Letters to the Editor

Reduction of Cu^{II} to Cu^{I} in reaction of Cu^{II} halides with 3,3-dimethyl-3,4-dihydrothioisocarbostyryl

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To search for biologocally active compounds we have been performing a systematic investigation of metal complexes of 3,3-dimethyl-3,4-dihydroisoquinoline derivatives. The present report concerns the reaction of CuX_2 (X = Cl, Br) with 3,3-dimethyl-3,4-dihydrothioisocarbostyryl (L^1). Potentially L^1 may be presented as thion (**A**) or thiol (**B**) tautomers.

A **B**

X = S (L^1), O (L^2)

In IR spectra of solid L^1 bands corresponding to stretching vibrations of the thiolactam group (1522, 1214, and 1122 cm^{-1}), a band at 3160 cm^{-1} assigned to NH stretching vibrations, and the absence of ν(SH) bands at 2580—2280 cm^{-1} in these spectra (see Refs. 1, 2) point to the existence of L^1 in the solid state as tautomer **A**. In solutions of inert solvents ($CDCl_3$ and CCl_4) L^1 is also present predominantly as tautomer **A**. In fact ^1H NMR spectra exhibit a signal of one acid proton (~8.3 ppm). Nonetheless IR spectra of solutions with a concentration of $1 \cdot 10^{-2}$—$2.5 \cdot 10^{-3}$ mol L^{-1} that were recorded in a 5—20 mm cuvette show a broad, multicomponent, low intensity band at ~2400 cm^{-1}, which may be assigned to S—H stretching vibrations. Based on these data one may conclude that L^1 is present in the solutions as a mixture of tautomers **A** and **B**, and their equilibrium is strongly shifted to form **A**.

This allows one to suggest that in the reactions of CuX_2 with dimethyldihydrothioisocarbostyryl L^1 the latter forms $[CuL^1_4X_2]$ complexes by coordination of a metal atom *via* the S atom of the thiolactam group, similarly to 3,3-dimethyl-3,4-dihydroisocarbostyryl (L^2).[3]

Monophase crystal precipitates of complexes were prepared in ~30 % yield by the reaction of partially

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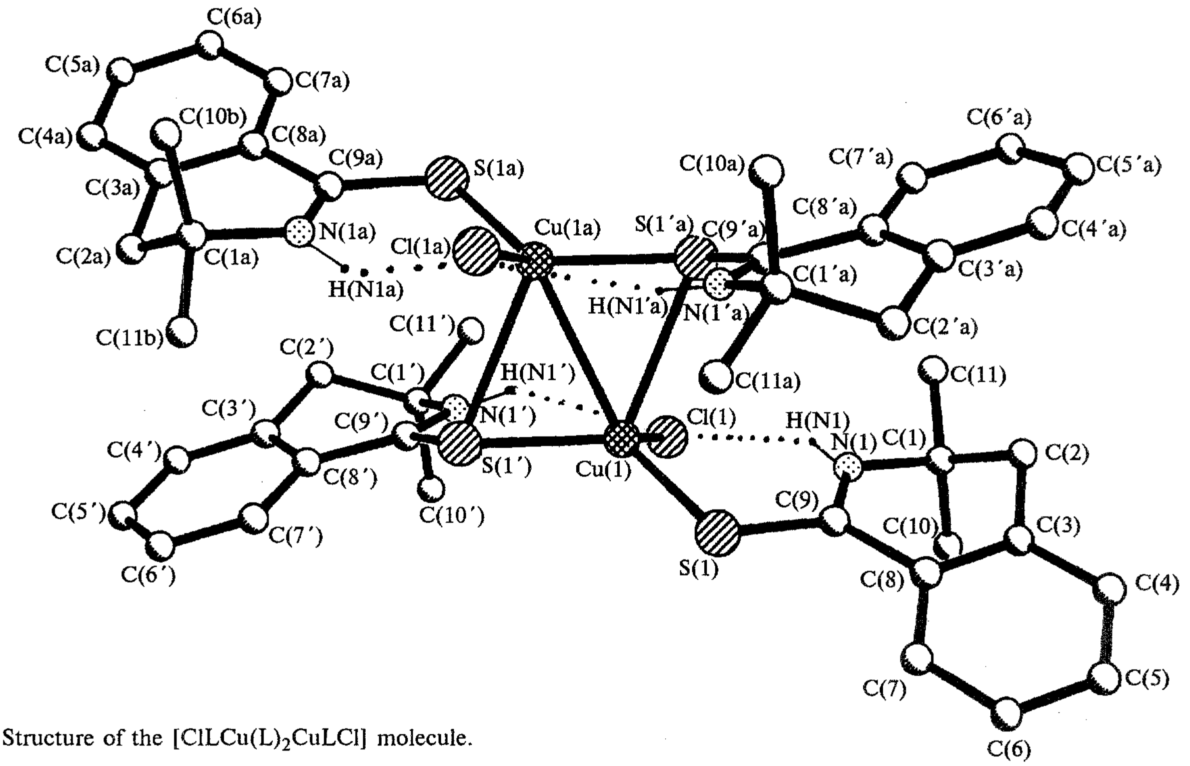

Fig.1. Structure of the $[ClLCu(L)_2CuLCl]$ molecule.

dehydrated CuX_2 crystal hydrates (X = Cl, Br) with L^1 (acetone, M : L = 1 : 1). The X-ray analysis data show that $CuCl \cdot 2L^1$ (**1**) and $CuBr \cdot 2L^1$ (**2**) are isostructural and Cu^{II} is reduced to Cu^{I} during the complex formation. Although, according to ^1H NMR and IR spectral data, L^1 exists in solutions almost completely as thiolactam tautomer **A,** the reduction of Cu^{II} to Cu^{I} indicates that a small amount of tautomer **B** is present under the synthesis conditions, since it is thiols that possess reductive ability[1] and can reduce Cu^{II} to Cu^{I}.

Structures **1** and **2** consist of binuclear $[XL^1Cu(L^1)_2CuL^1X]$ (X = Cl, Br) complexes. In each complex two molecules of L^1 serve as bridges (Fig. 1), resulting in shortening of the $Cu \cdots Cu$ distances to 2.790(1) and 2.789(3) Å in **1** and **2**, respectively. The coordination Cu^{I} polyhedron of each complex is a distorted CuS_3X tetrahedron. The ligand L^1 exists in each complex as tautomer **A** because the presence of H atoms attached to N atoms was found in difference maps (R = 0.028 for **1** and 0.058 for **2**). Tetrahydropyridine rings of dimethyldihydrothioisocarbostyryl molecules possess a half-chair conformation. Intramolecular H-bonds between X atoms and NH groups of L^1 ligands favor stabilization of the complexes.

Thus, taking into account the reductive ability of thiols, which oxidize to disulfides[1] during the reaction, one can suggest that the distinction revealed in the reactions of Cu^{II} halides with L^1 and L^2 are related to the ability of L^1, unlike L^2 to react as a thiol tautomer, reducing Cu^{II} to Cu^{I}.

References

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