Oxidation of phosphine by sulfur or selenium involving a catalytic cycle in the interconversion of monomer and tetramer forms of copper–maleonitriledithiolate complexes

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Abstract.   The addition of triphenylphosphine (PPh$_3$), into [Et$_4$N]$_4$[Cu$_4$(mnt)$_4$] shifted its characteristic electronic spectral band at 377 nm to 372 nm which is identical to that of the monomeric species, [Et$_4$N][Cu(mnt)(PPh$_3$)]. This reaction was followed by electrochemical study and also by ^{31}P NMR spectroscopy. Such interconversion with the participation of breaking of bridging copper-μ_3-sulfur bond with the formation of new copper–phosphorous bond led to the development of a catalytic cycle using excess PPh$_3$ and S or Se as the reacting substrates. The turnover number for the oxidation of PPh$_3$ by S was found to be $0·8 \times 10^{-2}$ s^{-1} and that with Se was $0·6 \times 10^{-2}$ s^{-1} using this catalytic system.

Keywords.   Monomer ↔ tetramer interconversion; catalytic cycle; phosphine oxidation reduction; sulfur; selenium.

1.   Introduction

Transition metal-sulfur bonds are ubiquitous not only in metalloenzymes but also present in man-made functional materials, in catalysts with various architectures for structural interest.[1] The sulfur atoms present in these entities serve as terminal or bridging ligands to metal ions to construct various types of molecular structures.[2–3]

Cu^I ion with 1,1- or 1,2-dithiolene chelating ligands is known to form multinuclear or polynuclear complexes.[4,5] Sources of dithiolene sulfur ligands span like maleonitriledithiolate, (mnt), dithiosquarate (dts), benzene-1,2-dithiolate (bdt), *iso*-maleonitriledithiolate (*i*-mnt) (scheme 1). The two sulfurs present in these dithiolene ligands contribute diverse bridging mode like μ_1-S and μ_2-S.

{Cu$_8$S$_{12}$} core is a common feature in what appear to be a typical class of cluster obtained by the reaction of cuprous ions and bidentate sulfur chelating ligands. An outstanding common structural feature in [Cu$_8$(*i*-mnt)$_6$]$^{4-}$, [Cu$_8$(dts)$_{12}$]$^{4-}$, and [Cu$_8$(mnt)$_6$]$^{4-}$ clusters[4,5] is the similarity of cubic structure where all the coordinated sulfurs are attached as μ_2-S bridging mode. Recently, we have reported the tri-

nuclear, [Cu$_3$(mnt)$_3$]$^{4-}$ and tetranuclear, [Cu$_4$(mnt)$_4$]$^{4-}$ complexes[6,7] where the coordinated sulfurs vary their attachment in μ_1-S and μ_2-S bridging modes with their interconversion leading to octanuclear complex.

The cubane dithiolene cluster with *iso*-maleonitriledithiolate (*i*-mnt) ligand on oxidation by elemental sulfur led to sulfur rich copper-dithiolene cluster.[4a] The added sulfurs in turn may be removed from this sulfur-rich cluster by using PPh$_3$ to yield tetranuclear cluster with SPPh$_3$ as a by-product (scheme 2).

We were interested to explore similar chemistry using maleonitriledithiolate (mnt) ligand. The teranuclear and mononuclear Cu^I-mnt complexes are structurally characterized by us.[6] Here, we report a clean inter conversion between tetramer and monomer complex using elemental sulfur (and also independently with selenium) and PPh$_3$ to invoke a catalytic cycle that has been characterized by spectroscopic methods such as UV/Vis, ^{31}P NMR and by cyclic voltammetric study.

2.   Experimental

All spectroscopic measurements were performed under argon atmosphere to prevent aerial oxidation of the complexes. Solvents used for the spectro-

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Scheme 1.

$[Bu_4N]_4(Cu_8(i\text{-}mnt)_6) + S \rightarrow [Bu_4N]_6[Cu_6(S, i\text{-}mnt)_6]$

$[Bu_4N]_6(Cu_6(S,i\text{-}mnt)_6) + PPh_4 \rightarrow$

$\qquad\qquad [Bu_4N]_4[Cu_4(i\text{-}mnt)_4] + SPPh_3$
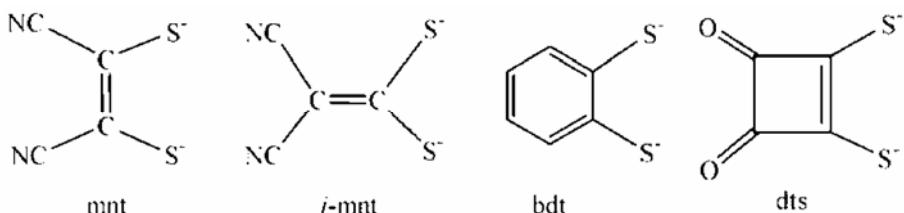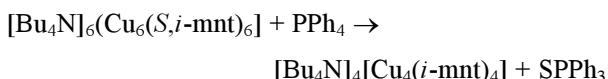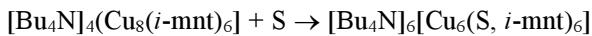
Scheme 2.

scopic measurements were of spectroscopic grade and were used as procured. Acetonitrile (HPLC grade) used for UV/Vis, cyclic voltammetry and for ^{31}P NMR spectroscopy was distilled twice over P_2O_5 and once over CaH_2. The complexes, $[Et_4N]_4$ $[Cu_4(mnt)_4]$ and $[Et_4N][Cu(mnt)(PPh_3)]$ were synthesized by previous procedure.[6]

Cyclic voltammetry (CV) and Differential pulse polarographic (DPP) studies were made by using an Epsilon EC-20 machine. The electrolytic cell used was a conventional three compartment cell, in which a GCE working electrode, a Pt auxiliary electrode, and an Ag/AgCl reference electrode were employed. The CV and DPP measurements were performed at room temperature using $0 \cdot 2$ (M) $^{n}Bu_4NClO_4$ as the supporting electrolyte in CH_3CN normally under a scan rate of 100 mV s^{-1} for CV and at 20 mV s^{-1} scan rate for DPP respectively. The ferrocenium/ferrocene couple was used as the internal standard ($E_0 = 0 \cdot 53$ V under experimental condition). Electronic absorption spectra were recorded with the help of a USB2000 UV/Vis Spectrometer and ^{31}P NMR spectra were recorded on JEOL JNM-LA 400 FT–NMR machine.

3. Results and discussion

Figure 1 represents the interconversion between tetramer and monomer Cu-mnt complex under sufficient excess of the substrates like PPh$_3$ and elemental sulfur or selenium. To understand this catalytic cycle, a representative forward part of the reaction in the conversion of tetramer to monomer on the addition of PPh$_3$ was followed by electronic spectroscopy and also by electrochemical study. Furthermore

backward or the reverse reaction like the conversion of monomer to tetramer by the addition of S or Se powder was monitored by ^{31}P NMR spectroscopy.

3.1 *Electronic absorption spectra*

The forward reaction in the conversion of tetramer to monomer in the presence of PPh$_3$ was monitored by UV/Vis spectroscopy as shown in figure 2. The electronic spectrum of tetramer exhibits a strong absorption band at 377 nm whereas monomer shows a strong absorption band at 372 nm. The characteristic electronic spectral band at 377 nm of the tetramer is shifted to 372 nm on the addition of PPh$_3$ in acetonitrile (figure 2). This indicates the rupture of the bridging copper–sulfur bond (μ_2-S) involved in the formation of the tetramer. The monomer {–Cu(S$_2$–mnt)} structural unit is now stabilized by the formation of a new copper–phosphorous bond as found in $[Et_4N][Cu(mnt)(PPh_3)]$.

3.2 *Electrochemistry*

The change in the form of tetramer to monomer can also be followed by electrochemical study as shown in figure 3. The cyclic voltammetric and differential pulse polarographic studies were performed to distinguish the electronic environment of copper center in monomer and tetramer compounds. In tetramer, each copper is coordinated by three sulfurs arising from trigonal planar geometry whereas in monomer, copper has non-equivalent environment due to the presence of two sulfur and one phosphorous donor atoms. In a typical cyclic voltammogram (CV) of the tetramer, an anodic peak potential (E_{Pa}) was observed at $+0 \cdot 32$ V followed by a reversible peak at $+0 \cdot 41$ V vs Ag/AgCl. Its differential pulse polarogram (DPP) exhibits the oxidation processes at $0 \cdot 26$ V and $0 \cdot 36$ V, close to $E_{1/2}$ values of the two processes as found in its CV study. The monomer complex displayed only one irreversible peak at

+0·34 V vs Ag/AgCl and its DPP exhibits that oxidation process at 0·29 V. Therefore the electrochemical responses for the tetramer and monomer differ and we used the DPP to follow a tritrimetric study using stoichiometric amount of PPh$_3$ per copper atom present in the tetramer. After the addition of one equivalent PPh$_3$ in the tetramer, the DPP of the resultant solution is drastically changed. The first oxidation peak of the tetramer is now almost disap-peared with the appearance as a shoulder and the second oxidation peak shifted from 0·36 V toward a lower value (see figure 3c) with the increase in current flow. Further addition of two, three and four equivalent of PPh$_3$ respectively resulted the completion of the trend in drifting of the 0·36 V to the lower value with the final position at 0·29 V which is the DPP potential measured for the monomer (figure 3). The current of this peak now equals to the four equivalent of monomer which is expected to form from one equivalent of tetramer interacting with four equivalent of PPh$_3$. These results indicate that the tetramer is ruptured by opening the bridging copper-μ_2-sulfur bond under free PPh$_3$ resulting the formation of new copper–phosphorous bond as present in the monomer.

3.3 ^{31}P NMR study

The backward reaction of the catalytic cycle in the conversion of monomer to tetramer by the addition of S or Se powder was monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR experiments were carried out with the monomeric compound in CH$_3$CN medium (figure 4). ^{31}P NMR showed resonance at
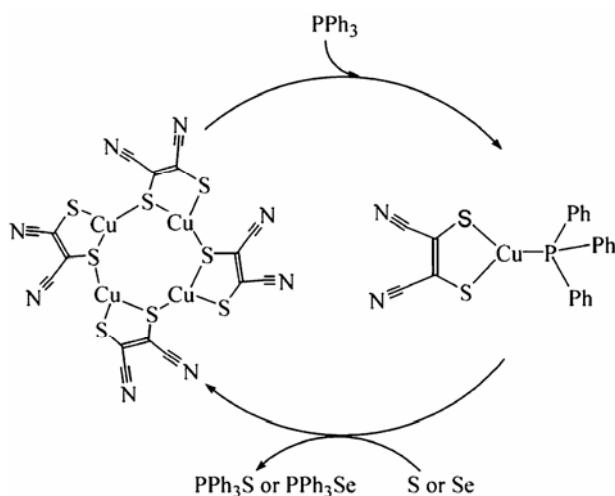
Figure 1. The catalytic cycle.
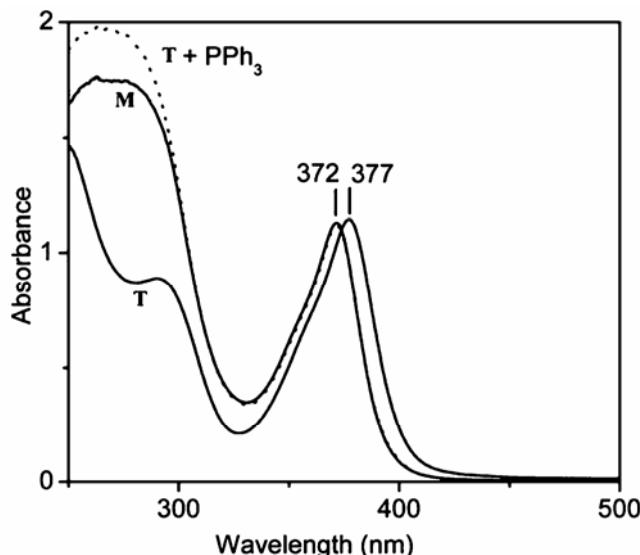
Figure 2. Conversion of [Et$_4$N]$_4$[Cu$_4$(mnt)$_4$] (T) to [Et$_4$N][Cu(mnt)(PPh$_3$)] (M) as monitored by absorption spectroscopy: Solid line indicates the UV/Vis spectra of tetramer (0·25 × 10^{-4} M) (T) and monomer (1 × 10^{-4} M) (M); and broken line indicates the spectrum of the tetramer (0·25 × 10^{-4} M) (T) with PPh$_3$ (1 × 10^{-4} M) in CH$_3$CN leading the shift of 377 nm peak of T to 372 nm for M almost overlaid with stoichiometric M.
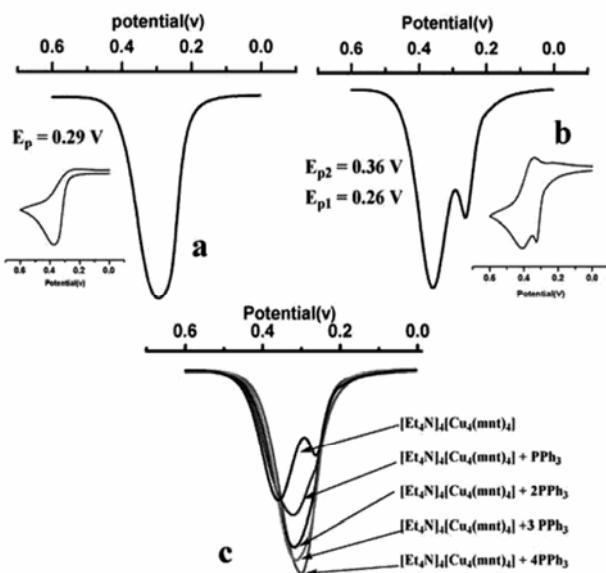

Figure 3. CV and DPP of monomer and tetramer were recorded at a scan rate of 100 mVs^{-1} over the potential range of interest, 0 to +0·60 V in acetonitrile solvent with 0·2 M Bu$_4$NClO$_4$ as supporting electrolyte. (**a**) CV and DPP of [Et$_4$N][Cu(mnt)(PPh$_3$)] (4 × 10^{-3} M); (**b**) CV and DPP of [Et$_4$N]$_4$[Cu$_4$(mnt)$_4$] (1 × 10^{-3} M) and (**c**) DPP scans of [Et$_4$N]$_4$[Cu$_4$(mnt)$_4$] with successive addition of four equivalent PPh$_3$.
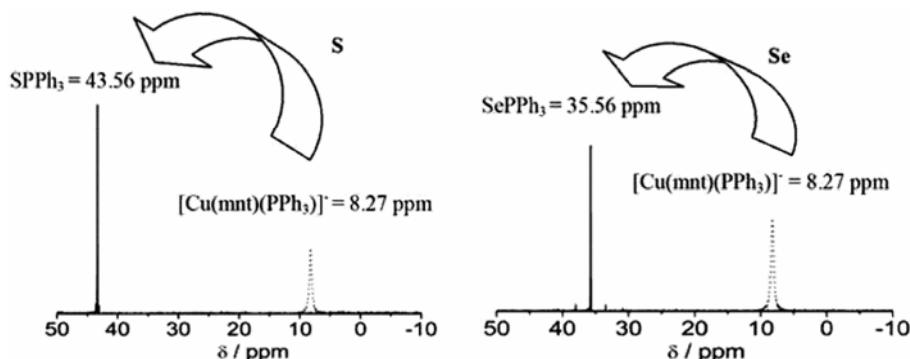
Figure 4. Left: ^{31}P NMR spectra of monomer at 8·27 (broken line) shifted to 43·56 ppm (solid line) on addition of one equivalent S in CH$_3$CN; right: ^{31}P NMR spectra of monomer (broken line) at 8·27 ppm shifted on addition of one equivalent Se to 35·56 ppm (solid line).

8·27 ppm which is due to copper bound phosphorus of PPh$_3$ ligand. This peak at 8·27 ppm was completely replaced by the appearance of another peak at 43·56 ppm (or 35·56 ppm) when stoichiometric amount of S (or Se) was added into the solution of the monomer in the NMR tube. These later peaks are assigned to the phosphorus present in PPh$_3$S (or PPh$_3$Se).[8,9] This result indicates that the coordinated PPh$_3$ in the monomer is not very stable in solution which re-organizes to form the tetramer with the formation of new bridging copper–sulfur bond once the PPh$_3$ is removed.

The tetramer losts its cluster structure in the presence of PPh$_3$ to afford PPh$_3$ coordinated monomer. This species further reacts with S or Se and activates the reactivity of these halogens by binding with the adjoining sulfur attached with copper. In this respect, the tetramer is first cleaved by PPh$_3$ to form the all important [Cu(mnt)(PPh$_3$)]– responsible for catalysis. This catalytic oxidation reaction of PPh$_3$ with S/Se thus occurred rapidly under mild conditions to produce PPh$_3$S/PPh$_3$Se.[9]

In a typical experiment when the tetramer (0·01 mmol, 14 mg) was treated with PPh$_3$ (0·1 mmol, 26 mg) in the presence of S (0·1 mmol, 3 mg) or Se (0·1 mmol, 8 mg) in DCM at RT for 10 min, the yield of PPh$_3$S was 86·20%, (25 mg). However, subtracting the amount of PPh$_3$S formed from the un-catalysed reaction (11 mg) the catalytic turnover number was found to be $0·8 \times 10^{-2}$ s^{-1}. Similarly for PPh$_3$Se the total yield was 82%, (28 mg) but after the subtraction of the product formed from the uncatalysed reaction (15 mg) the turnover number was found to be $0·6 \times 10^{-2}$ s^{-1}. The recovery of tetramer after these reactions was around 86%.

4. Conclusion

All spectroscopic and electrochemical results support a clean interconversion between tetramer and monomer complex in the presence of PPh$_3$ with S/Se resulting catalytic oxidation reaction of PPh$_3$ with S/Se under mild conditions to produce PPh$_3$S/ PPh$_3$Se.

Acknowledgments

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