

DELIBRATION OF ONE ELECTRON REDUCTION OF TRIMER $K_5[Mo_3S_4(CN)_9] \cdot 2H_2O$ TO TETRAMER $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$

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ABSTRACT

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 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 $2e$ orbital and thus achieve an unstable tri-nuclear $[Mo_3^{III}]^9$ 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 oxidises back to the starting material during work-up procedure.

Keyword: *Mechanistic Studies , Electronic Population, Trimer-cuboidal, Tetramer cubane type, Molybdenum-sulfur cluster.*

I 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 $\{Mo_3\}^6$ 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 water⁶⁻⁷ compared to the our step.

reduction of $[\text{Mo}_3^{\text{IV}}\text{S}_4(\text{CN})_9]^{5-}$ at very 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 $\{\text{M}'\text{Mo}_3\text{S}_4\}^{n+}$ core has been made by reacting $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ 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 $[\text{Mo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$, $[\text{Sn}.\text{Mo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$ and $[\text{Hg}.\text{Mo}_6\text{S}_8(\text{H}_2\text{O})_{18}]^{8+}$, have also been synthesized¹³⁻¹⁵. These are very 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 $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ achieved by the reduction of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ with NaBH_4 in 0.3M HCl under nitrogen atmosphere. However, this cubane cluster containing $\{\text{Mo}_4\text{S}_4\}^{n+}$ core gets slowly revert back to the starting material $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ on keeping in air for days

Though the complex $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}].4\text{H}_2\text{O}$ (2) has been isolated in poor yield (2.5%) long back as by-product of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9].5\text{H}_2\text{O}$ (1) by Muller and co-worker²⁰. It is a time taking long process and require seven 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 $(\text{NH}_4)_2[\text{Mo}_3\text{S}_{13}]$ with strong reducing agents like Na/Hg or $\text{NH}_2\text{NH}_2.\text{H}_2\text{O}$ in presence of KCN

II EXPERIMENT

2.1 Physical Measurements

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 $\square \square$ 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 298⁰K 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 100mV/s was used for discussion. The X-ray powder patterns were recorded on a Siefert-isodebyeflex-2002 diffractometer using Cu-K $\square \square$ radiation with Ni filter. The powdered sample was packed on a perspex sample holder.

Materials:

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 $9 \times 10^{-9} \square \square \square \text{Cm}^{-1}$. 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 $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}]\cdot 4\text{H}_2\text{O}$

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

$(\text{NH}_4)_2[\text{Mo}_3\text{S}_4]$ (0.5 m mol ; 370 mg) and KCN (30.0 m mol ; 2.0 gm) were taken in 30.0 ml water and warmed up to $60^\circ\text{--}70^\circ\text{C}$ for 30 minutes. 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-Vis spectra was obtained. To this KOH (2.0 gm.); KCN (10.0 m mol ; 650 mg.) and $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$ (1.0 ml) were added. The resultant solution was allowed to warm slowly. The color of solution changed from green to red in the period of 15 minutes. The solution was kept warm (70°C) for an hour 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.

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)

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

A thoroughly mixed powder mixture containing $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]\cdot 2\text{H}_2\text{O}$; (1.0 m mol ; 880 mg); KCN (30 m mol ; 2.0 gm;) and KSCN (10.0 gm.) was heated up to 250°C in a closed vessel under dry nitrogen atmosphere on an oil bath. The green color of starting material started changing to brown and finally stopped to red. The temperature at 250°C was maintained for an hour. After cooling down the red product at room temperature, it was washed thoroughly with excess of $\text{MeOH-H}_2\text{O}$ 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 $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]\cdot 2\text{H}_2\text{O}$ and characterized as $\text{K}_8[\text{Mo}_4\text{S}_4(\text{CN})_{12}]\cdot 4\text{H}_2\text{O}$

2.2 Reaction Attempted for the synthesis of $\text{K}_4[\text{Mo}_3\text{S}_4(\text{CN})_9]$: an oxidized species of (1)

$\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]\cdot 2\text{H}_2\text{O}$ (1.0 m mol ; 880 mg) was dissolved in the minimum amount of water (20 ml) followed by addition of KOH (2.0 gram) to it. The reaction mixture was placed in a ice-bath to maintain the temperature at 0°C . Addition of H_2O_2 (17%; 1.0 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 4.0 minute. 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 (10.0 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 were characterized as $K_5[Mo_3(\mu_3-S)(\mu_2-S)_2(\mu_2-O)(CN)_9] \cdot 2H_2O$, (**3**), in spite of expected $K_4[Mo_3S_4(CN)_9]$. The identity of product was confirmed by electronic spectral and esr spectral studies.

III RESULT AND DISCUSSION

IR-spectrum of product obtained as $K_8[Mo_4S_4(CN)_{12}] \cdot 4H_2O$ shows vibration at 2123 cm^{-1} for ν_{CN} , 1620 (m) for δH_2O , 3490(s) and 3570(s) for νH_2O , 370 , 340 , 310 and at 228cm^{-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 $K_8[Mo_4S_4(CN)_{12}] \cdot 2H_2O$ which has already been well characterized by Muller and co-workers using several physical measurements.²⁰

3.1 IR spectral Data

IR-spectrum of product obtained shows vibration at 2123 cm^{-1} for $\square\square CN^\dagger$, 1620 (m) for δH_2O , 3490 (S) and 3570 (S) for $\square H_2O$, 370 , 340 , 310 and 228 cm^{-1} for \square MoS and $\square\square$ MoMo.

According to the X-ray structure analysis $[Mo_4S_4(CN)_{12}]^{8-}$ 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 $[Mo_4S_4(CN)_{12}]^{8-}$ 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

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

The designations are explained in the following manner, where the multiplicity of each type is shown in parenthesis:

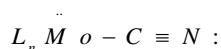
d = MC stretching (12), γ = CMC bending (12); r = M-S stretching (12) $\square\square$ = M \square M bending (12); $\square\square$ = SMC bending (24); t = CN stretching (12); $\square\square$ = MCN linear bending in a plane through the model centre (12); \square = MCN linear bending in a plane perpendicular to the one through the model centre (12) where the given designations d, \square , r, $\square\square$, $\square\square$, t, \square , $\square\square$ are various types of valence coordinates used for the construction of a set of independent symmetry coordinates for the $[Mo_4S_4(CN)_{12}]^{8-}$ with T_d symmetry. \square

The bands in the region of the \square (CN) vibrations (2100 cm^{-1}) are easy to locate. It seems to be possible to distinguish between the Mo-S stretching vibrations less than 370cm^{-1} ($<370\text{ cm}^{-1}$) on the one hand and the vibrations of the Mo-C-N linkage on the other hand (Mo-C stretching and \square MoCN bending those lying at more than 370 cm^{-1} ($>370\text{cm}^{-1}$), which are strongly coupled. A_1 fundamentals are the strongest bands in the Raman and T_2 bands the strongest bands in the IR.

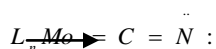
There are 24 \square -type bending but only 12 combinations were used in the construction of the symmetry coordinates. The rest of them are present as redundancies, since all \square -bending were included in the basis of the force field. In a similar way only 6 combinations of 12 \square bending are used in the symmetry coordinates. The agreement between the

observed and calculated $\nu(\text{Mo-C})$ and $\nu(\text{Mo-CN})$ vibrations was not expected to be good as they are strongly coupled.

The measurements of intensities of the $\nu(\text{CN})$ 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 $\nu(\text{CN})$ band and halfwidth under the assumption of Lorentz function band shape. The $\nu(\text{CN})$ frequencies are dependent on the oxidation state of molybdenum. The correlation between the oxidation state and the $\nu(\text{CN})$ frequencies and their band intensities can be explained by the concept of π donation and π 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.



I



II

With an increasing number of (formal) Mo 4d electrons, the valence structure II gains more importance. Therefore, the intensity per CN⁻ ligand is higher in $\text{K}_6[\text{Mo}_2^{\text{III}}\text{S}_2(\text{CN})_8]$ than in the almost iso-structural $\text{K}_4[\text{Mo}_2^{\text{IV}}\text{S}_2(\text{CN})_8]$, but also higher in $\text{K}_8[\text{Mo}_4^{\text{III}}\text{S}_4(\text{CN})_{12}]$ than in $\text{K}_5[\text{Mo}_3^{\text{IV}}\text{S}_4(\text{CN})_9]$, where both having a comparable coordination of Mo which means $[\text{Mo}(\text{CN})_3]$ moieties are linked by Mo-Mo single bonds. The latter comparison is very rough since the variations involved are not of the same species.

The most interesting vibrations are those of the Mo_4S_4 cube which can be classified according to the species



3.2 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 $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{5-}$ changes from pattern (A) to (C). The electronic spectrum C of the fully reduced species $[\text{Mo}_3\text{S}_4(\text{CN})_9]^{7-}$ changed back to A on exposure of its reduced yellow solution to air. This quantitative conversion occurs via two distinct stage of oxidation showing two different isobestic point - (1) at 733 nm followed by 620 nm and (2) at 576 nm. UV-Vis Spectrum shows $\lambda_{\text{nm}} (\epsilon)$: 1125 (152), 660 (580), 500(sh), 388(sh), 316(14400); 270(32100); 220(25000).

3.3 ESR-Spectral Study

The partially oxidized species **E** in solution with λ_{max} at 660 nm 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 $g_1 = 1.985$). 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.

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

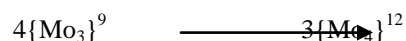
3.4 Electrochemical Study

The reported $E_{1/2} = -1.49\text{V}$ 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 -0.74V using KCl ($\Delta E = 100\text{mV}$) and KOH-KCN ($\Delta E = 80\text{mV}$) as supporting electrolyte respectively. In the latter case, this two more successive reduction peak Potentials appeared around -1.20V and -1.40V respectively.

When $\text{KOH-KCN-K}_2[\text{Zn}(\text{CN})_4]$ 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.

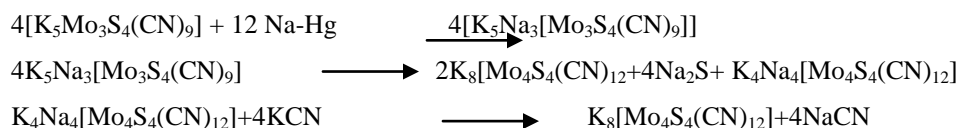
Anaerobic chemical reduction of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ in KOH-KCN medium by Zn powder led to the change of colour from bright green to yellow via olive-green. Oxidative scan of this species (resting potential at -1.5V) showed an identical voltammogram to that observed in the reductive scan (resting potential at 0.00V) for $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ with $\text{KOH-KCN-K}_2[\text{Zn}(\text{CN})_4]$ as the supporting electrolyte. Then reduction of the starting material $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ was accomplished by the using aluminium powder instead of Zn , the reverse scan (oxidative, resting potential at -1.55V) of the yellow solution was identical to what the observed in the reductive scan of $\text{K}_5[\text{Mo}_3\text{S}_4(\text{CN})_9]$ with KOH-KCN as supporting electrolyte.

For a trinuclear cluster having d^6 electronic configuration, the electrons responsible for three metal-metal bonds will be accommodated in $1a_1^2 - 1e^4$ orbitals³ The diamagnetism of these complexes can thus readily be explained using this quantitative M.O. Interesting lying non-bonding molecular orbital, the low $2a_1$ under reducing environments may be populated, thus showing the possibilities of having $\{\text{Mo}_3\text{S}_4\}^{4+}$ 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 $\{\text{Mo}_3\}^6$ to $\{\text{Mo}_3\}^8$ configuration, the extra two electrons are populated in mainly non-bonding orbital $2a_1$ 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 M_3 -core will be destabilized. Thus, with the electronic configuration $\{\text{Mo}_3\}^9$, each metal atom now acquires one electrons more and for its stabilization core rearrangement like



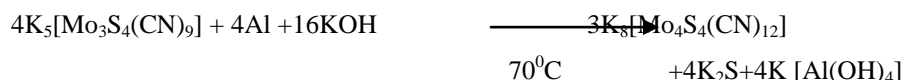
should occur leading to the formation of a complete cubane core like $3\{\text{Mo}_4\}^{4+}$.

The electron balanced reaction can be summarized as follows:

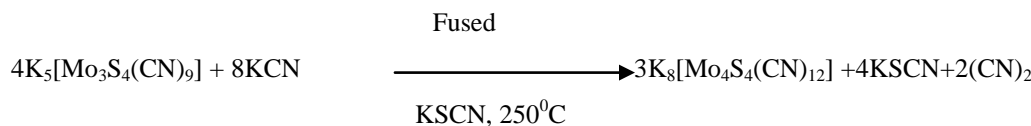


or

Water



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

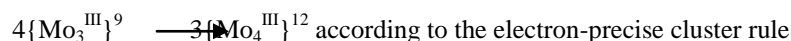


The X-ray powder diffraction data of (**2**) synthesized by adopting the alternative route are almost matching to that reported in literature²⁰. The similarities between the model substances for the ferredoxins and the complexes under study regarding their formal electron-transfer properties are striking. 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 KCN²⁰. 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.

IV 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 :



Interesting, the fully reduced species $K_8[Mo_4S_4(CN)_{12}]$ on subject to oxidation using H_2O_2 or Cl_2 -water, it does not revert back to the oxidized starting material $K_5[Mo_3S_4(CN)_9]$. The oxidation responses to the generation of oxo-species of Mo_3 -trimer or Mo_2 -dimer core.

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