Tetragonal Cubanoid Cu_4X_4 in the Isostructural π-Complexes with Divinyltetramethyldisiloxane: $[Cu_4X_4(C_8H_{18}OSi_2)]$ (X = Cl, Br)

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Abstract—The formation of the heterocubanoid fragmen Cu_4Y_4 (Y = Cl, Br, I, O, S) in the structure of the Cu(I) complexes is often associated with the appearance of valuable properties (catalytic, thermal, chemilumines-cence, and others) of these compounds. The Cu_4X_4 cluster (X = Cl, Br) found in the isostructural π-complexes with divinyltetramethyldisiloxane (DVTMSO) (space group $P\bar{4}$, Z = 1, a = 10.2330(2) Å, c = 7.6877(3) Å for $[Cu_4Cl_4(DVTMSO)_2]$ and a = 10.2633(1) Å, c = 7.9514(3) Å for $[Cu_4Br_4(DVTMSO)_2]$) makes it possible to discuss the homological chain of the Cu_4X_4 cuprohalide fragments from the viewpoint of steric (conforma-tional, symmetric) and electronic ($d_{Cu} \longrightarrow \pi^*(C=C)$) properties of an organic ligand.

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INTRODUCTION

The use of divinyltetramethyldisiloxane (**DVTMSO**) as a diolefin ligand in the complexes with d^{10}-metal centers (**M**) is interesting from several points of view. First, this is a rather labile ligand capable of changing the π–π-bridging function to the chelating one in the ligand exchange reactions to form a stable six-membered cycle, for example, $Pd(0)(CH_2=CH–Si)_2O$ [1]. Second, DVTMSO is the first representative of the series of unsaturated polysiloxanes, whose complexes, including those with Cu(I), serve as precursors for the production of thin copper films by thermal disproportionation [2]. In addition, from the recent time the Pt(0) complexes with DVTMSO have intensively been studied as catalysts for alkene hydrosilylation [3]. From our point of view, possibilities of this remarkable ligand are not restricted by the above properties, especially in the context of continuation of our investigation of the olefinic copper(I) halide π-complexes. It is known that the latter often act as intermediates in catalytic and stoichiometric reactions involving olefins. However, their negligible solubility induced by the polynuclear structure almost excludes the homophase character of similar processes. A different situation is observed for the "immobilized catalysts," the use of which makes it possible to combine certain advantages of homogeneous and heterogeneous systems. In this case, the problem of choosing the optimum matrix arises, and from this point of view the recent studies of polysiloxane supports [4, 5] seem to be more than interesting. Since it is reasonable to begin structural studies of nanosystems from the modeling of the simplest aggregates, we used DVTMSO for the synthesis of two isomorphic π-complexes $[Cu_4X_4(DVTMSO)_2]$ (X = Cl (**I**) and X = Br (**II**)), which were structurally characterized.

EXPERIMENTAL

Synthesis. Complexes **I** and **II** were synthesized by the direct interaction of the components: freshly synthesized CuX (0.05 g, ~0.5 mmol) was dissolved in DVTMSO (0.40 ml, ~2 mmol). Some time after (30 min for complex **I** and 2 h for complex **II**), the beginning of the growth of qualitative colorless pseudocubic crystals was observed using a microscope. The growth ceased within one day with an almost quantitative yield. The dissolution of a larger amount of CuX accelerates the crystallization and quality losses of the crystalline material. Single crystals of complex **I** are characterized by the unusual (for this class of compounds) stability in air at room temperature.

X-Ray diffraction analysis. The experimental data for complexes **I** and **II** were obtained on a Xcalibur CCD diffractometer (graphite monochromator, MoK_α radiation, λ = 0.71073 Å) at 293(2) K. The reflection intensities were corrected to the Lorentz, polarization, and absorption factors.

The initial model was obtained by direct methods (SHELXS-97) [6] and supplemented by the atoms localized from the difference Fourier syntheses (SHELXL-97) [6]. When the initial model was refined, it became necessary to take into account racemic twinning, which made it possible to decrease the *R* factor by 10%. Hydrogen atoms were determined from the geometric concepts and were taken into account during the refinement of non-hydrogen atoms. The parameters of all non-hydrogen atoms were refined by least squares in

Table 1. Crystallographic data and conditions of X-ray experiment for complexes **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_8H_{18}Cl_2Cu_2OSi_2$	$C_8H_{18}Br_2Cu_2OSi_2$
M	384.40	473.30
$F(000)$	1136	651
Space group	$P\bar{4}$	$P\bar{4}$
$a = b$, Å	10.2330(2)	10.2633(1)
c, Å	7.6877(3)	7.9514(3)
V, Å^3	805.01(4)	837.56(3)
Z	2	2
Crystal sizes, mm	$0.15 \times 0.10 \times 0.10$	$0.15 \times 0.15 \times 0.15$
ρ(calcd), g/cm^3	1.586	1.877
μ_{Mo}, cm^{-1}	65.69	129.83
Detection method	ω scan	ω scan
$2\theta_{max}$; $2\theta_{min}$, deg	58.4; 5.6	58.2; 5.6
Index ranges	$-13 \le h \le 13$, $-10 \le k \le 13$, $-10 \le l \le 10$	$-13 \le h \le 11$, $-11 \le k \le 13$, $-10 \le l \le 10$
Number of reflections:		
measured	2022	2071
independent with $I > 2\sigma(I)$	1094	1301
Number of refined parameters	91	91
R; R_w (for $I > 2\sigma(I)$)	0.0461; 0.0845	0.0355; 0.0452
R; R_w (for whole array)	0.0887; 0.0974	0.0652; 0.0538
Goodness-of-fit	0.962	0.944
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.38/−0.37	0.60/−0.52

the full-matrix anisotropic approximation. The experimental conditions and X-ray diffraction data are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The coordinates of atoms and other parameters for structures **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (nos. 704920 (**I**) and 704921 (**II**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The high symmetry of the considered complexes under the conditions of rather small unit cells of complexes **I** and **II** assumes that the structures contain the symmetric molecule DVMTSO. Axis 2 passing through the oxygen atom provides the bridging function of this diolefin ligand, which coordinates with the copper(I) atoms to bind the Cu_4X_4 units (Fig. 1). The island inorganic fragments are associated according to the tetragonal symmetry law along the directions [100] and [010], which forms the layered structure. It is interesting that the layers (010) of the complexes are separated by the methyl groups and have no weak hydrogen bonds C–H$\cdots$X (H$\cdots$X > 3.3 Å), although these bonds are usual for this class of compounds. This fact is a prerequisite, most likely, for the polysynthetic twinning of

the enantiomeric forms found at the stage of structure determination.

The disiloxane group of DVMTSO predetermines the flexibility of the organic ligand, which, in addition to the symmetry 2 revealed in the discussed structures, can also crystallize with the local symmetry m and even $\bar{1}$. The matter is the ability of the d orbitals of the silicon atoms to be π-overlapped with the p orbitals containing electron pairs of the oxygen atom. This formally corresponds to the change in the hybridization of the orbitals of the oxygen atom toward sp, which undoubtedly increases the SiOSi bond angle to a boundary value of 180°. This phenomenon is not new and has been studied in rather detail for the silicates [7]. We are interested in the influence of this electronic factor on the conformation of the coordinated organosilicon ligand. In the previously studied π-complex of DVMTSO with copper(I) trifluoromethylacetylacetonate [8], the siloxane ligand is centrosymmetric at the unfolded SiOSi angle. In this case, the Si–O distance is shortened to 1.597(2) Å and the Cu$\cdots$Si distance (3.149(2) Å) is shorter than the sum of the van der Waals radii of Si and Cu. This allowed the authors [8] to assume a possibility of the additional interaction $\pi(d_{Cu}) \longrightarrow \pi(d_{Si}$–$p_O)$), which is less proba-

Table 2. Bond lengths and bond angles in structures **I** and **II***

Bond	d, Å		Angle	ω, deg	
	I	**II**		**I**	**II**
Cu–X	2.277(2)	2.403(1)	XCuX[i]	103.60(6)	106.07(3)
Cu–X[i]	2.301(2)	2.423(1)	XCuX[ii]	85.50(6)	87.94(4)
Cu–X[ii]	2.970(2)	3.103(1)	X[i]CuX[ii]	93.95(7)	96.54(3)
Cu–C(1)	2.050(5)	2.042(6)	XCum	130.16	129.32
Cu–C(2)	2.056(5)	2.063(6)	X[i]Cum	125.87	124.01
Cu–m**	1.931	1.935	X[ii]Cum	96.18	93.26
			C(1)CuC(2)	39.4(3)	39.0(4)
Si–O	1.619(2)	1.615(2)	SiOSi[ii]	163.3(5)	164.2(6)
Si–C(2)	1.872(7)	1.876(5)	OSiC(2)	105.6(3)	105.8(2)
Si–C(3)	1.85(1)	1.844(9)	OSiC(3)	109.7(4)	110.4(3)
Si–C(4)	1.82(1)	1.83(1)	OSiC(4)	111.1(5)	111.6(5)
			C(2)SiC(3)	107.0(4)	107.4(3)
C(1)–C(2)	1.388(8)	1.370(7)	C(2)SiC(4)	113.3(4)	112.6(3)
			C(3)SiC(4)	109.9(6)	108.9(5)
			SiC(2)C(1)	122.0(5)	121.6(5)

Notes: * Coordinates of equivalent atoms: [i] $1 - y, x, 1 - z$; [ii] $y, 1 - x, 1 - z$.
   ** m is the middle of the C(1)=C(2) bond.

ble, from our point of view, due to steric hindrance, because the Cu–(middle of Si–O bond) axis with the plane of the Cu(I) basal ligands forms an angle of 55° instead of 90°. In addition, the copper(I) atom is shifted by 0.08 Å from the above-mentioned plane to the side opposite to the hypothetical apical π-ligand (Si–O bond), which undoubtedly does not favor the discussed interaction. In other olefinic π-complexes of DVTMSO with the d^{10}-metal centers (Ni(0), Pd(0), Pt(0)), the silicon atom is more remote from the M atom. However, a correlation between the SiOSi angle value and Si–O bond length is well observed. Note that in the predominant majority of the complexes DVTMSO acts as a chelating ligand, which is accompanied by an insignificant change in the geometric characteristics under study. However, the few compounds with the bridging DVTMSO ligand, including complexes **I** and **II**, demonstrate an inversely proportional dependence of the discussed parameters (Fig. 2), which unambiguously agrees with the concept of changing the order of the Si–O bond. No noticeable difference was revealed between the lengths of the coordinated C=C bonds and the values of the corresponding bond angles C=C–E (E = C, Si) in the π-complexes with usual olefins, on the one hand, and the silicon derivatives, on the other hand, indicating the absence of conjugation of the Si–O and C=C bonds. However, in complexes **I** and **II** the olefinic bonds elongate to 1.388(8) and 1.370(8) Å and the CCuC angles achieve values of 39.4(3)° and 39.0(4)°, respectively. This indicates rather strong interaction Cu–(C=C), which is almost always accompanied by the substantial

pyramidal deformation of the tetrahedral coordination sphere of the central atom [12]. In our case, the Cu–X$_{ap}$ distance is 2.970(2) Å in complex **I** and 3.103(1) Å in structure **II**. In this case, the deviation of the copper atoms from the equatorial plane of two halogen atoms and the middle of the C=C bond to the apical ligand (X$_{ap}$) does not exceed 0.10 Å.

This decrease in the symmetry of the coordination polyhedron of the Cu(I) atom certainly affects the shape of the cuprohalide fragment, which is a concurrent part of the structure of this class of compounds. In complexes **I** and **II**, the cubane-like units Cu$_4$X$_4$ with the S_4 symmetry (according to A. Schoenflies) are formed in which the elongated Cu···X bonds are perpendicular to the $\bar{4}$ axis (Fig. 3c). Similar formations are rather rarely met in the olefinic Cu(I) π-complexes. For example, the tetragonally distorted cubane has previously been found only in the compounds with norbornadiene: in the series of isostructural adducts (1 : 1), namely, [Cu$_4$Cl$_4$(C$_7$H$_8$)$_4$] [13, 14], [Cu$_4$Br$_4$(C$_7$H$_8$)$_4$], and [Cu$_4$Br$_2$Cl$_2$ (C$_7$H$_8$)$_4$] [15], and in the 2 : 1 complex, namely, [Cu$_4$Cl$_4$(C$_7$H$_8$)$_2$] [14]. A more deformed cubane-like fragment with the axis 2 instead of $\bar{4}$ was observed in two other copper(I) chloride π-complexes with 1,4-pentadiene [15] and *endo*-dicyclopentadiene [Cu$_4$Cl$_4$(C$_{10}$H$_{12}$)$_4$] [16]. In this case, the Cu$_4$Cl$_4$ unit retains the perpendicular arrangement of the Cu···Cl elongated bonds due the doubling of the number of crystallographically independent atoms. The Cu$_4$Br$_4$
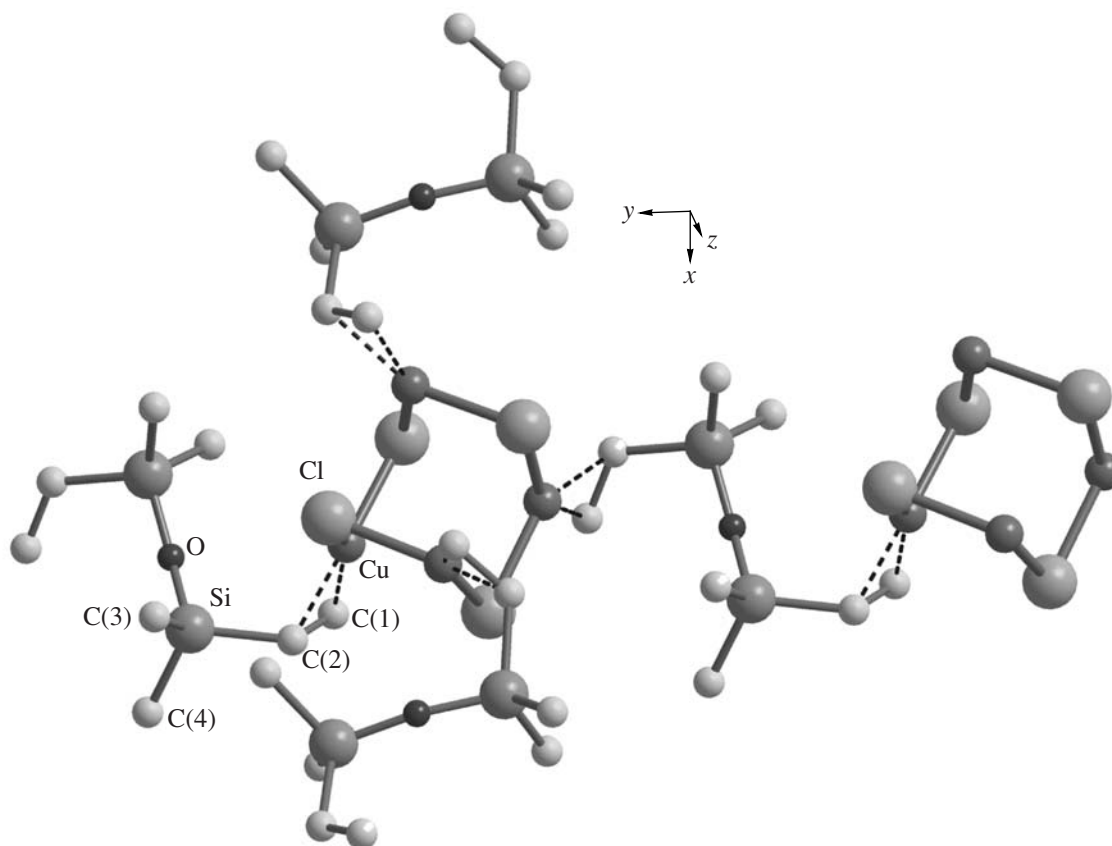
Fig. 1. Fragment of the crystal structure of complex **I**.

fragment of similar structure was found in the tetragonal structure of the olefinic π-complex with triallyl-1,3,5-triazine-2,4,6-trione [17].

However, it seems more interesting that the latter complex forms the orthorhombic modification (space group *Pbcn*) in addition to the mentioned above tetragonal modification (space group *P4/ncc*) [16]. In this orthorhombic modification the Cu···Cl contacts are oriented along the axis 2 of the Cu₄Cl₄ fragment (Fig. 3d). The pseudotetragonal prism that appears in this case can be presented more correctly as a combination of two nonplanar dimers Cu₂Cl₂. The intertransformation $c \longrightarrow d$ (Figs. 3c, 3d) according to the Burger classification is a distortion polymorphous transition of the second type [18], i.e., occurs without bond cleavage and does not change the coordination number of the copper(I) atom. These transitions occur rapidly and, hence, modification *d* (Fig. 3d) can be considered as intermediate in the processes of changing the cuprohalide fragments. The further redistribution of the weak Cu···Cl bonds easily allows the Cu₂Cl₂ dimers to associate into the polynuclear formations Cu$_n$Cl$_n$ (Fig. 3e) [19], which readily generate both corrugated ribbons with the cubane-like units (Fig. 3f) and stepped tetramers Cu₄Cl₄ (Fig. 3g). By the way, the latter pair (Figs. 3f, 3g)

of the cuprohalide fragments was also found in the polymorphous pair of the copper(I) chloride complexes with 1,5-hexadien-3-ol [20], and the redistribution of the weak Cu···Cl bonds of the fragment (Fig. 3f) was a reason for polymorphism of the CuCl compound with allyl cyanide [21, 22]. The both cases (Figs. 3f, 3g) confirm the low contribution of the enthalpy component to
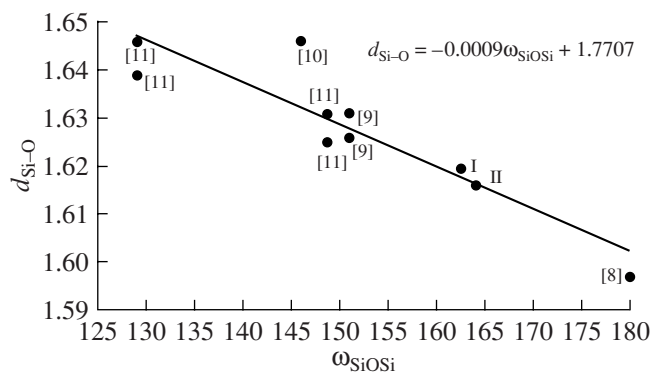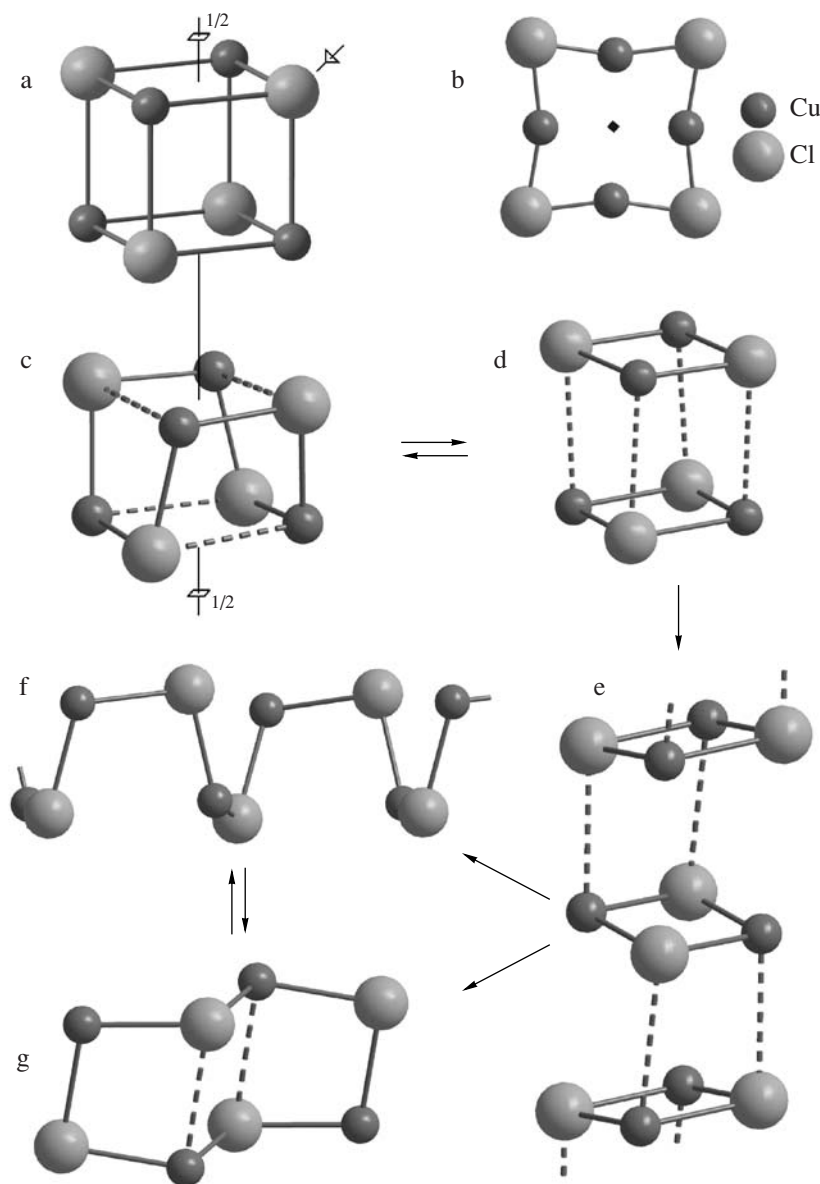

Fig. 2. Dependence of the Si–O distance on the SiOSi angle value in structures **I** and **II** and in other π-complexes with the bridging diallyldisiloxane ligand [9–11].

Fig. 3. Homology of the cuprohalide fragments: Cu_4Cl_4 with the symmetry (a) T_d, (b) D_{4h}, (c) S_4, (d) C_{2v}, (g) C_i, and (e, f) Cu_nCl_n.

the change in the free energy of the distortion transformations of this type.

The considered homological chain of the cuprohalide fragments can be supplemented by several important but, unfortunately, hypothetical units. First, one of the forms of gaseous copper(I) chloride is considered to be the Cu_4Cl_4 cluster with the symmetry T_d (Fig. 3a) and minimum Cu···Cu distances of 3.00(1) Å [23]. In this case, the coordination of the considered tetramer with four ligands in the complex decreases its ssymmetry from cubic (Fig. 3a) through tetragonal (Fig. 3c) and pseudotetragonal [15, 16] to the orthorhombic symmetry (Fig. 3d). Second, there is no single opinion concerning the structure of vaporous Cu_4Cl_4, because the data of IR spectroscopy [23] indicate in favor of the cir-

cular tetramer of the tetragonal symmetry (Fig. 3b). Continuing the considered distortion transformations, this planar cycle can be obtained from the stepped tetramer (Fig. 3g) via the maximum elongation of all transversal Cu···Cl bonds with the simultaneous increase in symmetry. Thus, it can be assumed that the cuprochloride tetramers in the gaseous state are also prone of transformations with a symmetry change and the above-considered transformation in the complexes will serve as the starting point for the explanation of these transformations.

In conclusion let us pay attention to reasons for the decrease in the symmetry of the Cu_4X_4 cubanoid in the structures of the complexes. First of all, this is caused

by the symmetry of the ligand, because the Cu$_4$ cubic tetrahedron can be retained only in the case of its coordination by the ordered molecule with the symmetry axis 3 (Fig. 3a). However, in this case, the accomplishment of the dense packing principle can result in an insignificant deformation of the inorganic cluster, as it takes place in the [{CuCl(PPh$_3$)}$_4$] structure [24]. In the olefinic π-complexes the C=C group initially does not correspond to the requirements of the symmetry discussed. However, the predominant influence on the further deformation of the Cu$_4$ tetrahedron is made by electronic factors rather than by steric ones. The occurrence of the $d_{Cu} \longrightarrow \pi^*(C=C)$ dative interaction is favored by the trigonal deformation of the tetrahedral coordination of the central atom [12, 15], which predicts the necessary elongation of one Cu⋯Cl bond and, as a consequence, the distortion of the trigonal symmetry of the CuCl$_3^{2-}$ group. That is why the Cu⟷(C=C) interaction should be considered as a method of efficient stabilization of coordination unsaturation of the Cu(I) atom in catalytic and stoichiometric reactions accompanied by distortion and constructive transformations of the cuprohalide fragments.

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