# Synthesis and Crystal Structure of the Tetranuclear Copper(I) Complex [$Cu_4I_4(MPTQ)_2$] with a *N,S,N′*-Tridentate Ligand(MPTQ=8-((2-Pyridylmethyl)thio)quinoline)

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Copper(I) iodide reacts with 8-((2-pyridylmethyl)thio) quinoline (MPTQ) to give the tetranuclear cluster complex [$Cu_4I_4(MPTQ)_2$] which has been structurally characterized, showing that the $Cu_4I_4$ core exists in a distorted chair-like structure with four copper atoms forming parallelogram which is bridged by iodine atoms on each short sides, by S, N-MPTQ on each long sides and with two additional iodine atoms face-bridging sets of three copper atoms on opposite sides of the parallelogram.

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There has been considerably growing interest in mono- and polynuclear complexes of $d^{10}$ metal centers due to their displaying interesting and rich luminescent and structural properties.[1] Extensively investigated members include copper(I) halide clusters of N/P donor Lewis base adducts, such as [$Cu_4I_4py_4$],[2] [$Cu_4I_4(pip)_4$],[3] [$Cu_4I_4(quin)_4$],[4] [$Cu_4X_4(dpmp)_4$],[5] [$Cu_4I_4(2Me\text{-}py)_6$],[6] ( py = pyridine, pip = piperidine, quin = quinoline, dpmp = 2-(diphenyl methyl)pyridine, X=Cl, Br, I) and [$Cu_4I_4(PPh_3)_4$],[7] some of which have been shown to be luminescent.[1c,1d,8] Such tetrameric clusters with $Cu_4X_4$ core generally exist in either a cubane or chair geometry with $Cu_2X_2$ moiety as the basic building blocks sharing edges. Herein, we report the preliminary structural results on [$Cu_4I_4(MPTQ)_2$] with the $Cu_4I_4$ core in chair-like form. The ligand MPTQ which incorporates both pyridine and quinoline heterocycles shows a special coordinating modes both of chelating and bridging.

The ligand MPTQ was prepared in 45% yield by the reaction of 2-chloromethylpyridine with sodium salt of 8-mercaptoquinoline and purified chromatographically. Its subsequent reaction with CuI in acetonitrile affords [$Cu_4I_4(MPTQ)_2$] in 94% yield.

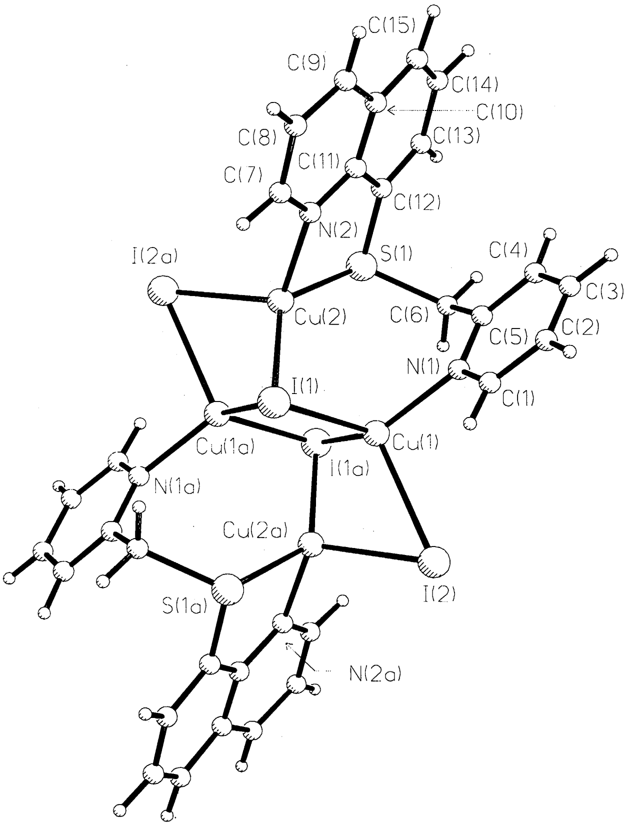

**Figure 1.** Crystal and molecular structure of [$Cu_4I_4(MPTQ)_2$].

The crystal and molecular structure of [$Cu_4I_4(MPTQ)_2$][9] illustrated in Figure 1 shows that the tetrameric $Cu_4I_4$ core exists in a distorted chair-like structure with crystallographically imposed $C_i(-1)$ symmetry. The chair-like structure is defined by three $Cu_2I_2$ moieties sharing Cu-I edges: the strictly planar Cu(1)-I(1)-Cu(1a)-I(1a), and the nonplanar Cu(1)-I(2)-Cu(2a)-I(1a) and Cu(1a)-I(2a)-Cu(2)-I(1) which are symmetry-related. The four Cu atoms and four iodine atoms are precisely coplanar respectively thus forming parallelograms which are depicted in Figure 2. It can be easily found that the Cu···Cu distances vary substantially from 2.607 (short sides) to 3.141 (long sides) with a short diagonal distance of 3.065 Å, which are comparable with those found in [$Cu_4I_4(Ph_2PCH_2PPh_2)_2$][10] (short sides, 2.682, long sides 3.108 Å) and [$Cu_4I_4(quin)_4$][4] (short sides, 2.582, 2.545; long sides 3.279, 3.325 Å). However, the I···I distances show less variation i.e. short sides, 4.360, long sides, 4.434 and short diagonal 4.481 Å. Similar results were also found in [$Cu_2I_4(PPh_3)_4$].[7] In addition, it has been noted that the Cu···Cu distance depend markedly on the nature of the bridging ligand.[10] In the present complex, the MPTQ ligand exhibits a special coordinating mode in which S(1) and N(2) chelates Cu(2) and N(1) bridges Cu(1). The iodine atoms bridge the copper atoms either in a $\mu_2$- asymmetrical mode or in a $\mu_3$- mode. If the chair–like structure is considered as derived from the cubane structure via rupture of two Cu–I bonds followed by rotation of $Cu_2I_2$ moiety by approximately 180°,[11] it may be considered that the rupture of Cu–I bonds in [$Cu_4I_4(MPTQ)_2$] results from the coordination of the sulfur atoms to the copper atoms of Cu(2) and Cu(2a). Thus the copper atoms are all four–coordinated while the iodine atoms are either two–coordinated($\mu_2$) or

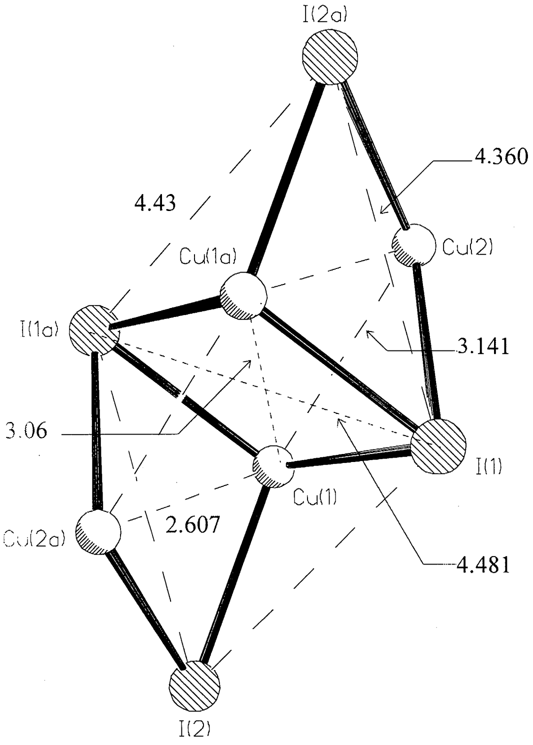

**Figure 2.** The $Cu_4I_4$ core of $[Cu_4I_4(MPTQ)_2]$.

three–coordinated($\mu_3$). From the above discussion it may well be that the formation of the chair–like structure owes its origin principally to the minimization of I···I interactions as well as the special nature of the bridging ligand .

The Cu–I bond distances show significant difference with the different copper environment. The Cu(1) bonds to three iodine atoms with Cu–I bond distances ranging from 2.666(2) to 2.761(2) Å (average 2.726 Å), while Cu(2) bonds to two iodine atoms with Cu–I bond distances 2.633(2) and 2.637(2) Å (average 2.635 Å), respectively. The relatively long Cu–I bond distances for the former may arise from the more I···I interaction and different coordinating behavior of MPTQ towards Cu(1) and Cu(2), which is an alternative of the finding that the Cu–I bond distances increase systematically as the coordination numbers of the component atoms increase.[7]

Similarly, the coordination polyhedron of Cu(1) and Cu(2) show varied distortion though they both have essentially tetrahedral geometry. The angles around Cu(1) are normal for a tetrahedron (range from 101.1(2) to 127.1(2)°) while those around Cu(2) deviated more(range from 85.4(2) to 136.18(10)°), therefor the Cu(2) atom exists in a more distorted tetrahedral environment.

The two Cu–N bond distances are nearly the same (2.037(9), 2.048(8) Å) and are comparable with those of other tetrameric clusters[4,5] with N donors. The Cu–S bond distance 2.362(3) Å is well within the range 2.302-2.382 Å of Cu–S for tetrahedral copper(I) coordination.[12]

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## References and Notes

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9 Crystal data: $C_{30}H_{24}N_4S_2I_4Cu_4$, triclinic, space group $P$-1, $a$ = 9.405(5), $b$ = 11.218(8), $c$ =9.115(6)Å, $\alpha$ = 99.14(6), $\beta$ = 106.45(4), $\gamma$ = 69.96(5)°, $U$ = 864(1)Å$^3$, $Z$ = 1, $D_c$ = 2.433g/cm$^3$, $F$(000) = 592, $\lambda$ = 0.71069Å, $\mu$ (Mo-K$\alpha$) = 6.15 mm$^{-1}$. Intensity were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K$\alpha$ radiation using ω-2θ scan technique to a maximum 2θ value of 45.0°. From the total 2224 reflections, 2056 were unique of which 1745 had $I$>3.0$\sigma(I)$ and were considered to be observed. The structure was solved by direct method and expanded using Fourier technique. The nonhydrogen atoms were refined anisotroscopically by full-matrix least squares on 1745 observed reflections and 200 variable parameters and converged with $R$ = 0.039, $Rw$ = 0.055 ($Rw = [\Sigma(w(|Fo|-|Fc|)^2/\Sigma wFo^2]^{1/2}$ ). Hydrogen atoms were included but not refined. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.75 and -0.82/e Å$^3$, respectively.

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