

Structure and reactivity of copper(I) oligomers

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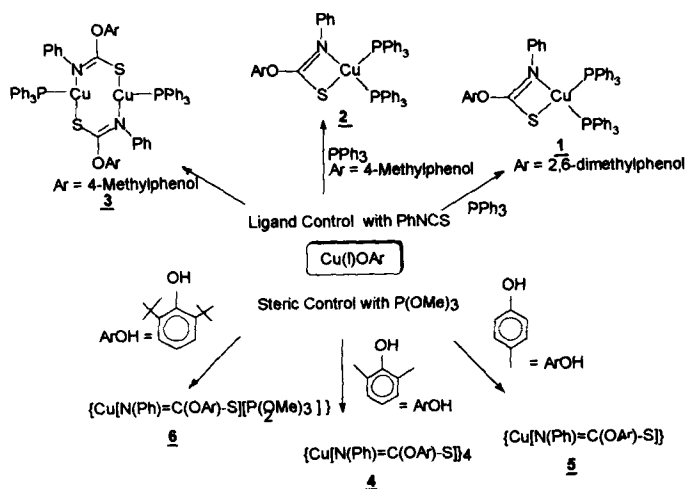
Abstract. The reactivity of oligomeric copper(I) complexes towards test electrophiles and hydrogen have been studied. The complexes exhibit similar reactivity patterns in most cases. Photochemical irradiation of the tetramer **4**, led to the isolation of the ligand **8**, 2,6-dimethylphenyl-N-phenylthionocarbamate, present in the tetramer. This compound crystallized in the monoclinic system in the $P2_1/n$ space group with $a = 11.992(5)$ Å, $b = 9.886(3)$ Å, $c = 12.783(6)$ Å, $\beta = 115.91(4)^\circ$, $V = 1360.37(4)$ Å³, $z = 4$. The comparison of the structure of the ligand with the tetramer shows the differences in the structure brought about by coordination. A comparison of the structures of the tetramer **4** and the hexamer **5** brings out the differences in the nature of bridging sulphide which considerably alters the properties of the complexes. Differences in the reactivity can be understood in terms of the type of the sulphide bridge present in the complexes. Similarities in the reactivity trends are the result of the dissociation of the oligomers in solution. ¹H NMR studies reveal that the structures of these complexes in the solution state are different from the solid state and account for the similarities in the reactivity patterns of these complexes.

Keywords. Copper(I) oligomers; reactivity patterns; ligand structure; photochemical reactivity.

1. Introduction

Cooperative interaction between metal centres in polynuclear complexes can result in altered reactivity patterns (Vahrenkamp 1983; Adams 1990; Werner 1990). To gauge the extent of such synergistic interactions between metal atoms one should be able to synthesize polynuclear complexes which do not differ greatly in their coordination environment. One such opportunity is provided by oligomeric complexes of copper(I) since they occur with varying nuclearity in a variety of coordination geometries (van Koten and Notles 1981; Munakata *et al* 1990; Castro *et al* 1992; Kitagawa *et al* 1992). The absence of ligand field effects makes copper(I) versatile and able to tolerate considerable deviation from ideal geometries. Hence, with steric and ligand control, copper(I) complexes of predetermined nuclearity can be synthesized. A particularly striking example is provided by the series of N-phenylimino(aryloxy)methanethiolato copper(I) complexes **1–6** (Narasimhamurthy *et al* 1989; Abraham *et al* 1993) in which a heterocumulene is anchored with aryloxy (scheme 1). Since variations occur only in the remote aryloxy group of the ligand, the electronic effect of the ligand can be assumed to be similar in all complexes. The tetramer and hexamer further stand out in that they have nearly identical coordination spheres around the metal ion. As a result of

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Scheme 1.

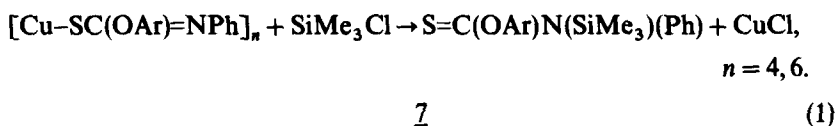
these unique features, these complexes serve as suitable candidates for comparing reactivity patterns as a function of nuclearity. We report here the results of our studies on the reactivity and stability of these complexes in solution.

2. Results and discussion

The reactivity of a metal centre and the ligand undergoes drastic changes on coordination. Depending on the extent of electron density transferred from the ligand to the metal one would expect the coordinated ligand to have reduced nucleophilicity. Similarly removal of an electron from the metal centre using oxidising agents or photons would be facilitated or retarded depending on the extent to which the oxidation state of the metal centre is stabilised by the ligand and the metal centres around it. Hence the reaction of electrophiles and oxidising agents are of interest while examining the reactivity changes. Also the presence of a heterocumulene in the coordination sphere of the complexes 1–6 prompted us to take hydrogenations in order to model the reactivity of CO_2 anchored in such multi-metal centres (Behr 1988).

2.1 Reaction with electrophiles

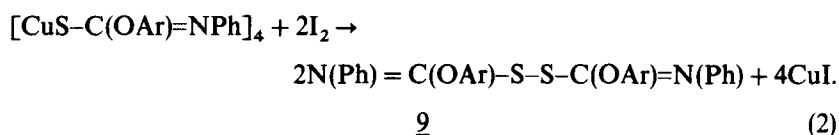
Attempts to react the coordinated ligand with MeI and tetramethylammonium iodide to produce an *N*-methylated thiourea failed in the case of the tetramer 4 and hexamer 5. However, when SiMe_3Cl was used as an electrophile a simple metathesis reaction occurs with $(\text{CuL})_n$ complexes,



The rapid reaction with SiMe_3Cl when compared to MeI is due to the greater electrophilicity of Me_3SiCl . The silylated ligand 7 is a poor ligand and falls off the coordination sphere of copper(I).

2.2 Oxidation with I₂

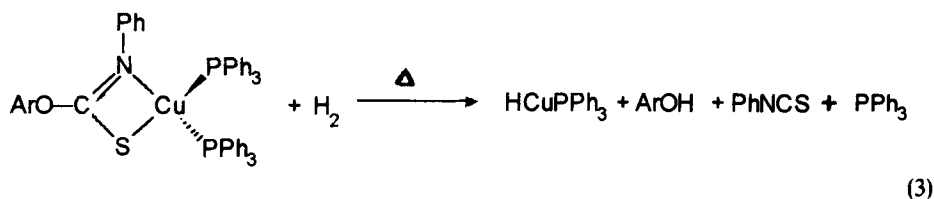
When the tetramer **4** was treated with I₂, an instantaneous reaction occurred. The pale yellow product isolated did not have copper and its spectral properties varied drastically from the tetramer. The IR stretching frequency of the C=N bonds appeared as two peaks at 1588 cm⁻¹ and 1641 cm⁻¹. The ¹H NMR spectrum revealed that the methyl groups of the 2,6-dimethylphenoxide which appeared as two singlets in the case of the tetramer now appeared as a singlet at δ 2.3. These spectral characteristics were also different from that of the ligand **8** of the tetramer (*vide infra*). The fact that this compound did not have copper led to the suspicion that a redox reaction occurred whereby iodine was reduced forming CuI and the ligand was oxidized, leading to the formation of the disulphide **9**. This was confirmed when the product **9** tested positive for the disulphide test (Fritz 1966).



In the case of the reaction of the hexamer **5** with I₂, the reaction was not as neat as in the case of the tetramer. A thin layer chromatographic (TLC) analysis indicated an intractable mixture of 6 products. This crude reaction mixture did not test positive for a disulphide. The IR stretching frequency of the C=N bonds appears at 1594 cm⁻¹ and 1640 cm⁻¹, shifted from the 1574 cm⁻¹ value of the hexamer. It was thus evident that the reactivity of the hexamer with I₂ varied drastically from that of the tetramer.

2.3 Reduction studies

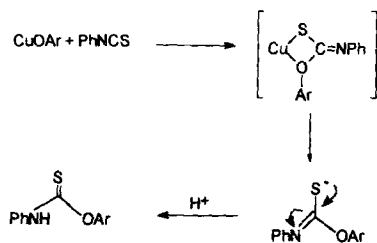
Hydrogenation of the complexes **1**–**5** was attempted without and with noble metal catalysts to no avail. Even when very drastic conditions of pressure were used hydrogenation did not occur. Increasing the temperature however led to the decomposition of these complexes and in some cases led to the extrusion of the heterocumulene PhNCS presumably through hydrogenolysis (3)



When an anionic hydride reagent was used, very rapid reaction of **4** and **5** occurred even at -78°C, leading to copper metal and an inseparable number of products arising from reduction of the ligand.

2.4 Photochemical studies

Photodissociation of the ligand occurs on irradiation of *d*¹⁰ metal complexes (Ford and Vogler 1993). However, the fact that each ligand in the sample is bridged to three metal ions and each metal atom is attached to three ligands in the tetramer **4** and hexamer **5** suggests that ready loss of the ligand may not be feasible in these complexes.



Scheme 2.

Prolonged irradiation of the tetramer **4** showed the formation of the ligand **8** in equilibrium with the complex. The photostationary state was reached after 12 hours. Preparative TLC allowed isolation of the ligand and characterisation (vide infra). In the case of the hexamer **5**, no decomplexation was apparent even after irradiation for 12 hours. The greater stability of the paddle wheel structure of the hexamer probably results in rapid recombination. When the hexamer was irradiated in air, decomposition of the complex was obvious suggesting oxidation of Cu(I). On the other hand irradiation of the tetramer in air, led to decomplexation of the ligand and no decomposition was apparent.

2.5 The ligand

The product isolated in the irradiation of the tetramer with UV light was also isolated from the reaction of copper(I) 2,6-dimethyl phenoxide with PhNCS. If the reaction was stopped at shorter reaction times, the formation of an intermediate could be detected. A TLC separation of the intermediate followed by characterization showed the intermediate to be the ligand **8**. A plausible explanation for the formation of the ligand is given in scheme 2.

The tetramer could be made by reaction of the ligand and CuCl suggesting an independent route to the formation of the oligomeric complexes. The structure of the ligand in the solid state was determined from a single crystal X-ray diffraction study in order to compare its structure with that of the tetramer and the hexamer (figure 1).

A comparison of the important bond lengths and bond angles in the ligand and the various complexes is made in table 1. The ligand has C–S and C–N bond distances atypical of thiourea (Caron and Donohue 1969). While thiourea itself binds to

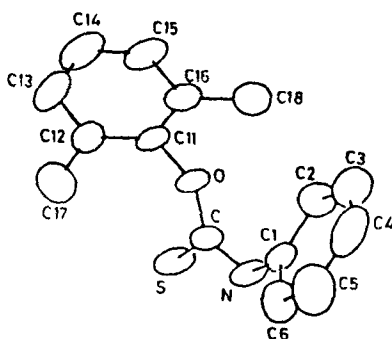
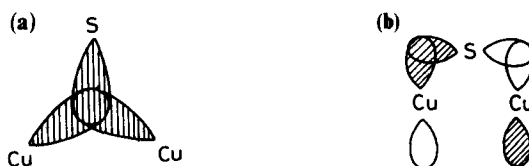
Figure 1. ORTEP view of the ligand **8**.

Table 1. Selected bond distances, Å (average) and bond angles, deg (average) for 1, 4, 5, 6, 8.

Distance/angle	Ligand <u>8</u>	Tetramer <u>4</u>	Hexamer <u>5</u>	Dimer <u>6</u>	Monomer <u>1</u>
C-S	1.665(2)	1.755(5)	1.752(8)	1.744(7)	1.703(3)
C-N	1.324(3)	1.281(6)	1.295(10)	1.275(9)	1.294(3)
C-OAr	1.339(2)	1.356(5)	1.345(9)	1.366(8)	1.374(4)
Cu-S	—	2.280(2)	2.245(2)	2.263(2)	2.469(2)
Cu-Cu	—	2.790(1)	2.957(1)	2.828(1)	—
S-C-N	123.7(2)	123.2(4)	122.0(5)	120.5(5)	119.8(2)
N-C-O	112.4(2)	119.1(3)	119.2(7)	120.0(5)	118.4(3)
O-C-S	123.9(2)	117.7(3)	118.8(8)	119.5(4)	121.8(3)
Cu-S-Cu	—	71.2(1)	90.2(1)	—	—

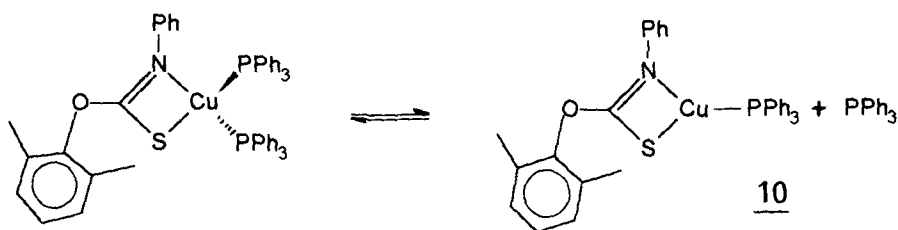
**Figure 2.** (a) Closed 3-centre-2-electron bond. (b) Open 3-centre-4-electron bond.

copper(I) in the neutral form, the ligand prefers coordination in the anionic form. Removal of the N-H proton by silylation results in decomplexation.

It is interesting to note that in spite of the nearly identical coordination around Cu in the tetramer and hexamer, the Cu-Cu bond distance and the Cu-S-Cu angles are significantly different. The acute angles in the tetramer are caused by the steric constraints resulting in the two dimeric tubs coming together in a perpendicular fashion in the tetramer. The acute angles at the sulphur result in a greater contribution to the electron-deficient 3-centre $2e^-$ bond (figure 2a). In the case of the hexamer the wide angles conform to the ideal angles predicted by MNDO calculations for an *RS*-, forming a 3-centre 4-electron bond (figure 2b) (Abraham *et al* 1993). The longer Cu-Cu bond distances in the hexamer are a result of greater contribution from the 3-centre $2e^-$ bond. The optimal Cu-L bond distances are consistent with the greater stability of the hexamer (*vide infra*). The electron deficiency in the tetramer and the long Cu-S distances should result in greater reactivity. Similarities in the reactivity suggested that solution state structures of these complexes are different. Hence a detailed study of the structure of the complexes in solution was taken up.

2.6 Solution state structures of the oligomeric Cu(I) complexes

2.6a The monomers (1, 2): Copper(I) complexes are expected to be labile. In fact the ^1H NMR of all the complexes showed interesting features indicative of a variety of structural changes. The monomeric complex 1 for example, invariably had two signals for the Me groups on the ligand at δ 2.21 and δ 1.87 ppm in the ratio 4.2:1.8. The non-integral ratio of the intensities led to the suspicion that in solution the monomer dissociates in accordance with the following reaction.



If such an equilibrium were to hold good, the addition of PPh_3 to a solution of the monomer should shift the equilibrium to the left, suppressing the dissociation of the monomer and giving rise to the pure monomer with only one peak corresponding to the dimethyl group. This was indeed the case. The addition of PPh_3 to a solution of the monomer **1** led to the disappearance of the smaller peak in the room temperature spectrum of the monomer.

Increasing the temperature aids the dissociation of the monomer while lowering the temperature suppresses its dissociation. The effect of temperature on a solution of the monomer was monitored by a variable temperature ^1H NMR experiment. Below room temperature, the intensity of the smaller peak decreases, while that of the larger peak increases and at a temperature of 223 K, the smaller peak completely disappears. Below this temperature only the monomer **1** is present in solution. When the temperature is

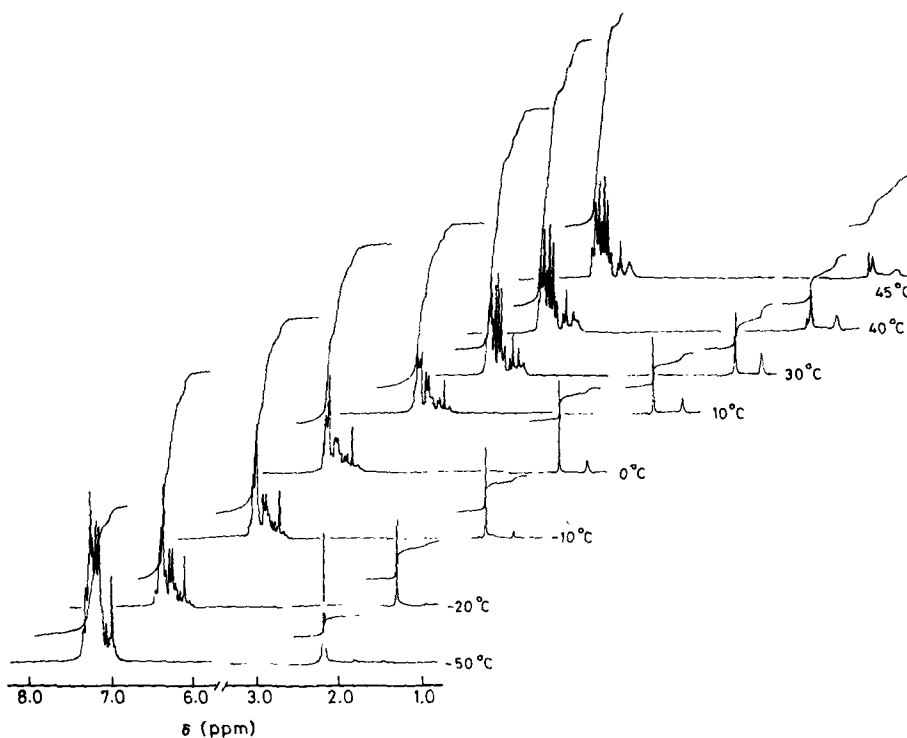
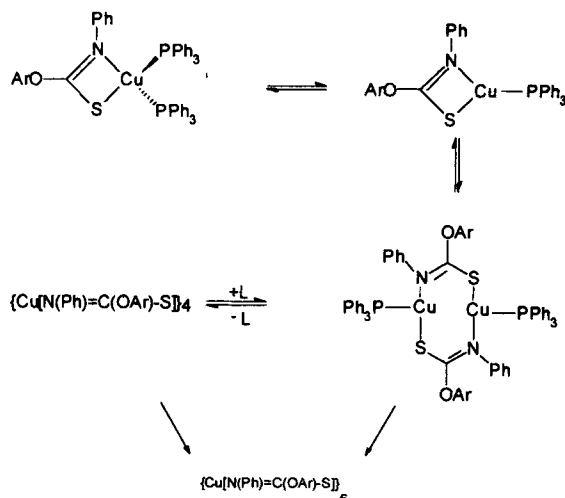


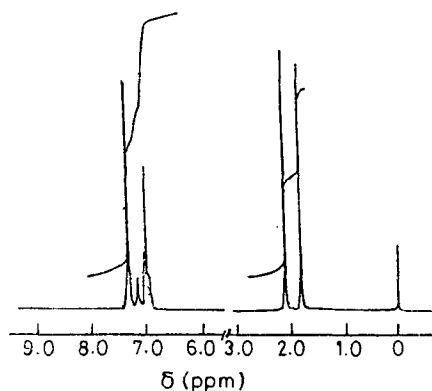
Figure 3. Variable temperature ^1H NMR spectrum of the monomer **1**.



Scheme 3.

raised above the room temperature, the formation of another species is indicated at 313 K by the appearance of another signal at δ 2.24. At 318 K, this peak becomes more prominent. This spectrum is similar to the NMR spectrum of the product obtained in the reaction of copper(I) 2,6-dimethylphenoxide with PhNCS in the presence of one equivalent of PPh₃ (figure 3) suggesting that the new peak at δ 2.24 corresponds to the species formed by the loss of the ligand from the monomer (10).

The reaction in the presence of one equivalent of the ancillary ligand leads to the isolation of the dimer 3. The N-phenylimino(aryloxy)-methanethiolate ligand prefers to bridge copper atoms through S rather than act as a chelating ligand. So even in the presence of 1 equiv of PPh₃ it would bridge two coppers rather than chelate (see scheme 3). However, in solution it exists in equilibrium with the monomer. This clearly suggests that Cu(I) prefers to coordinate to PPh₃ rather than form an oligomeric species. Only in the absence of strong donors such as PPh₃, it tends to form the tetramer and the hexamer where the coordination sphere of Cu is satisfied by N and S. A large excess of triphenylphosphine arrests the oligomerisation at the first step in the

Figure 4. ¹H NMR spectrum of the tetramer 4 (room temperature).

case of copper(I) 4-methylphenoxide leading to the isolation of the monomer where two phosphines are coordinated to the Cu(I) in addition to the ligand. Surprisingly the $^1\text{H NMR}$ of the monomer **2** did not show any additional signals indicative of an equilibrium with a phosphine dissociated species in solution. While it is tempting to assume that the monomer did not dissociate in solution, a more likely explanation is the coincidence of the two signals.

2.6b The tetramer (4): The $^1\text{H NMR}$ spectrum of the tetramer **4** at room temperature shows that the 2,6-dimethyl groups resonate at 1.78δ and 2.21δ with equal intensities (figure 4). These two signals arise due to the inequalities of the methyl

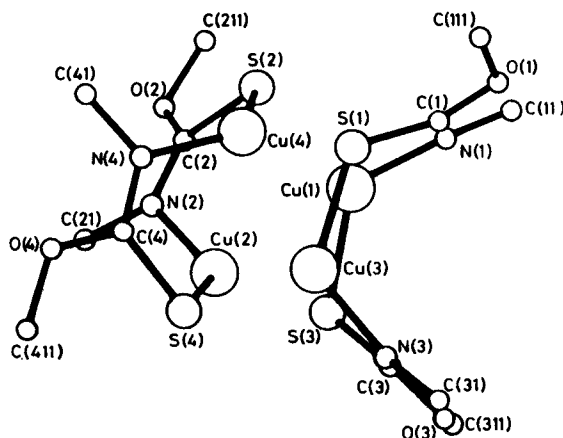


Figure 5. Dimeric tubs comprising the tetramer.

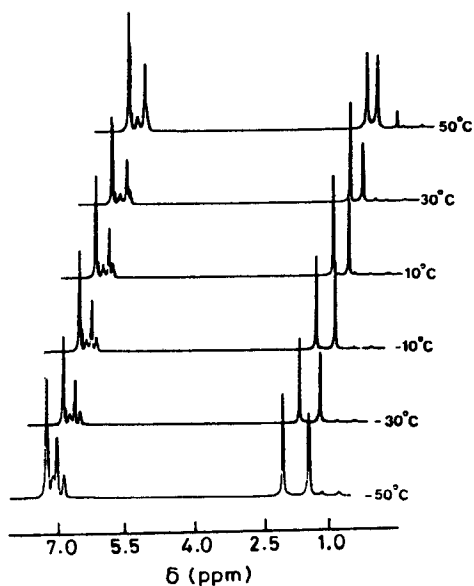


Figure 6. Variable temperature $^1\text{H NMR}$ spectrum of the tetramer **4**.

groups. The tetramer could be considered to be made up of two dimeric tubs (figure 5). The 2,6-dimethylphenoxide groups present in each of these tubs are in different environments and hence resonate at different frequencies. At a temperature of 323 K, the two methyl groups still resonate with equal intensities but at two frequencies, with a peak separation smaller than that observed in the room temperature spectrum (figure 6). When the temperature is lowered to 223 K, the intensities of the two peaks do not change but the peak separation becomes larger. This suggests that the two tubs are interconverting at a rate comparable to the NMR timescale ($\approx 10^{-7}$ s). Such a fast rotation is consistent with weak bonds formed by the bridging sulphides in the tetramer configuration. Throughout the range of temperatures the ratio of the intensities of the dimethyl groups is always 1:1. This indicates that there is no dissociation taking place and it is a rotational process responsible for the two peaks. To supplement the ^1H study, a variable temperature ^{13}C NMR experiment was carried out on a CDCl_3 solution of the tetramer. The room temperature ^{13}C NMR spectrum is shown in figure 7. The two methyl groups appear as two singlets. As the temperature is progressively lowered, each of the two peaks are split into two and four peaks corresponding to the methyl carbons. This can be attributed to the fact that the rapidly rotating dimeric tubs of the tetramer are slowed down at temperatures below 243 K and signals corresponding to the four dimethyl groups present in the two tubs resonate at different frequencies (figure 8). The ^{13}C chemical shift is more sensitive to the environment of the methyl groups than the ^1H chemical shift of the methyl group. At higher temperatures, the tubs rapidly rotate and the dimethyl groups resonate at

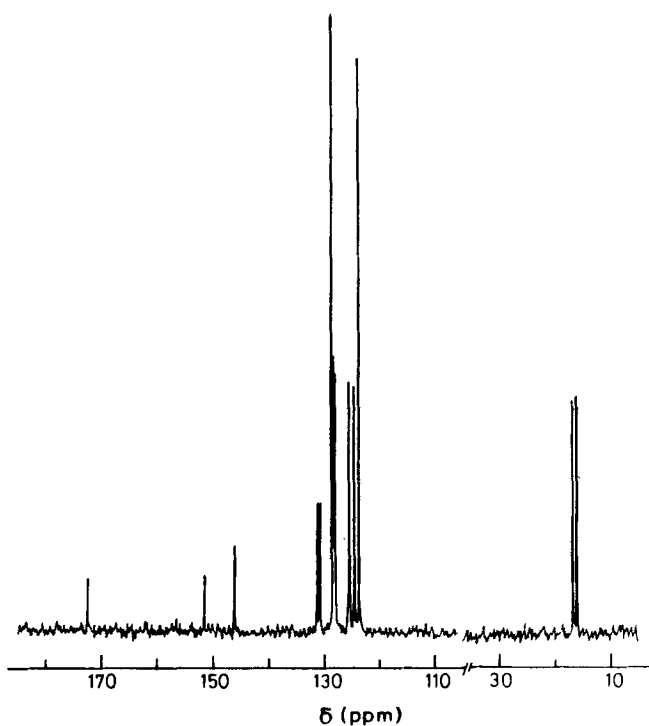


Figure 7. ^{13}C NMR spectrum of the tetramer **4** (room temperature).

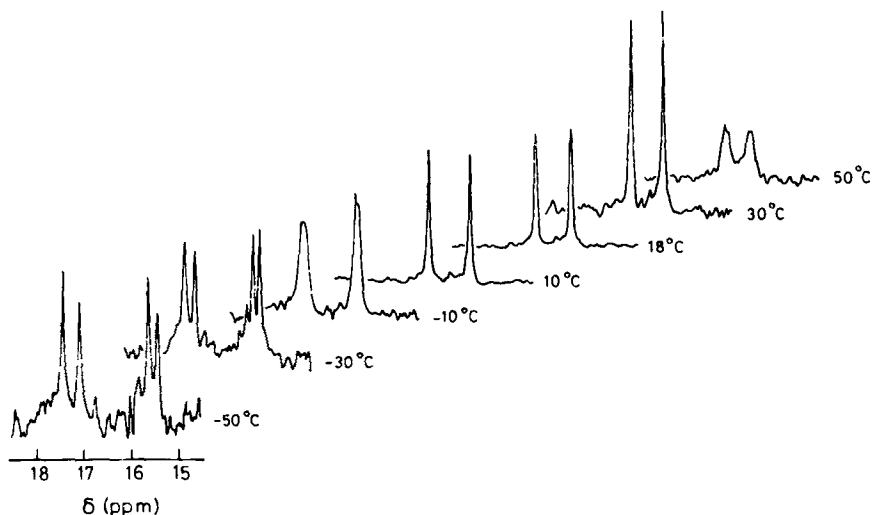


Figure 8. Variable temperature ^{13}C NMR spectrum of the tetramer **4**.

averaged out frequencies. When the temperature is raised to 323 K, the two peaks in the room temperature spectrum tend to coalesce. All these findings are consistent with the proposal that rotational effects and not dissociation predominate the behavioural pattern of the tetramer in solution.

2.6c The hexamer (5): Initial studies indicated that the hexamer **5** dissociated in solution (Abraham *et al* 1993a). Dissociation of the hexamer in solution can in principle lead to an equilibrium mixture of a tetramer and a dimer. An attempt was made to isolate the dissociated species. A solution of the hexamer was heated at 313 K for 24 hours and the resulting mixture was concentrated and the orange precipitate obtained was recrystallized. The cell parameters of the crystal obtained matched that of the hexamer. This showed that the hexamer was the most stable form in the solid state although dissociation was obvious in solution. To probe the structural differences of the hexamer in solution, a variable temperature NMR study was conducted. The room temperature ^1H NMR spectrum of the hexamer **5** indicates that the signal due to the methyl substituent of the 4-methylphenoxide group appears as two singlets at δ 2.31 and δ 2.26. When the temperature of the CDCl_3 solution of the hexamer was lowered to 223 K, only one peak was observed (figure 9). On the contrary, raising of the temperature to 323 K, the two peaks for the *p*-methyl group which were initially in the ratio 2:1 now appeared with equal intensity. The non-integral values of the ratios of the signals corresponding to the methyl group indicated a dissociation process. As the temperature is lowered, the thermodynamically stable product (the pure hexamer) predominates and as expected, only one signal for the *p*-methyl group is observed. When the temperature is raised, the equilibrium is shifted to the right and two signals for the methyl substituents are detected. The variable temperature ^1H NMR study indicated that the hexamer probably dissociated in solution (figure 9).

A variable temperature ^{13}C NMR study was then conducted to confirm the findings. In the case of the ^{13}C NMR spectrum (figure 10), the two peaks that appear at room temperature (corresponding to the methyl group) coalesce and resonate at a single

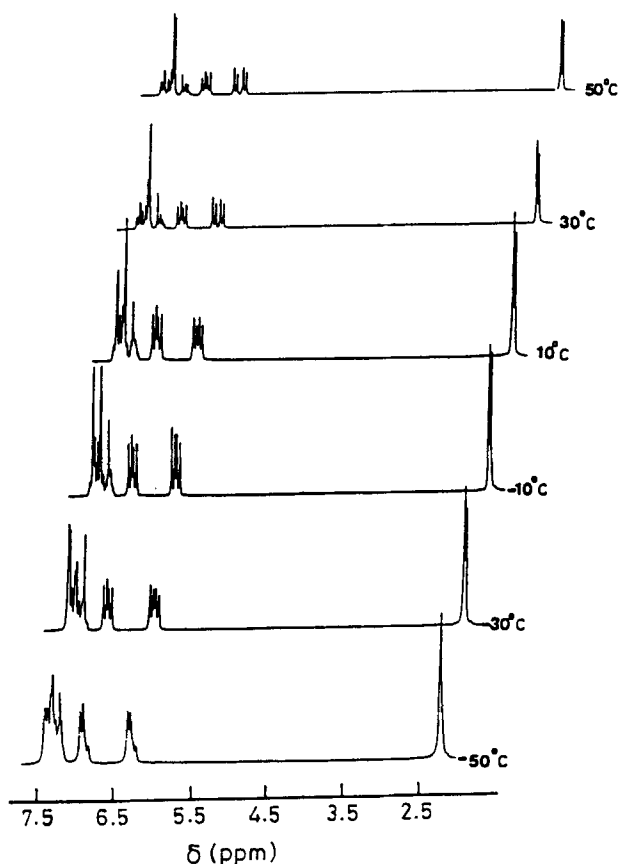


Figure 9. Variable temperature ^1H NMR spectrum of the hexamer 5.

frequency when the temperature of the solution is lowered to 263 K. However, when the temperature is lowered to 223 K, two peaks appear. Though the spectrum indicated the probability of a second species being formed, the roughly 1:1 ratio of the two species formed indicated that this variation of the spectrum with temperature could be a result of a concerted bond alternation in the Cu_3S_3 chairs present in the hexamer. This would be in accordance with the single resonance for the methyl group in the less sensitive ^1H NMR at low temperature.

3. Experimental

Solvents were purified by conventional methods and distilled under N_2 prior to use. All solvents were purged with N_2 for 30 m before use. The complexes 4 and 5 were prepared by procedures previously reported (Abraham *et al* 1993a). SiMe_3Cl (Fluka) and NaBH_4 (Merck) were used as such. I_2 was sublimed before use.

All IR spectra were recorded in the region 4000 cm^{-1} – 400 cm^{-1} on a Bio-Rad FTS7 spectrophotometer. The ^1H NMR spectra were recorded on a Bruker WH-200 FT spectrophotometer operating at 200 MHz. ^{13}C NMR spectra were recorded on the same spectrophotometer operating at 50 MHz. Chemical shifts in ppm were measured

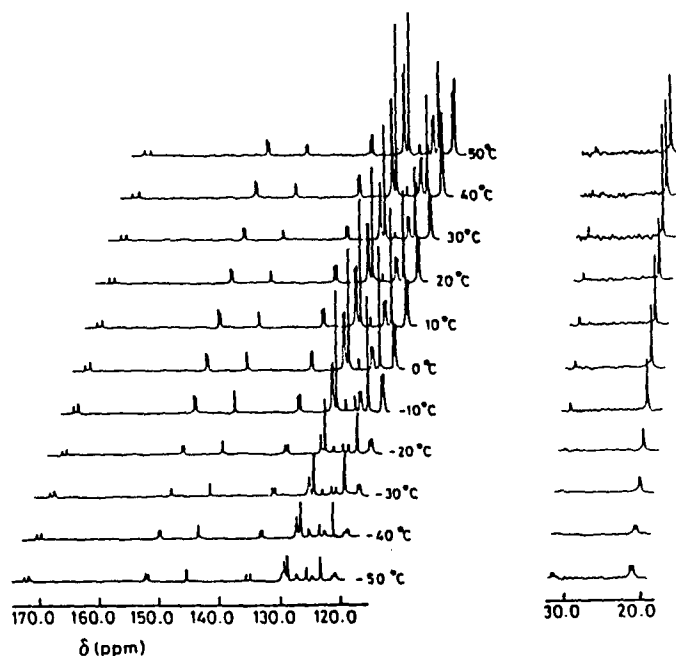


Figure 10. Variable temperature ^{13}C NMR spectrum of the hexamer **5**.

Table 2. Crystallographic data for the ligand **8**.

Chem formula	$\text{C}_{15}\text{H}_{15}\text{SON}$	$\lambda, \text{\AA} (\text{Mo-K}\alpha)$	0.7107
Crystal system	Monoclinic	$T, ^\circ\text{C}$	17
fw	257.35	Scan method	$\omega/2\theta$
space group	$P2_1/n$	2θ range (data collection)	$2^\circ \leq 2\theta \leq 50^\circ$
$a, \text{\AA}$	11.992(5)	2θ range (cell determination)	$24^\circ \leq 2\theta \leq 36.0^\circ$
$b, \text{\AA}$	9.886(3)	Unique reflections	2395
$c, \text{\AA}$	12.783(6)	Observed reflections	2045
β, deg	115.91(4)	Criterion for being observed	$ F_o \geq 6\sigma F_o $
$V, \text{\AA}^3$	1360.37(4)	Final (shift/esd) $_{\text{max}}$	0.03
Z	4	Weight (w)	0.000001
$\rho_{\text{calcd}}, \text{g cm}^{-3}$	1.250	R^a	0.0479
μ, cm^{-1}	1.83	Rw^b	0.0545

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}; w = [\sigma^2 |F_o| + g|F_o|^2]^{-1}$$

with respect to tetramethylsilane on the δ ppm scale. Photochemical studies were carried out using a high pressure mercury vapour lamp (500 W) in a quartz reaction vessel.

All hydrogenation reactions were carried out in a Parr Series 4560 Bench Top Reactor. Hydrogenation reactions were tried with two catalysts, either 10% Pd deposited on activated charcoal or Adam's catalyst. To a solution of the complex, 20% by weight of the catalyst was added. The suspension was purged with H_2 for 20 minutes and the progress of the reaction was monitored by removing 5 ml aliquots from the

Table 3. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) for the non-hydrogen atoms of **8**.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
S	0.9593(1)	0.1301(1)	0.1157(1)	528(3)
C	1.0006(2)	-0.0178(2)	0.1847(1)	381(8)
N	1.0307(2)	-0.1258(1)	0.1410(1)	432(7)
O	1.0057(1)	-0.0416(1)	0.2898(1)	400(5)
C1	1.0673(2)	-0.2569(2)	0.1932(2)	397(8)
C2	1.1666(2)	-2.2719(2)	0.3011(2)	576(10)
C3	1.2006(3)	-0.4019(3)	0.3460(2)	741(13)
C4	1.1359(3)	-0.5141(3)	0.2823(3)	804(18)
C5	1.0403(3)	-0.4966(2)	0.1743(3)	834(17)
C6	1.0054(2)	-0.3677(2)	0.1283(2)	619(12)
C11	0.9863(2)	0.0681(2)	0.3515(1)	393(7)
C12	0.8686(2)	0.0886(2)	0.3410(2)	500(9)
C13	0.8570(3)	0.1951(3)	0.4099(2)	688(13)
C14	0.9570(3)	0.2712(3)	0.4804(2)	737(15)
C15	1.0720(3)	0.2447(2)	0.4888(2)	633(12)
C16	1.0899(2)	0.1406(2)	0.4236(2)	455(9)
C17	0.7616(2)	0.0053(3)	0.2637(2)	744(12)
C18	1.2154(2)	0.1098(3)	0.4327(2)	641(10)

Table 4. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) for the hydrogen atoms of **8**.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
H	1.0255(23)	-0.1191(24)	0.0724(22)	548(69)
H2	1.2205(24)	-0.1849(24)	0.3478(21)	678(67)
H3	1.2722(21)	-0.4199(26)	0.4238(20)	774(66)
H4	1.1544(23)	-0.6107(25)	0.3150(22)	804(70)
H5	0.9954(22)	-0.5657(27)	0.1164(18)	843(66)
H6	0.9358(23)	-0.3548(24)	0.0448(22)	882(71)
H13	0.7840(22)	0.2179(24)	0.4118(21)	777(68)
H14	0.9445(23)	0.3513(24)	0.5230(23)	777(70)
H15	1.1479(23)	0.2992(25)	0.5417(21)	668(66)
H171	0.7500(21)	0.0029(24)	0.1807(20)	633(68)
H172	0.6876(23)	0.0305(26)	0.2409(19)	015(67)
H173	0.7718(22)	-0.0815(27)	0.2883(20)	771(66)
H181	1.2750(23)	0.1728(26)	0.4813(22)	882(67)
H182	1.2366(23)	0.0158(24)	0.4647(20)	749(65)
H183	1.2192(24)	0.1148(24)	0.3640(22)	731(70)

reactor, removing the solvent under reduced pressure and recording the IR spectra of the residue.

3.1 Reaction with I_2

To a solution of tetramer **4** in CH_2Cl_2 , was added a solution of I_2 in excess. An instantaneous reaction occurred as indicated by the formation of a greyish white

Table 5. Anisotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) for the non-hydrogen atoms of **8**.

Atom	U11	U22	U33	U23	U13	U12
S	925(5)	340(4)	384(4)	88(2)	346(3)	142(2)
C	511(11)	342(10)	304(9)	-1(7)	190(8)	-9(8)
N	707(12)	322(9)	320(9)	23(6)	274(8)	68(7)
O	636(9)	316(7)	300(6)	39(5)	253(6)	62(6)
C1	551(12)	320(10)	424(11)	37(8)	310(9)	61(8)
C2	750(15)	483(13)	481(12)	58(10)	255(11)	147(12)
C3	995(21)	733(17)	607(16)	270(14)	453(15)	431(16)
C4	1112(24)	443(15)	1223(25)	323(16)	850(22)	300(15)
C5	853(19)	323(12)	1358(26)	-7(14)	514(20)	-33(13)
C6	613(14)	391(13)	832(18)	-32(11)	296(13)	6(10)
C11	614(12)	325(10)	310(9)	59(8)	267(9)	75(9)
C12	612(13)	485(11)	489(12)	131(10)	319(10)	86(10)
C13	908(18)	639(16)	793(17)	166(14)	626(16)	272(14)
C14	1240(25)	471(14)	768(18)	-74(13)	687(19)	50(15)
C15	1008(20)	465(13)	544(14)	-97(10)	448(14)	-66(12)
C16	671(13)	385(11)	352(10)	3(8)	264(10)	-26(9)
C17	610(15)	850(20)	726(16)	130(14)	250(13)	-2(14)
C18	616(14)	665(16)	615(15)	-51(12)	244(12)	-116(12)

Table 6. Bond distances (\AA) with their estimated standard deviations for **8**.

Atoms	Distance	Atoms	Distance
S-C	1.665(2)	C2-H2	1.083(23)
C-N	1.324(3)	C3-H3	1.006(20)
C-O	1.339(2)	C4-H4	1.025(25)
N-C1	1.434(2)	C5-H5	0.977(23)
C1-C2	1.381(3)	C13-H13	0.914(29)
Cl-C6	1.377(3)	C14-H14	1.007(28)
C2-C3	1.392(4)	C15-H15	1.018(23)
C11-C12	1.373(4)	C17-H171	1.008(23)
C11-C16	1.380(3)	C17-H172	0.842(26)
C12-C13	1.416(4)	C17-H173	0.902(27)
C12-C17	1.480(3)	C18-H181	0.946(23)
C13-C14	1.367(4)	C18-H182	1.001(23)
N-H	0.854(30)	C18-H183	0.900(31)

precipitate. Upon filtration and removal of the solvent under reduced pressure, a pale yellow compound resulted. $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 6.8–7.2 (m, 8H, $\text{C}_6\text{H}_5\text{NCS}$, $-\text{OC}_6\text{H}_3$), δ 2.3 (s, 3H, CH_3).

To a solution of the hexamer **5** in CH_2Cl_2 was added a solution of I_2 in excess. A greyish white precipitate was formed. A TLC analysis indicated the formation of 6 products. Upon filtration and removal of the solvent under reduced pressure, a pale yellow solid was obtained. $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 6.9–7.4 (m), δ 2.2–2.3 (m).

3.2 Reaction with SiMe_3Cl

To a solution of the tetramer **4** in CH_2Cl_2 was added SiMe_3Cl in excess. The white

Table 7. Bond angles (deg) with their estimated standard deviations for **8**.

Atoms	Angles	Atoms	Angles
S–C–O	123.9(2)	C–N–H	117.4(16)
S–C–N	123.7(2)	C1–N–H	114.7(17)
N–C–O	112.4(2)	C1–C2–H2	120.8(13)
C–N–C1	127.9(2)	C3–C2–H2	120.4(14)
C–O–C11	118.6(2)	C2–C3–H3	122.7(15)
N–C1–C6	117.5(2)	C4–C3–H3	117.1(15)
N–C1–C2	121.1(2)	C3–C4–H4	122.3(15)
C2–C1–C6	121.3(2)	C5–C4–H4	117.8(15)
C1–C2–C3	118.7(2)	C6–C5–H5	110.8(13)
C2–C3–C4	120.2(3)	C4–C5–H5	128.2(15)
C3–C4–C5	119.8(3)	C5–C6–H6	120.5(14)
C4–C5–C6	120.6(3)	C1–C6–H6	120.2(13)
C1–C6–C5	119.3(2)	C12–C13–H13	123.7(16)
O–C11–C16	116.7(2)	C16–C15–H15	117.3(17)
O–C11–C12	118.0(2)	C14–C13–H13	114.9(15)
C12–C11–C16	125.2(2)	C13–C14–H14	119.5(17)
C11–C12–C17	122.5(2)	C15–C14–H14	119.5(16)
C11–C12–C13	115.1(2)	C14–C15–H15	122.1(15)
C13–C12–C17	122.4(3)	C12–C17–H173	110.4(16)
C12–C13–C14	121.4(3)	C12–C17–H172	122.9(17)
C13–C14–C15	120.9(3)	C12–C17–H171	113.4(15)
C14–C15–C16	120.6(3)	H172–C17–H173	111.3(25)
C11–C16–C15	116.8(3)	H171–C17–H173	106.3(21)
C15–C16–C18	121.1(2)	H171–C17–H172	90.2(22)
C11–C16–C18	122.1(2)	C16–C18–H183	113.1(21)
C16–C18–H181	111.4(17)	H182–C18–H183	109.7(22)
H181–C18–H183	105.0(24)	H181–C18–H182	110.9(21)

precipitate that settled down was filtered and the filtrate yielded a product with the following spectral features $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 7.09–7.77 (*m*, 8H, $\text{C}_6\text{H}_5\text{NCS}$, $-\text{OC}_6\text{H}_3$), δ 2.21 (*s*, 6H, CH_3), δ 0.06 (*s*, 9H, SiMe_3).

To a solution of the hexamer **5** in CH_2Cl_2 was added SiMe_3Cl in excess. The white precipitate that settled down was filtered and the filtrate yielded a product with the following spectral features $^1\text{H NMR}$ (CDCl_3 , 298 K): δ 7.02–7.65 (*m*, 9H, $\text{C}_6\text{H}_5\text{NCS}$, $-\text{OC}_6\text{H}_3$), δ 2.36 (*s*, 3H, CH_3), δ 0.06 (*s*, 9H, SiMe_3).

3.3 Reaction with CH_3I

To a solution of the tetramer **4** or hexamer **5** in CH_2Cl_2 was added CH_3I in excess. The reaction was heated under reflux for 24 h. A TLC analysis revealed that no reaction had taken place and the complex was quantitatively recovered.

3.4 Experimental details of structure determination

A suitable crystal of the compound **8** was mounted and the three dimensional intensity data were collected on an Enraf Nonius CAD-4 diffractometer. Three intensity control reflections, monitored every 3600 seconds of exposure time, showed no intensity decay. Lorentz and polarization corrections were applied but no absorption correction. The structure was solved by direct methods using the SHELXS-86 (Sheldrick 1986)

program. The H atoms were located from the Δ map. Non-hydrogens were refined anisotropically and the hydrogen atoms isotropically by the full matrix least squares method using the program SHELX-76 (Sheldrick 1976) converged to an R factor for 0.0479. The ORTEP diagram is given in figure 1 and the data collection parameters and details of the crystallographic analysis are summarized in the tables 2–7.

4. Conclusions

The differences in the reactivity patterns of the tetramer **4** and the hexamer **5** varied significantly and can be summarized as follows: These complexes have identical coordination around the metal ions and have ligands which are similar but for the substituents on the aryloxy group. However there are wide ranging differences in their structure, the most prominent being the Cu–S–Cu bridges. In the tetramer, the Cu–S–Cu bridges are acute [70.1(1)–73.0(1)°] when compared to the larger bridge angles of the hexamer [86.2(1)–92.6(1)°].

The reactivity changes can be attributed primarily to this difference. The tetramer appears to be generally more reactive when compared to hexamer; its reaction with PPh_3 for example results in the monomer **1**. This is a reflection of the weaker Cu–S–Cu bridges. The hexamer on the other hand has optimum metal-ligand bonding and is less reactive; attempts to break it down by reacting it with PPh_3 led to incomplete conversion, even after long reaction times.

The difference in the reactivity patterns was reflected in the photochemical properties of these complexes. Irradiation of the tetramer with UV light led to decomplexation and the isolation of a ligand **8**, while in the case of the hexamer there appeared to be a reversible decomplexation in the absence of air. However, in the presence of O_2 decomplexation was accompanied by oxidation due to the electron-rich nature of the cluster. This is a reflection on the 3centre– $4e^-$ bonding present in the Cu–S–Cu bridges. This is again reflected in the reactivity trends of the tetramer **4** and the hexamer **5** with I_2 . The hexamer is very readily oxidized and leads to a mixture of products. However, the tetramer is less readily oxidized and gives CuI and the disulfide.

In contrast, reactions with electrophiles are similar in the case of the hexamer and the tetramer. These complexes underwent a metathesis reaction with SiMe_3Cl , but they did not react with CH_3I and tetramethylammonium iodide.

All the complexes **1**–**5** resisted reduction with hydrogen under ambient conditions; drastic conditions like elevated pressures and temperature led to the decomposition of the complexes. When a strong reducing agent like NaBH_4 was employed, the tetramer **4** and the hexamer **5** underwent complete reduction to yield a mixture of products.

The tetramer and the hexamer exhibit significantly different behaviour in solution. Both the hexamer and the tetramer show fluxional behaviour even at low temperatures consistent with the absence of crystal field stabilization energy to favour unique coordination geometries. In addition to the fluxional behaviour, the hexamer dissociates in solution and is in equilibrium with the dimer.

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