 combinations were used in the construction of the symmetry coordinates. The rest of them are present as redundancies, since all δ-bending were included in the basis of the force field. In a similar way only 6 combinations of 12 α bending are used in the symmetry coordinates. The agreement between the observed and calculated ν(Mo-C) and δ(Mo-CN) vibrations was not expected to be good as they are strongly coupled.

The measurements of intensities of the ν(CN) infrared bands in solution is of special interest. The integrated absorption coefficient K has been calculated from the molar extinction coefficient ε_m measured at the absorption maximum of the strong ν(CN) band and half-width under the assumption of Lorentz function band shape. The ν(CN) frequencies are dependents on the oxidation state of molybdenum. The correlation between the oxidation state and the ν(CN) frequencies and their band intensities *c* be explained by the concept of donation and M→π (CN) back-bonding. The intensity is a measure of the degree of M-C π-bonding *i.e.* of the increasing importance of value structure-II.



With an increasing number of (formal) Mo 4*d* electrons, the valance structure II gains more importance. Therefore, the intensity per CN⁻ ligand is higher in K₆[Mo₂^{III}S₂(CN)₈] than in the almost iso-structural K₄[Mo₂^{IV}S₂(CN)₈], but also higher in K₈[Mo₄^{III}S₄(CN)₁₂] than in K₅[Mo₃^{IV}S₄(CN)₉], where both having a comparable coordination of Mo which means [Mo(CN)₃] moieties are linked by Mo-Mo single bonds. The latter comparison is very rough since the variations involved are not of the same species (Table-1).

The most interesting vibrations are those of the Mo₄S₄ cube which can be classified according to the species.

$$\nu(\text{Mo-S}): A_1 + E + T_1 + 2T_2; \quad \nu(\text{Mo-Mo}): A_1 + E + T_2$$

Electronic spectral data: The electronic spectrum is quite helpful to understand this core transformation from trimer to tetramer under this reducing atmosphere. Under the reducing environment of Na/Hg or Al-powder, the spectrum A of the starting material [Mo₃S₄(CN)₉]⁵⁻ changes from pattern (A) to (C). The electronic spectrum C of the fully reduced species [Mo₃S₄(CN)₉]⁷⁻ changed back to A on exposure of its reduced yellow solution to air. This quantitative conversion occurs *via*

TABLE-1
CALCULATED VIBRATIONAL FREQUENCIES
(cm^{-1}) AND THEIR ASSIGNMENTS

Species	$^{92}\text{Mo}^{32}_4\text{S}_4(\text{CN})_{12}^{8-}$	$^{100}\text{Mo}^{32}_4\text{S}_4(\text{CN})_{12}^{8-}$	$^{92}\text{Mo}^{34}_4\text{S}_4(\text{CN})_8^{8-}$	Assignments
A1	2123	2123	2123	$\nu(\text{CN})$
	527	520	527	$\nu(\text{Mo-C})$
	447	444	447	$\nu(\text{Mo-CN})$
A2	433	433	433	$\delta'(\text{Mo-CN})$
	2123	2133	2133	$\nu(\text{CN})$
E	495	492	495	$\nu(\text{MoC})$
	455	452	455	$\nu(\text{MoCN})$
	407	405	406	$\delta'(\text{CMo-CN})$
	119	119	119	$\nu'(\text{CMoC})$
T_1	2123	2123	2123	$\nu(\text{CN})$
	492	490	492	$\nu(\text{Mo-C})$
	453	449	452	$\delta'(\text{Mo-CN})$
	436	436	436	$\delta'(\text{MoCN})$
	404	403	404	$\delta'(\text{MoCN})$
	151	149	150	$\delta'(\text{CMoC})$
	113	113	113	$\delta'(\text{CMoS})$
	83	83	83	$\delta'(\text{CMoS})$
T_2	2123	2123	2123	$\nu(\text{CN})$
	521	514	519	$\nu(\text{MoC})$
	503	500	502	$\nu(\text{MoC})$
	466	464	465	$\delta'(\text{MoCN})$
	437	434	438	$\delta'(\text{MoCN})$
	404	403	404	$\delta'(\text{MoCN})$
	125	124	125	$\delta'(\text{CMoC})$
	118	118	118	$\delta'(\text{CMoC})$
75	75	75	$\delta'(\text{CMoS})$	

two distinct stage of oxidation showing two different isobestic point-(1) at 733 nm followed by 620 nm and (2) at 576 nm. The electronic spectra of these species are shown in Fig. 1. For fully reduced species we could not locate the appearance of band beyond 1100 nm due to the limitation of spectrophotometer used.

UV-visible spectrum shows λ_{nm} (ϵ): 1125 (152), 660 (580), 500 (sh), 388 (sh), 316 (14400); 270 (32100); 220 (25000).

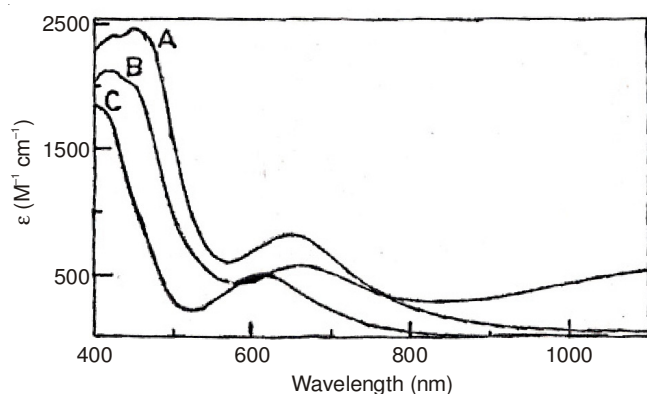


Fig. 1. Electronic absorption spectra of (A) $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{7-}$, (B) $[\text{Mo}_3\text{S}_4(\text{SN})_9]^{6-}$ and (C) $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ in aqueous 0.35 MKOH+ 0.1 M KCN+ 0.05 M $\text{K}_2[\text{Zn}(\text{CN})_4]$

ESR-spectral study: The partially oxidized species E is solution with λ_{max} at 660 nm (curve B, Fig. 1) when *vacuum*

dried and diluted with diamagnetic $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ complex ion show room temperature, ESR spectrum ($g_{11} = 2.073$ and $g_1 = 1.985$) as shown in Fig. 2. 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 $\{\text{Mo}_3\}^9$ core may indicate the presence of $\{\text{Mo}_3\}^7$ core in this half oxidized species⁶. The electron accepting property of water from the nitrogen atoms in the cyano ligated group 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 dimethyl sulphoxide.

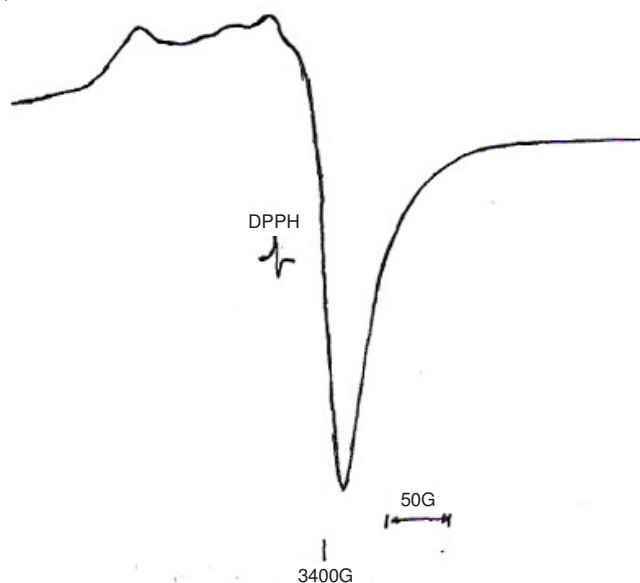


Fig. 2. Room temperature X-band ESR spectrum (modulation amplitude 5G, microwave power 10 mW) of $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{6-}$ diluted with KCN-KOH- $\text{K}_2[\text{Zn}(\text{CN})_4]$ and $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9] \cdot 2\text{H}_2\text{O}$

Thus, a regular shift of half-wave potential to a less negative value for $\{\text{Mo}_3\}^6$ to $\{\text{Mo}_3\}^7$ and to a more positive one for $\{\text{Mo}_3\}^6$ to $\{\text{Mo}_3\}^5$ steps due to increase of the percentage of water in dimethyl sulphoxide has been observed, demonstrating the role of a protic solvent in cyanoligated species^{21,22}.

Electrochemical study: Cyclic voltammogram of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ in water with different supporting electrolyte compositions (KCl, KOH-KCN, KOH-KCN- $\text{K}_2[\text{Zn}(\text{CN})_4]$) are shown in Fig. 3(A-F). The reported $E_{1/2} = -1.49$ V vs. NHE for one electron reduction of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ in DMSO⁹ is drastically shifted to -0.74 V using KCl ($\Delta E = 100$ mV) and KOH-KCN ($\Delta E = 80$ mV) as supporting electrolyte respectively. In the latter case, this two more successive reduction peak potentials appeared around -1.20 V and -1.40 V respectively.

When KOH-KCN- $\text{K}_2[\text{Zn}(\text{CN})_4]$ combined supporting electrolyte was used the appearance of second reduction process became by the third irreversible reduction. The quasi-reversible nature of the first reduction step in KCl changed to the fully reversible form in KOH-KCN supporting electrolyte. All the reductions steps are diffusion controlled in nature.

Anaerobic chemical reduction of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ in KOH-KCN medium by Zn powder led to the change of colour

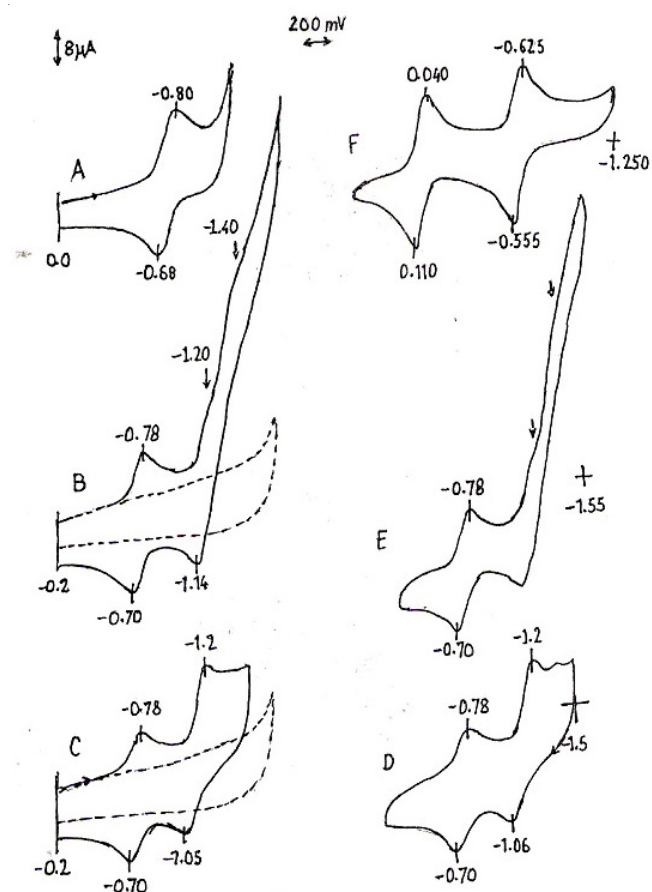
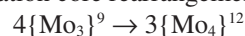


Fig. 3. Cyclic voltammograms of 0.98 mM K₅[Mo₃S₄(CN)₉] in different supporting electrolyte compositions: (A) KCl; (B) KOH-KCN, (C) KOH-KCN-K₂[Zn(CN)₄]. Broken lines in B and C were blank scans. Voltammograms of chemically generated 0.98 mM [Mo₃S₄(CN)₉]⁷⁻ by zinc (D) and aluminium (E) (see text for electrolyte compositions). Voltammogram of 1 mM solution of [Mo₄S₄(CN)₁₂]⁸⁻ in 0.5 MKCl (F). All scan rates, 100 mV s⁻¹ at 25 ± 1 °C

from bright green to yellow *via* olive-green. Oxidative scan of this species (resting potential at -1.5 V) showed an identical voltammogram to that observed in the reductive scan (resting potential at 0.00V) for K₅[Mo₃S₄(CN)₉] with KOH-KCN-K₂[Zn(CN)₄] as the supporting electrolyte. Fig. [3C, 3D]. Then reduction of the starting material K₅[Mo₃S₄(CN)₉] was accomplished by the using aluminium powder instead of Zn, the reverse scan (oxidative, resting potential at -1.55 V) of the yellow solution was identical to what the observed in the reductive scan of K₅[Mo₃S₄(CN)₉] with KOH-KCN as supporting electrolyte (Fig. 3B, 3E).

For a trinuclear cluster having *d*⁶ electronic configuration, the electrons responsible for three metal-metal bonds will be accommodated in 1a₂¹-1e⁴ orbitals³. The diamagnetism of these complexes can thus readily be explained using this quantitative M.O. scheme (Fig. 4). Interesting lying non-bonding molecular orbital, the low 2a₁ under reducing environments may be populated, thus showing the possibilities of having {Mo₃S₄}⁴⁺ core with *d*⁷ or *d*⁸ electronic configuration. The relative energies of these orbitals, suggest that the absorption within these orbitals will occur under visible region and these transitions are symmetry allowed. They should have higher intensities than the *d-d* transition like L → M and M → L are expected to occur only at higher energy. It is interesting to take a note that

on going from {Mo₃}⁶ to {Mo₃}⁸ configuration, the extra two electrons are populated in mainly non-bonding orbital 2a₁ with respect to the metal-metal bond. If by any chemical means, extra electrons are being populated to the next anti-bonding orbitals 2e and so on in relation to the M-M bond, the M₃-core will be destabilized. Thus, with the electronic configuration {Mo₃}⁹, each metal atom now acquires one electrons more and for its stabilization core rearrangement like.



should occur as shown in **Scheme-I** leading to the formation of a complete cubane core like 3{Mo₄}⁴⁺.

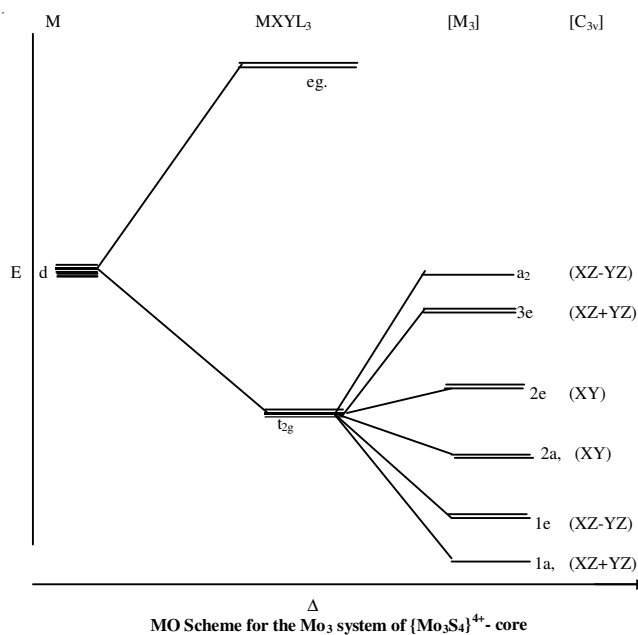
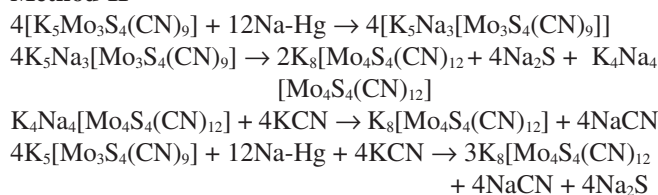


Fig. 4

The electron balanced reaction can be summarized as follows:

Method-II

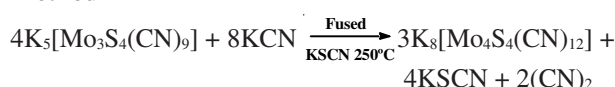


Method-III



A model reaction to achieve such core conversion which has been made under the solid reaction state also as follows:

Method-B



The cyclic voltammogram of the isolated compound by this process (Fig. 3F) is identical to that of K₈[Mo₄S₄(CN)₁₂] obtained by the authentic method.

The X-ray powder diffraction data of (2) synthesized by adopting the alternative route are almost matching to that reported in literature²⁰. The similarities between the model substances for the ferredoxins and the complexes under study

regarding their formal electron-transfer properties are striking. Since all known cyanothiomolybdates undergoes reversible electrochemical redox reaction.

It is important to realize that $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ and $[\text{Mo}_4\text{S}_4(\text{CN})_{12}]^{8-}$ have been obtained by the reaction of amorphous MoS_3 with excess of KCN in aqueous solution. Where the major product was $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ (yield = 10 % based on the starting material). The tetramer complex ion $[\text{Mo}_4\text{S}_4(\text{CN})_{12}]^{8-}$ was obtained as a by-product of the reaction in the very low yield (Can 1.25 % based on starting material). The high yield of **1** and very low yield of **2** suggest that the trinuclear cluster units are already present in the amorphous MoS_3 a part of which gets slowly convert to the tetramer unit **2** under the available reducing atmosphere of KCN^{20,21}. The phenomenon of this core conversion has also been confirmed experimentally by the another that on reducing the aqueous solution of **1** with KOH and Al-powder it generates **2** in near quantitative yield.

Conclusion

Tuning of reduction potential of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ with $\{\text{Mo}_3\}^6$ core in aqueous medium led to the media-dependent electron transfer steps using KOH-KCN- $\text{K}_2[\text{Zn}(\text{CN})_4]$ ternary system as supporting electrolyte. We have identified the species containing $\{\text{Mo}_3\}^8$ cores by electro chemicals and spectroscopic techniques. It is important to note, that the unstable reduced $\{\text{Mo}_3^{\text{III}}\}^9$ core is rearranged to yield an electron-precise tetrahedral $\{\text{Mo}_3^{\text{III}}\}^{12}$ core containing $[\text{Mo}_4^{\text{III}}\text{S}_4(\text{CN})_{12}]^{8-}$ ion by the core expansion:

$4\{\text{Mo}_3^{\text{III}}\}^9 \rightarrow 3\{\text{Mo}_4^{\text{III}}\}^{12}$ according to the electron-precise cluster rule. Interesting, the fully reduced species $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}]$ on subject to oxidation using H_2O_2 or Cl_2 water, it does not revert back to the oxidized starting material $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$. The oxidation responses to the generation of oxo-species of Mo_3 -trimer or Mo_2 -dimer core.

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