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Molecular Structure of the Macrocyclic Copper(II) Chelate with 6,7,13,14-Tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11 According to Quantum-Chemical DFT Calculations

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Abstract—The key parameters of the molecular structure of macrotetracyclic (*NNNN*)-coordinated chelate of Cu(II) with 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11 have been calculated by means of the DFT-based B3LYP6-31G(d) method in GAUSSIAN-09 software. The complex may be formed via self-assembly of Cu(II), thiocarbohydrazide, and diacetyl in the gelatin-immobilized matrix implants. The bond lengths, bond angles, and torsion angles are presented; it has been shown that the metal chelate and the chelating ligand are almost planar.

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Previously [1] we discovered the template synthesis (self-assembly) in the system Cu(II)–thiocarbohydrazide–diacetyl in the copper(II) hexacyanoferrate(II) gelatin-immobilized matrix implants. By means of various physicochemical methods it was proved that the complex formation in that ternary systems resulted in the Cu(II) chelate with tetramethyl-substituted 3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11, the chelating ligand being coordinated to Cu(II) via four donor nitrogen atoms. The molecular structure of the complex, however, remained unknown, in particular due to the failed attempts to grow the complex monocrystal suitable for X-Ray diffraction analysis. Modern non-empirical quantum-chemical computational methods allow reliable estimation of the molecular structure of the chelate complexes; the quantum-chemical estimations of the key structural parameters (bond lengths, bond angles, torsion angles) are in general practically identical to the experimentally determined ones, as was demonstrated in [2, 3] in the cases of Ni(II) chelates with hydrazinomethanethioamide and phthalocyanine complexes of 3*d*-elements. Basing on this, this work was aimed at determination of the above-mentioned macrotetracyclic Cu(II) chelate by means of quantum-chemical calculations.

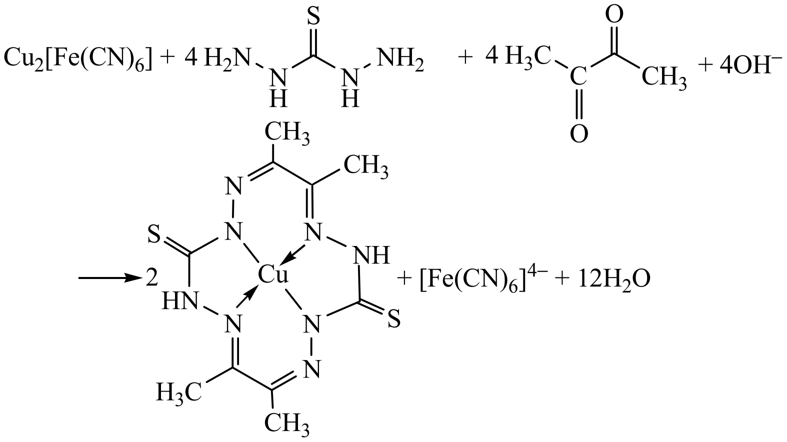

Table 1. Bond lengths, bond angles, and torsion angles in the Cu(II) complex with 66,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11

Bond, angle	pm, deg	Bond, angle	pm, deg	Bond, angle	pm, deg	Bond, angle	pm, deg
Bond lengths in the MN_4 chelate node							
M^1–N^1	188.0	M^1–N^3	188.0	M^1–N^2	190.2	M^1–N^4	190.2
Individual bond lengths out of the chelate node							
C^1–S^1, C^2–S^2	166.4	C^5–N^7, C^6–N^8	131.0	N^2–N^6, N^4–N^5	136.0	C^4–C^{10}, C^7–C^2	151.0
C^1–N^5, C^2–N^6	140.2	C^6–C^8, C^5–C^9	151.7	C^4–C^5, C^3–C^6	147.7	N^1–C^1, N^3–C^2	
Bond angles in the MN_4 chelate node							
$N^1M^1N^2$	94.4	$N^3M^1N^4$	94.4	$N^2M^1N^3$	85.6	$N^4M^1N^1$	85.6
Nonvalent angles in the N_4 group							
$N^1N^2N^3$	89.3	$N^3N^4N^1$	89.3	$N^2N^3N^4$	90.7	$N^4N^1N^2$	90.7
Bond angles in the 5-membered chelate cycles							
$M^1N^4N^5$	109.2	$M^1N^2N^6$	109.2	$C^1N^1M^1$	114.5	$C^2N^3M^1$	114.5
$N^4N^5C^1$	120.1	$N^2N^6C^2$	120.1	$N^1M^1N^4$	85.6	$N^3M^1N^2$	85.6
$N^5C^1N^1$	110.5	$N^6C^2N^3$	110.5	Sum of the bond angles VAS^{51}	540.0	Sum of the bond angles VAS^{52}	540.0
Bond angles in the additional 6-membered chelate cycles							
$M^1N^1N^7$	127.6	$M^1N^3N^8$	127.6	$C^4N^2M^1$	126.9	$C^3N^4M^1$	126.9
$N^1N^7C^5$	121.9	$N^3N^8C^6$	121.9	$N^2M^1N^1$	94.4	$N^4M^1N^3$	94.4
$N^7C^5C^4$	129.2	$N^8C^6C^3$	129.2	Sum of the bond angles VAS^{61}	720.0	Sum of the bond angles VAS^{62}	720.0
$C^5C^4N^2$	120.0	$C^6C^3N^4$	120.0				
Bond angles out of the chelate cycles							
$N^1C^1S^1$	131.0	$N^3C^2S^2$	131.0	$C^8C^6N^8$	113.1	$C^9C^5N^7$	113.1
$N^5N^4C^3$	121.0	$N^6N^2C^4$	121.0	$C^6C^3C^7$	121.2	$C^5C^4C^{10}$	121.2
$N^4C^3C^7$	118.8	$N^2C^4C^{10}$	118.8	$N^6C^2S^2$	118.5	$N^5C^1S^1$	118.5
$C^3C^6C^8$	117.7	$C^4C^5C^9$	117.7				
Torsion angles							
$M^1N^3N^8C^6$	0.0	$M^1N^4N^6C^2$	0.7	$M^1N^2C^4C^5$	0.4	$N^2M^1N^4C^3$	90.3
$M^1N^4C^3C^6$	0.4	$M^1N^3C^2N^6$	0.4	$M^1N^1C^1N^5$	0.4	$N^3M^1N^1N^7$	89.9
$M^1N^1N^7C^5$	0.0	$N^1M^1N^3N^8$	90.0	$M^1N^4N^5C^1$	0.7	$N^4M^1N^2C^4$	90.1

According to [1], the following reaction occurred in the course of template synthesis in the ternary system Cu(II)–thiosemicarbazide–diacetyl.

The calculated geometry parameters (bond lengths, bond angles, and torsion angles) of the studied complex are collected in Table 1; its spatial structure and atoms numeration is shown in Fig. 1. The ground state of the complex according to the theoretical studies is a spin doublet, its energy difference with the closest quartet state being 241.2 kJ mol^{-1}. The energy difference corresponds to the gaseous state, however, its high difference value makes it possible to suggest that in the solid phase the doublet state should also be the most stable, and the calculated geometry parameters should be relevant.

From the common theoretical considerations, a planar geometry could be expected for the studied complex. However, DFT quantum-chemical studies of some (5656) macrotetracyclic chelate complexes of 3*d*-elements, in particular, those of Cu(II) with 5,5,7,12,12,14-hexamethyl-2,3,9,10-tetrathio-1,4,8,11-tetraazacyclotetradeca-1,7-diene and 1,8-dioxa-3,6,10,13-

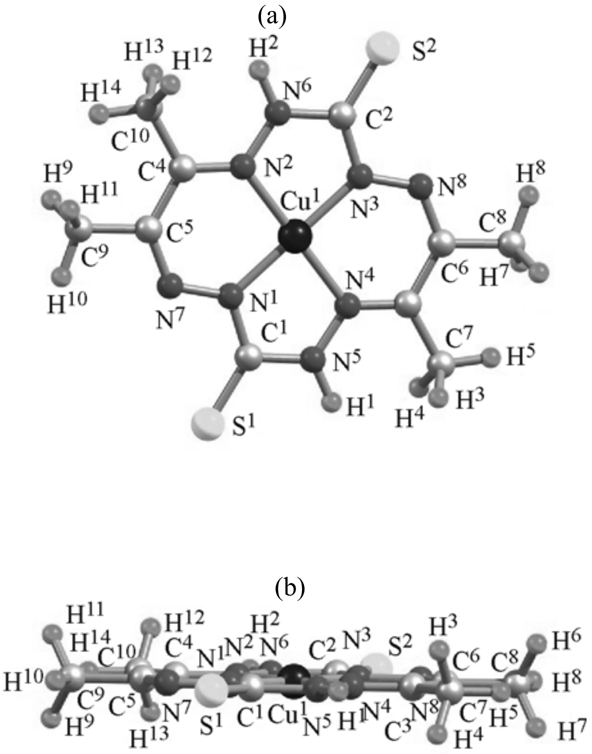

Fig. 1. Molecular structure of Cu(II) complex with 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11. (a) Front view and (b) side view.

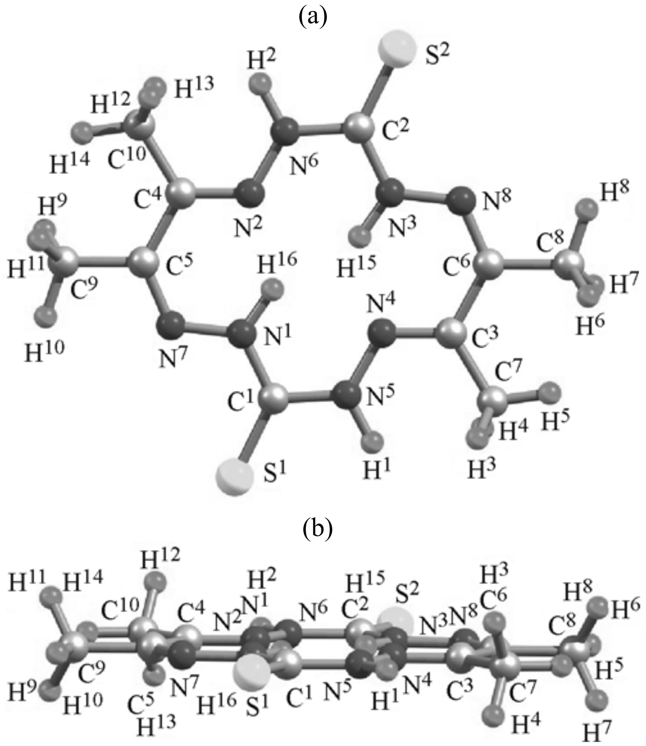

Fig. 2. Molecular structure of 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11. (a) Front view and (b) side view.

tetraazacyclotetradeca-4,5,11,12-tetrathione [4–6], showed their significant deviations from planarity. Thus, we could not state *a priori* whether the structure of the Cu(II) chelate with 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11 was planar or not. The computation showed that in the case of the studied complex the MN_4 chelate node was planar, as its sum of bond angles and nonvalent angles was exact equal to the sum of inner angles of a planar tetragon (360°). The sum of bond angles in each of the 5-membered chelate cycles equaled the sum of inner angles of a planar pentagon (540°), whereas the sum of bond angles in each of the 6-membered chelate cycles equaled the sum of inner angles of a planar hexagon (720°). Thus, all those metal cycles were planar, and the macrocyclic fragment of the Cu(II) chelate with 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11 was coplanar. That was additionally confirmed by the torsion angles, being close either to 0° or 90° (Table 1). Moreover, from the values of the bond angles, the 5-membered cycles were identical, and so were the 6-membered rings. Note that the respective bond angles out of the chelate cycles, for instance, $N^1N^7C^5$ and $N^3N^8C^6$, $C^3C^6C^8$ and $C^4C^5C^9$, $N^6C^2S^2$ and $N^5C^1S^1$ were pairwise equal as well; and so were the lengths of the bonds forming those angles. However, the copper–nitrogen bonds in the metal chelate cycle were slightly different (188.0 and 190.2 pm), but pairwise equal; the bond angles were also equal in pairs $N^1M^1N^2$ and $N^3M^1N^4$, $N^2M^1N^3$ and $N^4M^1N^1$ (Table 1). As seen in Fig. 1, the studied metal complex had only the second order symmetry axis, a mirror plane, and an inversion point, thus its symmetry group was C_{2h}. The dipole moment should be close to zero for that symmetry group, indeed, our calculations led to the value of 0.02 D.

It was of interest to compare the structures of the studied metal chelate and the respective macrocyclic organic ligand, 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11. The ligand geometry parameters are compiled in Table 1 and its spatial structure is shown in Fig. 2. It should be noticed that the 14-membered macrocycle in the ligand structure was almost planar as well (its sum of inner bond angles was of 2159.8°, almost equal to the

Table 2. Bond lengths, bond angles, and torsion angles in 6,7,13,14-tetramethyl-3,10-dithio-1,2,4,5,8,9,11,12-octaazatetradecatetraene-1,5,7,11 molecule

Bond, angle	pm, deg	Bond, angle	pm, deg
Individual bond lengths			
C^1–S^1, C^2–S^2	166.2	C^5–N^7, C^6–N^8	130.2
C^1–N^5, C^2–N^6	139.0	C^6–C^8, C^5–C^9	151.4
N^2–N^6, N^4–N^5	135.1	C^4–C^{10}, C^7–C^3	151.3
C^4–C^5, C^3–C^6	148.5	N^1–C^1, N^3–C^2	136.3
Nonvalent angles in the N_4 group			
$N^1N^2N^3$	93.9	$N^3N^4N^1$	93.9
$N^2N^3N^4$	86.1	$N^4N^1N^2$	86.1
Bond angles in the 14-membered macrocycle			
$N^4N^5C^1$	122.8	$N^2N^6C^2$	122.8
$N^5C^1N^1$	112.6	$N^6C^2N^3$	112.6
$N^1N^7C^5$	119.7	$N^3N^8C^6$	119.7
$N^7C^5C^4$	128.2	$N^8C^6C^3$	128.2
$C^5C^4N^2$	118.7	$C^6C^3N^4$	118.7
$C^3N^4N^5$	240.1	$C^4N^2N^6$	240.1
$C^1N^1N^7$	237.8	$C^2N^3N^8$	237.8
Sum of bond angles in the macrocycle			2159.8
Bond angles out of the macrocycle			
$N^1C^1S^1$	128.1	$N^3C^2S^2$	128.1
$N^4C^3C^7$	120.9	$N^2C^4C^{10}$	120.9
$C^3C^6C^8$	118.5	$C^4C^5C^9$	118.5
$C^8C^6N^8$	113.2	$C^9C^5N^7$	113.2
$C^6C^3C^7$	120.4	$C^5C^4C^{10}$	120.4
$N^6C^2S^2$	119.3	$N^5C^1S^1$	119.3

sum of inner angles in a planar 14-gon, 2160°). That fact was of special interest, as even 8-membered organic cycles are rarely planar. Note that the sum of inner bond angles in the studied Cu(II) complex was equal to that of the free ligand (even though the respective individual inner angles could be significantly different). That led to conclusion that the energy required to form the Cu(II) metal chelate complex with that ligand was negligibly low.

EXPERIMENTAL

Quantum-chemical calculations were performed with the DFT hybrid method, B3LYP with a standard basis, 6-31G(d). The calculations were performed using GAUSSIAN-09 [7] software. The correspondence of the found stationary points to the energy minima was proved by calculation of the energy second derivatives over the atom coordinates; all the frequencies were found to be positive.

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