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# Probing the limits of steric constraints in the oligomerization of copper(I) complexes: structures of two sterically congested oligomers

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#### Abstract

Oligomeric copper(I) clusters are formed by the insertion reaction of copper(I) aryloxides into heterocumulenes. The effect of varying the steric demands of the heterocumulene and the aryloxy group on the nuclearity of the oligomers formed has been probed. Reactions with copper(I)2-methoxyphenoxide and copper(I)2-methylphenoxide with PhNCS result in the formation of hexameric complexes hexakis[*N*-phenylimino(aryloxy)methanethiolato copper(I)] **3** and **4** respectively. Single crystal X-ray data confirmed the structure of **3**. Similar insertion reactions of  $CS_2$  with the copper(I) aryloxides formed by 2,6-di-*tert*-butyl-4-methylphenol and 2,6-dimethylphenol result in oligomeric copper(I) complexes **7** and **8** having the (aryloxy)thioxanthate ligand. Complex **7** was confirmed to be a tetramer from single crystal X-ray crystallography. Reactions carried out with 2-mercaptopyrimidine, which has ligating properties similar to *N*-alkylimino(aryloxy)methanethiolate, result in the formation of an insoluble polymeric complex **11**. The fluorescence spectra of oligomeric complexes are helpful in determining their nuclearity. It has been shown that a decrease in the steric requirements of either the heterocumulene or aryloxy parts of the ligand can compensate for steric constraints and facilitate oligomerization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copper(I); Aryloxide; Heterocumulene; Oligomeric structures; Fluoresence

# 1. Introduction

The prolific nature of copper(I) to form oligomeric complexes with nuclearities ranging from two to eight is well documented [1-30]. A wide variety of coordination numbers and geometries are encountered in these systems. The plasticity imparted by the spherical symmetry of the copper(I) ion permits considerable variations in the steric and electronic characteristics of the surrounding ligands [31]. Hence, it is extremely difficult to predict a priori the nuclearity of a complex that would be formed with a ligand. Subtle variations in the electronic and steric characteristics of the substituents on a ligand can result in changes of nuclearity [18,25,32-42]. A systematic study of the steric and electronic factors responsible for changes in the nuclearity of copper(I) complexes would go a long way in building copper(I) complexes with predefined structure and properties.

Electronic factors play an important role in determining the nuclearity of copper(I) clusters [18–21,25–29,32,33]. An example is provided by oligomers formed by the ligands diethyldithiocarbamate and dipropylthiocarbamate [32,33]. The former, with a  $S_3$  coordination yields a tetrameric complex, while the latter with a  $S_2O$  coordination gives rise to a hexameric complex. Furthermore, an examination of the C–S bond distances in both complexes show that the tetrameric complex has shorter distances (1.70–1.72Å) compared to the hexamer (1.75–1.81Å). Similarly, in a series of oligomeric complexes formed by heterocyclic thiones, shorter C–S distances are associated with the tetrameric complexes while longer C–S bonds are present in the hexameric complexes [18–21,25–29]. This suggests that ligands having short C–S bonds would favor the formation of a tetrameric complex.

Steric factors play a vital role in determining the nuclearity of clusters with bridging ligands. For example, the nuclearity of complexes of 6-halo-2-hydroxypyridine with a methoxide bridge are dependent on the size of the halogen atom. The chloro substituted ligand yields a tetramer while the less bulky fluoro substituted ligand forms a polymeric complex [37]. Similarly, in copper(I) thiolate complexes, bulky substitution in the *ortho* position of thiophenols decreases the nuclearity of the clusters formed [38,39]. Steric control of the nuclearity has also

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Fig. 1. Possible Interactions Between the -OAr and R Groups in the Oligomeric Complexes.

been observed in ligands that form three atom bridges. The copper(I) cluster formed from diethyldithiocarbamate is tetrameric while the smaller dimethyldithiocarbamate forms a polymeric copper(I) complex [32].

Surprisingly, in a recent study on the oligomeric copper(I) complexes of N-alkylimino(aryloxy)methanethiolate  $(\mathbf{RN}=\mathbf{C}(\mathbf{OAr})\mathbf{S}^{-})$ , the nuclearity of the copper(I) clusters was shown to be dependent on only the bulk of the aryloxy group present and apparently independent of the substitution on the nitrogen atom. This is in spite of the fact that the **OAr** is fairly distant from the polynuclear copper core compared to  $\mathbf{R}!$  [40–42]. When the aryloxy group was *p*-cresol, a hexanuclear complex  $[Cu-S-C(OAr)=NR]_6$ (R=Ph or Me) was formed. When the bulk of the ligand was increased by introducing two methyl groups in the ortho positions of the phenol, the nuclearity of the resulting cluster was reduced to a tetramer [Cu-S-C(OAr- $=NR_{4}(R=Ph \text{ or } Me)$ . This prompted us to take a closer look at these systems. In the three atom bridged complexes, are the nuclearity of complexes really independant of the steric influences of R? Can the steric influences of the group in position 2 be compensated by reduction of steric demands of the group in position 1? (Fig. 1). What would be the effect of releasing steric congestion by an extreme reduction in the bulk of the ligand? In the present paper we discuss the results of our studies to probe these factors and the utility of solid state fluorescence data in assigning the nuclearity of the clusters examined.

## 2. Experimental section

General: Dichloromethane, pyridine and petroleum ether (bp  $60-80^{\circ}$ C) were purified and dried by conventional methods. They were distilled under nitrogen and deoxy-

genated before use. CuCl and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> (Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts should be prepared and this should be handled with great caution) were freshly prepared before use. Phenols, MeNCS, PhNCS,  $CS_2$  and  $P(OMe)_3$  were purified by distillation. A 60% suspension of NaH in mineral oil was washed with petroleum ether (b.p. 60-80°C) and used. <sup>1</sup>H NMR spectra were recorded with a Bruker ACF 200 MHZ spectrometer. IR spectra were recorded on a Bio-Rad FTS-7 spectrophotometer. Samples were examined as KBr pellets, neat (thin film) or as nujol mull. The absorption and emission spectra of the oligomeric copper(I) complexes in the solid state were recorded by grinding the solid sample in mineral oil (nujol) to give a fine suspension and the spectrum of a thin film of this suspension was recorded. Electronic spectra were recorded on a Hitachi Model U-3400 spectrophotometer and fluorescence studies were done on a Hitachi F-2000 fluorescence spectrophotometer. Elemental analyses were done with a Carlo Erba Elemental Analyzer model 1106.

### 2.1. Preparation of Copper(I) aryloxides

Copper(I) aryloxides were prepared by the reported procedure [40–44]. To a stirred suspension of NaH (0.12 g, 3 mmol) in about 40 ml of  $CH_2Cl_2$  or  $CH_3CN$ , the phenol (3 mmol) was added under an atmosphere of dry, oxygen-free nitrogen. When the evolution of  $H_2$  ceased, CuCl (0.297 g, 3 mmol) was added. A yellow precipitate of copper(I) aryloxide was formed which was used immediately for further reactions. [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> could be used instead of CuCl.

# 2.1.1. Preparation of $[Cu{\mu-SC(=NPh)(OC_6H_4-OMe-2)}]_6$ (3)

To copper(I) 2-methoxyphenoxide prepared as above in CH<sub>2</sub>Cl<sub>2</sub>, P(OMe)<sub>3</sub> (0.35 ml, 3mmol) was added and the solution stirred for half an hour. Then, PhNCS (0.36 ml, 3 mmol) was added and the stirring was continued for 8h. The mixture was filtered and the resulting deep orange colored solution was concentrated to about 10 ml. Layering with petroleum ether (bp 60-80°C) yielded yellow crystals of **3**. Yield 16%. Alternately, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> could be used instead of CuCl. A bright yellow precipitate of the aryloxide was formed. PhNCS was added to this and the solution stirred for 8h. Similar work up of the reaction mixture yielded yellow crystals of 3. Anal. Calcd for 3: C, 52.25; H, 3.73; N, 4.35. Found: C, 52.57; H, 3.96; N, 4.00. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ 7.41–6.61 (m, 9H, –O–  $\mathrm{C_6H_4-},\,\mathrm{C_6H_5NCS}),\,\delta$  3.63 (S, 2.68H, –OMe),  $\delta$  3.53 (S, 0.31H, -OMe). IR(neat): in cm<sup>-1</sup> 1589(w)( $\nu_{C=N}$ ), 1565(m), 1553(s), 1537(m), 1498(s), 1486(m), 1452(m), 1435(w), 1414(w), 1257(m), 1208(m), 1174(w), 1127(s), 1111(s), 1041(w), 1021(m), 751(s), 692(m).

# 2.1.2. Preparation of $[Cu{\mu-SC(=NPh)(-OC_6H_4-Me-2)}]_6$ (4)

To copper(I) 2-methylphenoxide prepared using  $[Cu(CH_3CN)_4]ClO_4$  in  $CH_2Cl_2$ , PhNCS (0.36 ml, 3 mmol) was added and the mixture was stirred for 8h. Then it was filtered and the resulting yellow colored solution was concentrated to about 10 ml. Layering with petroleum ether (bp 60–80°C) yielded yellow crystals of **4**. Yield 19%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  7.66–6.21 (m, 9H, –O–C<sub>6</sub>H<sub>4</sub>–, C<sub>6</sub>H<sub>5</sub>NCS),  $\delta$  1.99 (S, 2.46H, –Me),  $\delta$  1.89(S, 0.54H, –Me). IR(neat): in cm<sup>-1</sup> 3057(w), 3025(w), 1557(s)( $\nu_{C=N}$ ), 1486(s), 1452(m), 1222(s), 1127(s), 756(s), 690(m), 597(m).

# 2.1.3. Preparation of $[Cu\{\mu-S-C(=S)(-OC_{6}H_{2}-Bu^{t}-2,6-Me-4)\}]_{4}$ (7)

The cuprous aryloxide (2,6-di-tert-butyl-4methylphenoxide) was made by adding CuCl to the suspension of sodium aryloxide in CH<sub>2</sub>Cl<sub>2</sub>. P(OMe)<sub>3</sub> (3 equiv.) was added followed by  $CS_2$  (2 ml). The mixture was allowed to stir for 8h and then filtered. The solvent in the yellow-orange filtrate was evaporated and the residue was extracted with ether. A yellow solution was obtained. TLC of this solution showed the presence of a major product (yellow) in addition to unreacted 2,6-di-tert-butyl-4-methylphenol and some minor products. A column chromatographic separation was carried out and the yellow product was isolated. Slow evaporation of the solvent yielded yellow crystals of 7. Yield 12%. Anal Calcd. for 7: C, 53.54; H, 6.42. Found: C, 52.49; H, 6.63. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K):  $\delta$  7.07(s, 2H,  $-OC_6H_2$ ),  $\delta$  2.33(s, 3H, Me),  $\delta$  1.32(S, 18H, CMe<sub>3</sub>). <sup>13</sup>C NMR (CH<sub>2</sub>Cl<sub>2</sub>, 298K)  $\delta$ 232.74(S-C=S), δ 152.33(ipso -OC<sub>6</sub>H<sub>2</sub>), δ 141.20(ortho  $-OC_6$  H<sub>2</sub>),  $\delta$  135.69(meta  $-OC_6$  H<sub>2</sub>),  $\delta$  127.81(para  $-OC_6$  H<sub>2</sub>),  $\delta$  35.80(*para* CH<sub>3</sub>),  $\delta$  31.74(Bu<sup>t</sup>),  $\delta$ 21.24(CMe<sub>3</sub>). IR(nujol): in cm<sup>-1</sup> 1145(s,  $\nu_{C=S}$ ),1090(m,  $\nu_{\rm C-O}$ ), 1025(s,  $\nu_{\rm CS2}$ [asym])

# 2.1.4. Preparation of $[Cu{\mu-S-C(=S)(-OC_{6}H_{4}-Me_{2}-2,6)}]_{n}$ (8)

A yellow suspension of copper(I) 2,6-dimethyl phenoxide was made by adding  $[Cu(CH_3CN)_4]ClO_4$  to a suspension of the sodium aryloxide in  $CH_2Cl_2$ .  $CS_2$  (2 ml) was added to this and the mixture was stirred for about 8h. Filtration of this mixture yielded a clear orange solution which was concentrated and an orange solid was obtained from this on slow evaporation of the solvent. Repeated attempts to crystallize this orange solid using various solvent mixtures were unsuccessful. Yield 56%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 298K)  $\delta$  7.1(3H,  $-OC_6H_3$ ),  $\delta$  2.17(6H, CH<sub>3</sub>). <sup>13</sup>C NMR (CH<sub>2</sub>Cl<sub>2</sub>, 298K)  $\delta$  229.40(S–C12,137C=S),  $\delta$ 153.88(*ipso*  $-OC_6H_3$ ),  $\delta$  129.80(*ortho*  $-OC_6H_3$ ),  $\delta$ 128.87(*meta*  $-OC_6H_3$ ),  $\delta$  126.84(*para*  $-OC_6H_3$ ),  $\delta$ 15.96(*ortho* CH<sub>3</sub>).

# 2.1.5. Preparation of $[Cu(C_4H_4N_2S)]_n$ (11)

2-Mercaptopyrimidine (0.14 g, 1.1 mmol) was added to a suspension of NaH (0.037 g, 1.1 mmol) in CH<sub>3</sub>CN. Then CuCl (0.107 g, 1.1 mmol) was added to this. The mixture was stirred for 8h and then filtered. A yellow precipitate (11) was obtained; this was found to be insoluble in all the usual organic solvents. The reaction was carried out in ethanol. Sodium (0.019 g, 0.83 mmol) was added to absolute ethanol and 2-mercaptopyrimidine (0.093 g, 0.83 mmol) was added to this.  $[Cu(CH_3CN)_4]ClO_4$  (0.272 g, 0.83 mmol) or CuCl (0.82 g, 0.83 mmol) was added to the resulting mixture. The yellow suspension was filtered when a yellow insoluble precipitate and a colorless solution were obtained. The IR spectra of this yellow precipitate was identical to the one obtained in the previous reaction (11). Yield 72%. Anal Calcd. for 11: C, 27.49; H, 1.72; N, 16.04. Found: C, 26.19; H, 1.65; N, 15.02. IR (nujol) in cm<sup>-1</sup>: 2952 (s), 1565 (s), 1542 (s), 1245 (w), 1171 (s), 767 (m), 744 (m), 647 (m).

#### 2.2. Experimental details of crystallography

The reaction mixture from the insertion reaction of copper(I) 2-methoxyphenoxide and PhNCS was concentrated to about 10 ml and layered with petroleum ether (b.p. 60-80°C). Slow evaporation of this mixture yielded yellow crystals of **3** suitable for the diffraction study. The crystals were found to be extremely unstable outside the mother liquor and lost their crystallinity very rapidly. Hence a crystal of 3 was sealed in a Lindemann capillary along with the mother liquor and used for data collection. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Ka radiation. The intensity control reflections, measured once in every 3600 s of exposure time to the X-rays showed that the crystal was degrading with time. Data was collected with difficulty up to 60% decay. The structure was solved by the heavy atom method and subsequent Fourier syntheses using the SHELX system [43,44] of programs. The hydrogen atoms were geometrically fixed. Non-hydrogen atoms (except C12) were refined anisotropically while the hydrogen atoms isotropically. The refinement was carried out till a final R factor of 0.0964 was reached.

Crystallization of the yellow complex from a mixture of petroleum ether (bp 60–80°C) and  $CH_2Cl_2$  after the chromatographic separation of **7** afforded yellow crystals suitable for an X-ray crystallographic study. A yellow crystal was mounted on a glass fiber and data collected. No significant decay was indicated by the intensity control reflections. The compound crystallized in the space group  $-I4_1/a$  of the tetragonal crystal system. The structure was solved by the direct method and subsequent Fourier syntheses showed this to be a tetrameric complex. The heavy atoms were refined anisotropically. While an attempt at anisotropic refinement of the carbon atoms showed disorder, they were refined isotropically. The hydrogen

Table 1			
Crystallographic details for $[Cu{\mu-SC(=NPh)(O-C_6H_4-2-OMe)}]_6$ 3 and $[Cu{\mu-SC(=S)(O-C_6H_2-2,6-Bu_2^t-4-Me)}]_4$ 7			
	3		
Chem formula	$C_{84}H_{72}N_6O_{12}S_6Cu_6.4CH_2Cl_2$		

Chem formula	$C_{84}H_{72}N_6O_{12}S_6Cu_6.4CH_2Cl_2$	$C_{64}H_{92}Cu_4O_4S_8$
FW	2270.93	1436.02
Color	yellow	Yellow
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/C$	$I4_1/a$
a, (Å)	13.108(5)	28.56(3)
b, (Å)	28.402(3)	
c, (Å)	14.363(3)	34.31(3)
$\beta$ , deg	116.38(2)	
V, Å <sup>3</sup>	4790(2)	27983(40)
Ζ	2	16
$\rho_{\rm calcd}, {\rm g \ cm^{-3}}$	1.571	1.363
$\mu, \text{ cm}^{-1}$	17.23	14.81
T, ℃	20	-105
$\lambda$ , Å (Mo K $\alpha$ )	0.7107	0.7107
Independent reflections	4474	9748
Final R <sup>a</sup>	0.0964	0.1173
Final $R_{\rm w}^{\rm b}$	0.1950	0.1987

 $^{a}R(F_{o}) = (\Sigma F_{o} - F_{c})/(\Sigma F_{o}).$ 

$${}^{b}R_{w}(F_{o}) = [\Sigma w(F_{o} - F_{c})^{2} / (\Sigma w F_{o}^{2})]^{1/2}; w = [\sigma^{2}(F_{o}) + gF_{o}^{2}]^{-1}.$$

atoms were geometrically fixed. The high value of R (0.1173) could not be reduced even when the structure was solved using a fresh data set collected at  $-77^{\circ}$ C. The inherent disorder in the system can be primarily attributed to the steric constraints (vide infra). The crystallographic details and important bond distances and angles are listed

in Tables 1 and 2 for the hexamer **3** and in Tables 1 and 3 for the tetramer **7**. Particulars of the crystallographic analyses including positional coordinates for all the atoms, thermal parameters, bond distances and angles are given in Tables S1-S5 and Tables S6-S10 (Supplementary material) for **3** and **7** respectively.

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Table 2

List of Selected Bond lengths [Å] and angles [°] for **3**  $[Cu{\mu-SC(=NPh)(O-C_6H_4-2-OMe)}]_6$ 

Bond	Distance	Bond	Distance	
Cu(1)–N(3)	2.00(2)	Cu(20)–Cu(1A)	2.809(4)	
Cu(1)-S(40)	2.220(7)	Cu(20)–Cu(39A)	3.011(4)	
Cu(1)–S(2)	2.268(7)	S(21)–Cu(20A)	2.222(7)	
Cu(1)-Cu(20A)	2.810(4)	S(21)–Cu(39A)	2.257(6)	
Cu(1)–Cu(39A)	2.878(5)	Cu(39)–S(40)	2.238(7)	
S(2)-Cu(20)	2.266(7)	Cu(39)–S(21A)	2.257(6)	
Cu(20)–N(22)	1.95(2)	Cu(39)–Cu(1A)	2.878(5)	
Cu(20)–S(21A)	2.222(7)	Cu(39)–Cu(20A)	3.011(4)	
Atom	Angle	Atoms	Angle	
N(3)-Cu(1)-S(40)	128.8(5)	S(2)-Cu(20)-Cu(1A)	130.4(2)	
N(3)-Cu(1)-S(2)	120.0(6)	N(22)-Cu(20)-Cu(39A)	84.2(6)	
S(40)-Cu(1)-S(2)	107.1(3)	S(21A)-Cu(20)-Cu(39A)	133.4(2)	
N(3)-Cu(1)-Cu(20A)	87.8(6)	S(2)-Cu(20)-Cu(39A)	71.7(2)	
S(40)-Cu(1)-Cu(20A)	76.3(2)	Cu(1A)-Cu(20)-Cu(39A)	68.85(11)	
S(2)-Cu(1)-Cu(20A)	129.5(2)	N(41)-Cu(39)-S(40)	120.2(6)	
N(3)-Cu(1)-Cu(39A)	84.0(6)	N(41)-Cu(39)-S(21A)	118.7(6)	
S(40)-Cu(1)-Cu(39A)	129.7(2)	S(40)-Cu(39)-S(21A)	115.8(2)	
S(2)-Cu(1)-Cu(39A)	74.4(2)	N(41)-Cu(39)-Cu(1A)	84.2(6)	
Cu(20A)-Cu(1)-Cu(39A)	67.29(12)	S(40)-Cu(39)-Cu(1A)	133.2(2)	
N(22)-Cu(20)-S(21A)	125.9(6)	S(1A)-Cu(39)-Cu(1A)	74.9(2)	
N(22)-Cu(20)-S(2)	116.7(6)	N(41)-Cu(39)-Cu(20A)	85.7(6)	
S(21A)-Cu(20)-S(2)	112.4(3)	S(40)-Cu(39)-Cu(20A)	71.8(2)	
N(22)-Cu(20)-Cu(1A)	88.0(7)	S(21A)-Cu(39)-Cu(20A)	135.5(2)	
S(21A)-Cu(20)-Cu(1A)	76.9(2)			

(Symmetry transformations used to generate equivalent atoms: -x, -y, -z).

Table 3 List of Selected Bond lengths  $[\text{\AA}]$  and angles  $[^{\circ}]$  for  $[Cu{\mu-SC(=S)(O-C_6H_2-2,6-Bu_2^{\dagger}-4-Me)}]_4$  7

Bond	Distance
Cu(1)–Cu(2)	2.636(5)
Cu(1)–Cu(3)	2.644(5)
Cu(1)-Cu(4)	2.804(6)
Cu(2)-Cu(4)	2.663(5)
Cu(2)–Cu(3)	2.810(6)
Cu(3)-Cu(4)	2.656(6)
Cu(2)–S(6)	2.259(8)
Cu(2)–S(3)	2.272(9)
Cu(2)–S(7)	2.292(9)
Cu(3)–S(4)	2.246(9)
Cu(3)–S(1)	2.267(9)
Cu(3)–S(5)	2.272(9)
Cu(4)–S(8)	2.245(9)
Cu(4)-S(1)	2.249(9)
Cu(4)–S(3)	2.292(9)
Atoms	Angle
S(2)-Cu(1)-S(7)	124.2(3)
S(2)-Cu(1)-S(5)	111.6(3)
S(7)-Cu(1)-S(5)	123.3(3)
O(1)-C(1)-S(2)	120(2)
O(1)-C(1)-S(1)	109(2)
S(2)-C(1)-S(1)	131(2)
C(1)–O(1)–C(11)	118(2)
Cu(2)-Cu(1)-Cu(3)	64.3(2)

#### 3. Results and discussion

### 3.1. Reactions with PhNCS

Introduction of bulky groups in the ortho positions of the aryloxy group has been found to hinder the oligomerization process and result in the formation of a tetramer or a dimer. In order to investigate whether mono ortho substitution will have the same effect, insertion reactions of PhNCS were carried out using copper(I) aryloxides of mono-*ortho* substituted phenols-o-methoxyphenol (guaiacol) and o-cresol. An X-ray crystallographic analysis of the product formed from guaiacol revealed it to be a hexameric cluster 3. The molecular structure of the complex has six copper atoms in roughly octahedral geometry and the six N-phenylimino(2-methoxyphenoxy)methanethiolate ligands bridge these copper atoms resulting in a paddle-wheel structure very similar to the hexamer formed in the reaction with p-cresol. The molecular structure of this hexameric complex **3** is given in Fig. 2. A yellow crystalline product 4 was formed in the case of o-cresol; the yellow color suggests that 4 is also a hexameric complex (vide infra). The formation of hexameric clusters clearly show that the partial relief in steric congestion achieved by using a mono-ortho sublstituted phenol instead of a di-ortho substituted phenol can result in a cluster with a higher nuclearity. Even though mono substitution has resulted in the formation of a hexamer, the



Fig. 2. ORTEP Diagram of the Hexameric Complex 3.

steric congestion is reflected in the distortions present in the molecular structure.

A hexameric cluster 5 was formed from an insertion reactions with MeNCS and the copper(I) aryloxide of p-cresol just as in the case of PhNCS. This ligand has steric variation at another position in the ligand; the terminal nitrogen atom of the N-C-S bridge has a less bulky methyl group (compared to PhNCS). All the three hexameric copper(I) complexes, with ligands having varying steric requirements, have very similar paddle-wheel structures. Although there is no change in the nuclearity, a closer examination of their structural parameters reveals subtle differences that reflect the changes caused by the steric requirements of the substituents. The hexamer 5 (from MeNCS) crystallizes in the highly symmetric space group  $-R\bar{3}$ -while the other two (1 and 3 from PhNCS) crystallize in space groups of much lower symmetry (P1 and  $P2_1/c$  respectively). The hexameric structure of 5 is symmetry-generated from one-sixth of the molecule by a three-fold axis and an inversion center whereas the only symmetry element present in the other two hexamers is an inversion center in the molecule. 5 is less distorted than 1 and 3 and the six copper atoms are located at the vertices of an almost perfect octahedron. In 5, the steric repulsion between the aryloxide and the substituent on the nitrogen atom is minimal because of the smaller size of the methyl group and there are no ortho substituents on the -OAr group. On the other hand, the larger phenyl substituent on the nitrogen in 1 results in the formation of a more distorted structure. Steric congestion is maximum in the case of 3 which has the phenyl substituent on the nitrogen atom as well as a bulky ortho substituent on the -OAr. The extent of distortion found in the three hexamers can be ranked as 3>1>5. This is evident from Table 4 where the bond angles at the core atoms in the three hexamers are compared. Reduced steric constraints result in a more

Table 4									
List of bon	d angles(°)	for the	atoms	in the	core	of the	three	hexamers	

	Hexamer 5	Hexamer 1	Hexamer 3	
	(MeNCS- <i>p</i> -cresol)	(PhNCS- <i>p</i> -cresol)	(PhNCS-guaiacol)	
Cu–S–Cu	89.6	86.2–92.6	89.1–98.4	
S-Cu-S	115.5	113.5-116.8	106.9-115.6	
N-Cu-S	119.8; 117.9	114.8-124.5	116.9-127.7	
Cu-S-C	103.5; 103.2	100.5-107.4	98.6-106.4	
S-C-N	123.6	121.1-123.1	121.8-126.0	
N-C-O	117.9	117.7-120.9	113.6-121.4	
S-C-O	115.5	117.9–119.3	115.4–120.4	

regular structure and distortions are minimized due to steric relief. A reduction in the steric strain is reflected by greater symmetry in the molecular and crystal structure.

The <sup>1</sup>H NMR spectra of these complexes suggest that the steric effects impact the solution properties of the complex too. Studies carried out earlier [45] had shown that the dissociation of the hexamer into a tetramer and a dimer (Scheme 1) would offer relief from the steric constraints. Such dissociation into two different species is indicated by the room temperature <sup>1</sup>H NMR spectrum of 3, 4 and 1. Hexamer 3 shows two resonances for the –OMe group (3.63 ppm; 2.68 H and 3.53 ppm; 0.32H) and the two peaks have non integral ratios. Hexamer 4 with the mono ortho methyl substituent also has two signals for the methyl group with non integral ratios(1.99 ppm, 2.46H and 1.89 ppm, 0.54H). Similarly, there are two peaks corresponding to the *p*-methyl substituent of the aryloxide in the <sup>1</sup>H NMR spectrum of **1** suggesting the presence of two species in solution. The ratio of the intensities of the two closely spaced singlets was found to be temperature dependent. At higher temperatures, the intensities of the two signals were equal. At lower temperatures, only one peak was observed indicating the presence of only one species. These changes could be attributed to a dissociation of the hexamer to give a tetramer and a dimer. The presence of very little steric congestion in the hexamer 5 (from MeNCS) is confirmed by its behavior in solution, the <sup>1</sup>H NMR spectrum of 5 does not indicate any dissociation in contrast to 1, 3 and 4.

### 3.2. Reactions with $CS_2$

Further decrease in the steric requirements of the ligand was brought about by employing a ligand with no substituents on the terminal atom. To probe the limits of steric



constraints an insertion reaction with copper(I) 2,6-di-tertbutyl-4-methyl phenoxide was carried out on CS2. A yellow crystalline product 7 was formed and was identified as a tetramer from an X-ray crystallographic analysis. The tetramer has a tetrahedral arrangement of the four copper atoms which are bridged by S-C-S and sulfide bridges. The structure is similar to that of the tetramer 2 isolated in the reaction between PhNCS and copper(I) 2,6-dimethyl phenoxide. The ORTEP diagram of 7 is shown in Fig. 3. The reaction involving copper(I) 2,6-di-tert-butyl-4methylphenoxide and  $CS_2$  results in a tetrameric cluster 7 (the corresponding reaction with PhNCS gives only a dimeric complex). The reduction in the size of the heterocumulene ligand has compensated for the steric congestion due to the phenol and consequently oligomerization is made feasible.

Subsequently, reactions were carried out with  $CS_2$  and copper(I) 2,6-dimethyl phenoxide which has less bulky methyl groups. An orange product **8** was obtained which could not be crystallized and hence its nuclearity could not be determined from an X-ray study. The orange color of the complex suggests that it is a hexamer (vide infra). The role played by steric effects is distinctly brought out by the insertion reaction of  $CS_2$  with copper(I) 4-methylphenoxide where there is no *ortho* substitution in the phenol. In this case, there is a further reduction in the steric require-



Fig. 3. ORTEP Diagram of the Tetrameric Complex 7.

ment of the ligand and as a result, multiple insertions take place. The products that are finally isolated are either the orthocarbonate  $[C(OAr)_4]$ or the thioncarbonate  $[S=C(OAr)_2]$  and cuprous sulfide [46–49]. The absence of steric impediments in both p-cresol and CS<sub>2</sub> lead to multiple insertions since there is no hindrance to the insertion reaction. Attempts were made to prevent multiple insertion by synthesizing the ligand (a thioxanthate) and then reacting it with copper(I) instead of an in situ insertion reaction of the heterocumulene with copper(I) aryloxide. However only decomposition products (phenol and cuprous sulfide) could be isolated.

An alternative mode of reducing steric requirements of the ligand is to covalently link the substituents as in the case of heterocyclic thione systems. These have an N-C-S fragment similar to the systems mentioned earlier and the ligand would have minimum or negligible steric effects. Reactions were carried out with copper(I) and pyrimidine-2-thiolate. The resulting product 11 is highly insoluble in all common organic solvents which suggests a polymeric structure. This polymeric structure could be broken down with pyridine. However, the highly air sensitive and non crystalline nature of the products formed precluded further characterization. Therefore it can be concluded that when there is a great release in the steric congestion, oligomerization is made so facile that polymerization results. A possible sheet-like structure for this polymeric copper(I) complex 11 is shown in Fig. 4. These results clearly demonstrate the role played by steric factors in controlling the oligomerization process in copper(I) clusters.

#### 3.3. Fluorescence spectra

The absorption and fluorescence spectra of these oligomeric complexes were found to be useful in finding out or



Fig. 4. A Possible Sheet-Like Structure for the Polymeric Complex 11.

confirming the nuclearities of these oligomers. Even in cases where single crystals suitable for diffraction work are not available, it is possible to assign a nuclearity to the complex. In the solution phase all complexes had a broad absorption from 250 nm tapering down to 350 nm indicating dissociation of the oligomeric structures. However, the spectra recorded in the solid state were more informative and are discussed below.

An examination of the emission characteristics of these clusters (Table 5) shows that 1, 3, 4, 5, 8, 9 and 10 are very similar. Also, these cluster compounds are all either orange-yellow, orange or red in color. The structures of 1, 3, and 5 are confirmed to be hexameric in the solid state from crystallographic studies. From the similarity in the absorption and emission patterns of these molecules (absorbances from 270-500 nm and a fluorescence emission band at the long wavelength region from 600-700 nm) and their color, it can be concluded that 4, 8, 9 and 10 are also hexamers. The absorption and emission characteristics of the hexamers are markedly different from 2, 6 and 7. The latter are colorless/yellow compounds, have absorbances between 270-350 nm and do not have any emission band beyond 600nm. The structures of 2 and 7 are known to be tetrameric from single crystal structure determinations. On the basis of these similarities it might be concluded that 6 is also a tetramer.

The color in copper(I) compounds with sulfur donor ligands has been assigned to a ligand-to-metal charge transfer transition [50]. The difference in the emission pattern and the color of the hexameric and tetrameric complexes can be attributed to the difference in their structures. The Cu–S–Cu angles in the hexamers are around 90° while those in the tetrameric structure are acute indicating closed three centre bonding. As a result the interaction between the ligand and the metal is better in the case of the hexamers which is reflected in shorter Cu–S distances. Table 6 compares the Cu–S–Cu angles and the Cu–S distances in the structurally characterised hexamers and tetramers. This structural difference could be responsible for the very different emission properties of the hexamers.

#### 3.4. Modeling studies

Modeling studies [51] were also helpful in understanding the role of steric effects in controlling the nuclearity of oligomeric copper(I) complexes. These studies reveal the fact that although monosubstitution increases the nuclearity of the cluster, the resulting structure is considerably strained. In the hexamer **3** that is formed in the reaction with guaiacol, free rotation about the O–C(aryloxide) bond is not possible and severe intramolecular bumping is encountered, the hydrogen atoms of the –OMe group and the phenyl ring of the *N*-**phenyl**imino(aryloxy)methanethiolate belonging to two neighboring ligands .....

Table 5		
Fluorescence	Spectral	Data

No.	Structural	X=C=Y-ArOH	Color	Fluorescence spectra		
	Data			$\overline{\lambda_{\mathrm{ex}}}$ nm	$\lambda_{_{ m em}}$ nm	
1	Hexamer	PhNCS-p-cresol	Orange	274	418, 471, 494, 629	
		X	0	383	639, 777	
				421	629	
2	Tetramer	PhNCS-DMP <sup>a</sup>	White	284	384	
3	Hexamer	PhNCS-guaiacol	Orange-	365	617	
		U	Yellow	400	603, 626	
				414	621	
4	Hexamer <sup>c</sup>	PhNCS-o-cresol	Yellow	374	438, 631	
5	Hexamer	MeNCS-p-cresol	red-orange	275	424, 474, 496	
		*	0	310	470, 491, 533	
				497	747	
6	_	MeNCS-DMP <sup>a</sup>	White	275	351, 388, 470, 493	
7	Tetramer	$CS_2 - BHT^b$	Yellow	312	471, 534	
		2		348	413, 469, 520, 571	
				363	413, 469, 513, 570	
				375	416, 468, 508, 567	
8	-	$CS_2$ -DMP <sup>a</sup>	red-orange	322	416, 436, 468, 528, 552	
		-	_	441	656	
				494	747	
9	-	PhNCS-p-	red-orange	311	401, 470	
		chlorophenol	-	387	642	
		-		455	682	
				486	731	
10	_	MeNCS-p-	red-orange	310	404, 468, 532, 549	
		chlorophenol	· ·	491	739	

<sup>a</sup> DMP=2,6-dimethylphenol.

<sup>b</sup> BHT=2,6-di-tert-butyl-4-methylphenol.

° Unpublished.

come as close as 0.55 Å. These constraints are responsible for the distortions observed in the molecular structure.

The nuclearity of complex **6** that was formed in the insertion reaction between copper(I) 2,6-dimethylphenoxide and MeNCS could not be ascertained from an X-ray crystallographic study. Modeling studies were carried out on this system by introducing two *ortho*-methyl substituents in the –OAr groups of the hexamer **5**. Contrary to the results obtained in the PhNCS systems, the introduction of methyl groups appeared to be feasible. While the possibility of a hexamer being formed is suggested by the modeling studies, fluorescence studies indicate that complex **6** is indeed a tetramer. Similarly, the orange

Table 6 Comparison of the Cu–S–Cu angles and Cu–S distances

Cluster	Cu–S–Cu (°)	Cu–S (Å)	
Tetramer 2	70.1-73.0	2.25-2.32	
Tetramer 7	70.8-72.1	2.24-2.30	
Hexamer 1	86.2-92.6	2.23-2.28	
Hexamer 3	89.1-98.4	2.21-2.27	
Hexamer 5	89.6	2.24-2.24	

product formed from copper(I) 2,6-dimethyl phenoxide and  $CS_2$  could not be crystallographically characterized. Modeling studies carried out on this system by constructing a hypothetical hexameric complex showed that the formation of a hexameric complex would not be restricted by steric factors. In this case, the results from fluorescence spectra confirm that a hexamer is indeed formed in this reaction.

The nuclearity of the cluster formed with a three atom bridge in a tricoordinate geometry around the metal is limited by topological factors. The oligomeric cluster complexes can be viewed as a combination of tub shaped dimeric  $(CuNCS)_2$  units. These tubs are brought together in an orientation where the trigonal coordination requirement of copper(I) is met. The three  $(CuNCS)_2$  tubs are in a parallel orientation in the hexamer while the two dimeric tubs are oriented orthogonal to each other in the tetramer. An attempt to form an octanuclear cluster by bringing together four tubs increases the Cu–S–Cu angle significantly. Large deviations of the S–Cu–S angle would be energetically unfavorable. On the other hand, the formation of a non planar sheet structure does not require deviations from trigonal coordination. Hence, in the absence of steric constraints, a hexamer or a sheet structure is preferred to an octanuclear complex.

### 4. Conclusions

From this study with ligands of varying steric demands, it can be concluded that the steric requirements of the ligand play a major role in determining the structure and hence the nuclearity of copper(I) complexes. It has been demonstrated that mono-ortho substitution instead of disubstitution results in the formation of a hexamer. The replacement of a phenyl group by a methyl group on the nitrogen atom of the -NCS- bridge does not bring about a change in nuclearity although it does affect the structure. The decreased congestion is evidenced by more symmetrical structural parameters. When the size is reduced further by exchanging the =NR group by a =S, the resulting -SCS- bridge leads to complexes of higher nuclearity. When the steric demands of the ligand are drastically reduced, by tying up the two ends of the ligand through covalent bonding, a polymeric sheet structure results. The thermodynamic stability of the oligomers seems to follow the order: hexamer/tetramer/dimer since release in steric strain results in a hexamer in all cases. Fluorescence studies could be used for determining nuclearity of some of these complexes that could not be studied using X-ray crystallography. Modeling studies are valuable in gauging the source of steric congestion in these structures, although they are not conclusive in predicting the nuclearity accurately. The structures of these copper(I) clusters are predominantly controlled by steric factors and fine tuning of steric parameters can lead to complexes of predictable nuclearity.

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