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Synthesis and structural characterization of a tetracopper(I) complex of 2,6-(bis(3-dimethylamino)-propyliminomethyl)-4-methylthiophenolate

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Abstract—The compound 2,6-diformyl-4-methylphenyl disulfide (**1**) has been made by hydrolysis of *S*-(2,6-diformyl-4-methylphenyl)dimethylthiocarbamate followed by oxidation with I_2. Condensation of **1** with 4 equiv. of 3-dimethylaminopropylamine and subsequent reduction with Na/benzophenone results in the sodium salt of the Schiff base binucleating ligand 2,6-(bis(3-dimethylamino)-propyliminomethyl)-4-methylthiophenolate (**2**, NaL). The ligand (L) binds 2 eq of Cu(I) and crystallizes from MeCN solution to give an air sensitive tetracopper(I) complex with the formula $[Cu_4L_2(MeCN)](PF_6)_2$ (**3**)·0.5 MeCN·0.25 MeOH as determined by X-ray crystallography. The complex contains three distorted trigonal planar and one distorted tetrahedral Cu^I centers with Cu—S bond lengths short for their respective coordination geometries. In DMSO solution, ^1H NMR spectra of **3** reflect free ligand symmetry suggesting dissociation into dimers. Cyclic voltammetry of **3** in MeCN reveals one irreversible oxidation at 110 mV (*vs* SCE). © 1997 Elsevier Science Ltd

Keywords: copper(I); thiolate; Schiff base; synthesis; crystal structure; trigonal.

Polynuclear copper centers play a wide variety of roles in biological systems [1]. A small and less studied subset of these copper centers contains one or more bridging cysteinyl thiolate ligands. The binuclear Cu_A site of both cytochrome *c* oxidase (CcO) [2] and nitrous oxide reductase (N_2OR) [3] has been well characterized as a dithiolate-bridged, fully delocalized mixed-valent $Cu^{1.5}Cu^{1.5}$ center. Other examples include multinuclear Cu^I-cysteinate clusters in the family of copper sequestering metallothionein (MT) proteins [4,5] and MT metalloregulatory proteins [6]. Cysteinate has also been implicated as a possible bridging ligand in the binuclear catalytic site of N_2OR (Cu_Z) [7].

Bio-mimetic chemistry of naturally occurring Cu-thiolate systems has been typically difficult due to the lack of specific structural information and the propensity of Cu^{II} to oxidize thiolate to disulfides. However, several thiolate-bridged mixed-valent complexes have been synthesized recently and compared structurally and electronically with Cu_A [8]. A handful of mono and bis(μ-thiolato) dicopper(II) complexes have also been made [9], some of which are shown by electrochemical methods to stabilize the mixed-valent state [9a,d]. In addition, numerous multinuclear monovalent copper–thiolate complexes have been characterized and related to the clusters in metallothioneins [5]. In accordance with the growing interest in biological Cu–thiolate systems, we have synthesized and isolated the sodium salt of a mixed imino/amino thiophenolate-based binucleating ligand which provides an N_2-(μ-S)-N_2 atom donor set per chelated Cu^I pair. In the absence of potential exogenous bridging ligands, we have successfully isolated a unique tetranuclear Cu^I 'dimer of dimers' complex of the ligand and herein report its structure and solution properties.

EXPERIMENTAL

Synthesis

THF, benzene, and ether were distilled over Na/benzophenone. All other solvents and reagents were used as purchased. Anaerobic manipulations were

carried out using standard Schlenk and glove box techniques.

2,6-*Diformyl*-4-*methylphenyl disulfide* (**1**). 1.85 g (7.36 mmol) of *S*-(2,6-diformyl-4-methylphenyl) dimethylthiocarbamate [10] were dissolved in 60 cm^3 of 1 M aqueous NaOH. The resulting bright orange solution was filtered and treated dropwise with 6 M HCl until the orange color disappeared and a white solid (thiol) precipitated. The solid was isolated by filtration, washed with distilled water, and redissolved in a minimal amount of CH_2Cl_2 (*ca* 50 cm^3). The tea colored solution was then dried over Na_2SO_4, filtered, and solvent was removed in vacuo. The residue was taken up in a minimal amount of THF (*ca* 10 cm^3) and treated with several drops of Et_3N to give a bright orange solution (deprotonated thiol). A 0.05 M I_2 solution in THF was added dropwise until the orange color disappeared. Addition of Et_3N followed by iodine solution was subsequently repeated until addition of the amine no longer afforded the orange colored solution, indicating reaction completion. About 80 cm^3 (4 mmol) of the iodine solution were added in total. THF was removed in vacuo and the residue was taken up in minimal CH_2Cl_2 (*ca* 50 cm^3), extracted with distilled water, and dried over Na_2SO_4. Solvent was removed in vacuo and the residue was taken up in benzene from which it was purified by recrystallization yielding 1.09 g of final product as a yellow crystalline solid (83%): ν_{CO} (KBr) 1690 cm^{-1}; mass spectrum (FAB+) *m/z* 358. Anal. Calcd for $C_{18}H_{14}O_4S_2$: C, 60.32; H, 3.94; O, 17.85; S, 17.89. Found: C, 60.46; H, 3.92; S, 17.82. ^{1}H NMR (benzene-d_6): δ 10.01 (formyl-H), 7.64 (phenyl-H), 1.69 (CH_3).

Sodium 2,6-*bis*(3-(*dimethylamino*)-*propyliminomethyl*)-4-*methylthiophenolate* (NaL, **2**). To a solution of 100 mg (279 μmol) of **1** in 15 cm^3 of THF (over activated 4 Å molecular sieve and under an atmosphere of N_2) was added to 142 μl (1.12 mmol) of 3-dimethylaminopropylamine to give a bright red solution. Solvent was removed in vacuo and the oily residue was redissolved in 20 cm^3 of ether. A 0.05 M solution of Na/benzophenone in ether was added dropwise to the solution until the red color disappeared and a bright yellow solid precipitated. The solid was collected by filtration, washed with ether, and redissolved in minimal THF (*ca* 5 cm^3). The resulting solution was filtered and treated with *ca* 50 ml of ether, thereby precipitating pure product which was isolated by filtration, washed with ether, and dried in vacuo to yield 80 mg (39%) of yellow solid; ν_{CN} (KBr) 1622 cm^{-1}; mass spectrum (FAB−) *m/z* 347. Anal. Calcd for $C_{19}H_{31}N_4SNa$: C, 61.59; H, 8.43; N, 15.12; S, 8.65; Na, 6.21. Found: C, 61.21; H, 8.59; N, 15.03; S, 9.02. ^{1}H NMR (MeOD-d_4): δ 9.36 (iminomethyl-H, s), 7.43 (phenyl-H, s), 3.62 (CH_2, t), 2.41 (CH_2, t), 2.25 (NMe_2, s), 2.33 (CH_3, s), 1.88 (CH_2, m).

$[Cu_4L_2(MeCN)](PF_6)_2$ (**3**). Under an inert atmosphere, a solution of 10 mg (27 μmol) of **2** (NaL) dissolved in 0.25 cm^3 MeCN was combined with a solution of 20 mg $[Cu(MeCN)_4](PF_6)$ [11] (54 μmol) in 0.25 cm^3 MeCN to give a red solution. Several volume equivalents of ether were diffused into the filtered solution over the course of 1 week producing orange block crystals with the formula **[3]**·0.5 MeCN·0.25 MeOH as determined by X-ray diffraction and white crystals of $NaPF_6$ which could be eliminated by successive recrystallization from MeCN. Coordinated MeCN and lattice solvent were readily removed in vacuo yielding 8.2 mg of pure product (61%): ν_{CN} (KBr) 1626 cm^{-1}. Anal Calcd for $C_{38}H_{62}N_8Cu_4F_{12}P_2S_2$: C, 36.83; H, 5.04; N, 9.04; Cu, 20.51; F, 18.40; P, 4.00; S, 5.17. Found: C, 36.73; H, 5.14; N, 9.12. ^{1}H NMR (DMSO-d_6): δ 8.4 (iminomethyl-H, s), 7.3 (phenyl-H, s), 3.8 (CH_2, t), 2.8 (CH_2, t), 2.6 (NMe_2, s), 2.3 (CH_3, s), 1.9 (CH_2, m).

X-ray structure determination

Data was collected using a Siemens SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3° per frame for 10 s, such that a hemisphere was collected. A total of 1271 frames were collected with a final resolution of 0.90 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data reduction was performed using SAINT software which corrects for Lp and decay. Absorption corrections were applied using SADABS supplied by George Sheldrick. The structures are solved by direct methods using the SHELXS-90 program and refined by the full-matrix least squares method on F^2 with SHELXL-93, incorporated in SHELXTL-PC V 5.03.

The structure of **3** was solved in the monoclinic crystal system, space group *C*2/*c*, by analysis of systematic absences, *E* statistics, and successful refinement of the structure. The asymmetric unit consists of the dicationic complex $[Cu_4L_2(MeCN)]^{2+}$, two hexafluorophosphates, 1/2 of an acetonitrile solvate molecule lying along a 2-fold symmetry site, and a methanol solvate molecule at 1/4 occupancy [12]. Due to disorder in one dimethyl amino group of the dicationic complex, methyl carbons C(13) and C(14) were each refined over 2 sites with 1/2 occupancy. All nonhydrogen atoms except those of the methanol solvate were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Selected crystallographic data and final R factors are given in Table 1.

Other physical methods

^{1}H NMR spectra were obtained with an AM400N Bruker spectrometer and IR spectra were recorded on a Nicolet Impact 400D spectrophotometer. Electro-

Table 1. Crystallographic data[a] for $[Cu_4L_2(MeCN)](PF_6)_2 \cdot 0.5\ MeCN \cdot 0.25\ MeOH$

Formula	$C_{40}H_{65}Cu_4F_{12}N_9P_2S_2 \cdot 0.5\ CH_3CN \cdot 0.25\ CH_3OH$
Formula wt	1308.77
Color	orange
Habit	block
Size, mm	$0.1 \times 0.1 \times 0.05$
T (K)	213
Crystal system	monoclinic
Space group	$C2/c$
Z	8
a (Å)	32.6089(4)
b (Å)	27.0775(4)
c (Å)	13.8764(2)
β (°)	108.801(1)
V (Å^3)	11598.7(3)
d_{calc} (g/cm^3)	1.499
2θ range (°)	4–45
$wR2^b$, $R1^c$	0.1528, 0.0563

[a] Obtained with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation.
[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

chemistry was investigated in 0.1 M solutions of tetrabutylammonium hexafluorophosphate (as supporting electrolyte) in MeCN with a platinum working electrode and saturated Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

Synthesis

Syntheses of **1–3** are outlined in Fig. 1. Compound **1** was prepared readily in air by hydrolysis of *S*-(2,6,-diformyl-4-methylphenyl)dimethylthiocarbamate [10] in aqueous NaOH solution followed by oxidation with I_2. Both steps were easily monitored for reaction completion by obvious color changes. Colorless *S*-(2,6,-diformyl-4-methylphenyl)dimethylthiocarbamate, insoluble in water, turns bright orange and dissolves upon hydrolysis in basic aqueous solution. Similarly, the orange colored thiolate, produced by deprotonation of the isolated thiol with tertiary amine, changes to pale yellow upon oxidation with I_2. The final disulfide product (**1**) is easily purified by crystallization from benzene and is stable in air. Synthesis of **2** is performed under a pure dinitrogen atmosphere as the ligand product is quite hygroscopic. Initially, **1** is treated with 4 eq of 3-dimethylaminopropylamine to form the Schiff base disulfide intermediate. Water generated in the condensation reaction is taken up by molecular sieves present in the reaction solution. The disulfide bond is then cleaved by reduction with Na/benzophenone in ether thereby generating the yellow, insoluble sodium salt of the ligand (NaL, **2**). Subsequent purification is accomplished by filtration of a THF solution of **2** followed by precipitation with ether. The relatively low yield (39%) may be due to

Table 2. Selected bond distances (Å) and angles (°) for $[Cu_4L_2(MeCN)](PF_6)_2 \cdot 0.5\ MeCN \cdot 0.25\ MeOH$

Cu(1)—N(2)	1.977(5)	Cu(3)—N(6)	2.010(5)
Cu(1)—N(1)	2.123(5)	Cu(3)—S(2)	2.151(2)
Cu(1)—S(1)	2.187(2)	Cu(4)—N(7)	1.969(5)
Cu(2)—N(9)	1.971(8)	Cu(4)—N(8)	2.088(7)
Cu(2)—N(3)	2.039(5)	Cu(4)—S(2)	2.184(2)
Cu(2)—N(4)	2.194(6)	S(1)—C(1)	1.788(6)
Cu(2)—S(1)	2.244(2)	S(2)—C(20)	1.796(5)
Cu(3)—N(5)	2.008(7)		
Cu(1)···Cu(2)	3.062	Cu(3)···Cu(4)	3.511
Cu(1)···SN$_2$[a]	0.1704	Cu(2)···SN$_2$[a]	0.9827
Cu(3)···SN$_2$[a]	0.0410	Cu(4)···SN$_2$[a]	0.0419
N(2)—Cu(1)—N(1)	103.1(2)	N(6)—Cu(3)—S(2)	104.2(2)
N(2)—Cu(1)—S(1)	142.1(1)	N(7)—Cu(4)—N(8)	98.9(3)
N(1)—Cu(1)—S(1)	112.6(2)	N(7)—Cu(4)—S(2)	144.6(2)
N(9)—Cu(2)—N(3)	112.7(2)	N(8)—Cu(4)—S(2)	116.3(2)
N(9)—Cu(2)—N(4)	100.6(3)	C(1)—S(1)—Cu(1)	107.1(2)
N(3)—Cu(2)—N(4)	93.5(2)	C(1)—S(1)—Cu(2)	106.3(2)
N(9)—Cu(2)—S(1)	134.6(2)	Cu(1)—S(1)—Cu(2)	87.43(6)
N(3)—Cu(2)—S(1)	97.9(2)	C(20)—S(2)—Cu(3)	107.4(2)
N(4)—Cu(2)—S(1)	110.4(2)	C(20)—S(2)—Cu(4)	108.8(2)
N(5)—Cu(3)—N(6)	105.7(3)	Cu(3)—S(2)—Cu(4)	108.20(7)
N(5)—Cu(3)—S(2)	150.0(2)		

[a] Distance from Cu to SN_2 coordination plane.

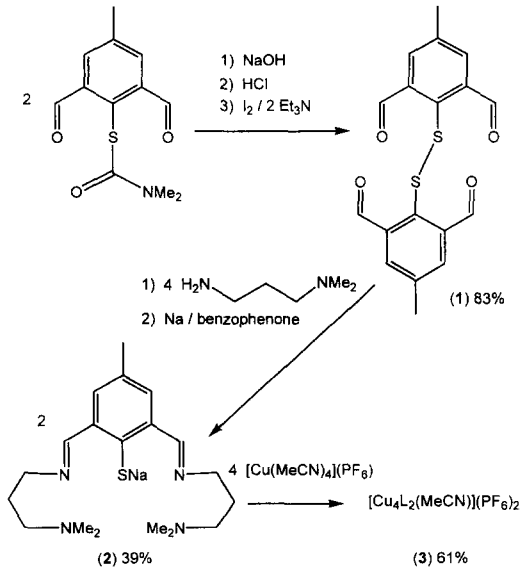

Fig. 1. Schematic for syntheses of **1**, **2**, and **3**.

incomplete removal of water from the reaction mixture after the Schiff base condensation step or instability of the Schiff base disulfide intermediate as evidenced by ^{1}H NMR [13]. The Cu^I tetramer **3** was prepared anaerobically by 1:2 stoichiometric combination of NaL (**2**) and [Cu(MeCN)$_4$](PF$_6$) [11], respectively in MeCN. Crystal formation was slow, often taking up to one week. White crystals of NaPF$_6$ also formed but could be eliminated by subsequent recrystallization from MeCN. Complex **3** is soluble in polar, coordinating solvents such as MeCN, DMSO, and DMF, and is quite air sensitive with both orange-red crystals and solutions decomposing upon exposure to give an intractable dark solid.

Structure analysis

The structure and atom labelling scheme for the Cu^I tetramer dication in **3** are shown in Fig. 2. Upon inspection one can observe that the complex is a

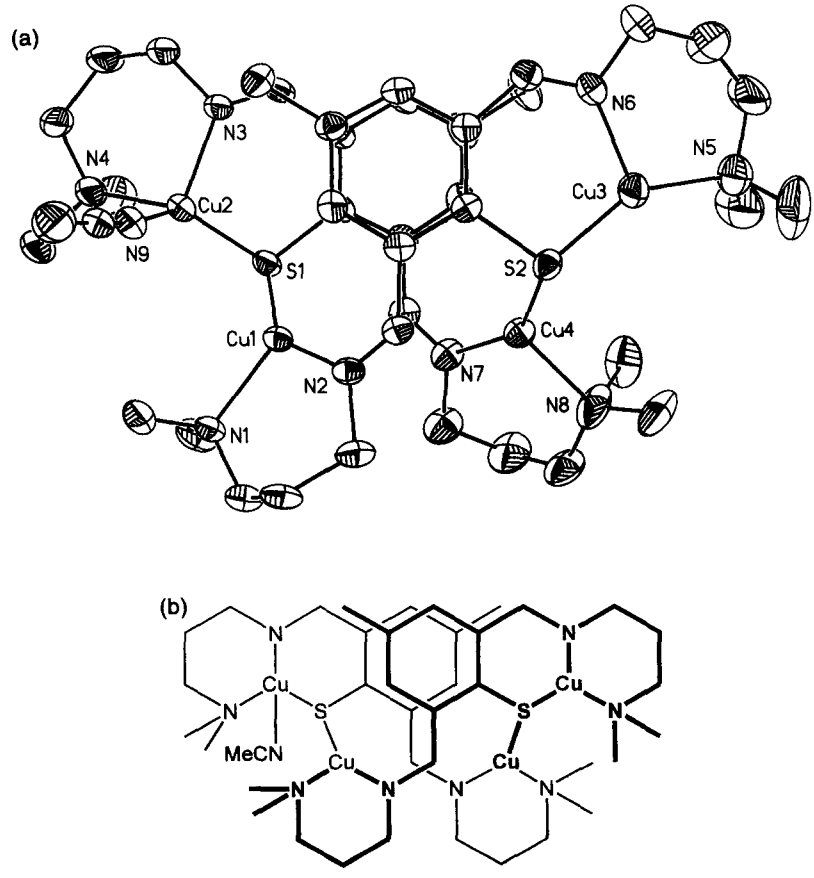

Fig. 2. (a) Structure of the dicationic complex [Cu$_4$L$_2$(MeCN)]$^{2+}$ in **3** showing 30% ellipsoids and the atom labelling scheme. (b) Schematic representation of the structure shown in (a). One Cu$_2$L fragment is emphasized in bold to show the relative positioning of the pendant ligand arms in **3**. Double bonds in the phenyl and imino groups have not been indicated for clarity.

'dimer of dimers' since the structure can be described as the combination of two Cu_2L complexes which interlock by exchange of pendant ligand arms. In this way, a 12-atom twisted ring structure is formed which includes both sulfur atoms, Cu(1), Cu(4), N(2), N(7), 4 phenyl, and 2 imino carbon atoms. The remaining two copper atoms, Cu(2) and Cu(3), are extracyclic. The copper atoms in each μ-S pair are sufficiently far apart (3.06 and 3.51 Å for Cu(1)···Cu(2) and Cu(3)···Cu(4), respectively) to preclude significant Cu^I–Cu^I interaction. Interestingly, the ligand phenyl groups are roughly parallel with a small dihedral angle of 5.2°. The eclipsed conformation of the phenyl rings in combination with an average interplanar distance of 3.82 Å suggests a small but favorable π-stacking interaction.

Of the four copper atoms in **3**, three have distorted trigonal planar coordination geometry while one, Cu(2), contains a bound acetonitrile which completes distorted tetrahedral coordination geometry. Trigonal coordination is rigorously planar for both Cu(3) and Cu(4) while Cu(1) deviates slightly from the N_2S plane by 0.17 Å. Probably due to steric constraints of the ligand, each trigonal copper contains one S—Cu—N angle that is significantly more open (142–150°) than the expected 120° thereby distorting coordination geometry towards a T-shape. Cu—S bond lengths for Cu(1), Cu(3), and Cu(4) are, in general, short for trigonally coordinated thiolate complexes of copper(I) [5] but are comparable to the Cu—S distances found in the tricoordinate CuN_2S fragments of Tolman's tricopper(I, II, I) complex [8b]. The Cu(3)—S(2) distance of 2.151(2) Å is exceptionally short but similar to the 2.19 Å Cu—S distance found in tetracopper(I) 'butterfly' clusters [14]. Also, the Cu—S bond distance of 2.244(2) Å for tetrahedral Cu(2) is short in comparison to other tetrahedral Cu^I—(μ-SR) bonds in similar compounds [15]. Cu—N_{amine} bond distances span a wide range in **3** [2.008(7)–2.194(6) Å] with the unusually short distances of 2.088(7) Å and 2.008(7) Å for Cu(4)—N(8) and Cu(3)—N(5), respectively finding precedence in only one other tricoordinate copper(I) complex containing a tertiary amine ligand [16]. Cu—N_{imine} bond distances [1.969(5)–2.039(5) Å] are unexceptional [17] and the Cu—$N_{acetonitrile}$ bond distance of 1.971(8) Å is well within the range found for $Cu(MeCN)_4^+$ [18].

Solution properties

^1H NMR spectra of **3** in DMSO solutions are not compatible with the asymmetric tetranuclear structure found in the solid state. Instead, the spectrum reflects free ligand symmetry but with slightly shifted and significantly broadened resonance peaks. These features together with the known lability of Cu^+ ions and the presence of coordinating solvent (DMSO) indicate a possible equilibrium between the $[Cu_4L_2]^{2+}$ tetramer and a dissociated $[Cu_2L]^+$ dinuclear species. The presence of a minute amount of Cu^{II}, generated through standard handling of air sensitive **3**, may also contribute to peak broadening and cannot be completely ruled out. Cyclic voltammetry of **3** in MeCN at scan rates of 100 mV/s reveals one irreversible oxidation wave at 110 mV (*vs* SCE) [19]. Faster scan rates made no improvement on wave reversibility implying that stability of mixed-valent and all oxidized copper complexes of L are compromised due to probable Cu^{II}/thiolate redox processes.

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12. One may wonder why MeOH is present in crystals of **3** since none was introduced to the crystallization solution. The MeOH solvate molecule is believed to be acquired through diffusion of MeOH present in the glove box atmosphere where the crystals were grown, which is consistent with the fairly long crystallization times and partial occupancy of the solvate molecule.
13. ^{1}H NMR of **1** after addition of 4 equiv. of 3-dimethylpropylamine ($CDCl_3$): δ 8.46 (imino-methyl-H, s); 7.75 (phenyl-H, s); 3.38 (CH_2, t); 2.28 (phenyl-Me, s); 2.22 (CH_2, t); 2.13 (amino-Me, s); 1.69 (CH_2, m). Resonances degraded over time giving an unrecognizable spectrum after 2 h.
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19. Potential obtained by differential pulse voltammetry.