# DFT Calculations on the Coordination and Hydrogen-Bonding Properties of Copper(I) Thiocyanate Complexes.

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## 1 Introduction

Three-coordination in metal complexes is relatively uncommon. It has been suggested that steric hindrance of the coordinating ligand itself is the main factor in limiting the coordination number to three. [1]

Surprisingly, there are two structural reports of discrete three coordinated complexes containing a transition metal and thiocvanate anion as ligand [2, 3], despite of the lack of steric hindrance (see Figure 3) [14]. There is a basic question connected with the possible coordination of a thiocyanate anion to copper(I) cation: is the ligand S- or N- coordinated? The HSAB principle simply states that hard acids prefer to coordinate to hard bases and soft acids to soft bases.[4, 5] Because copper(I) cation is classified as a soft Lewis acid, the coordination to sulfur of the thiocyanate anion is favoured. In general, bending of a thiocyanate anion is connected with concomitant change in the electronic configuration. If the carbon atom has a pure sp hybridization, the anion is linear. A change of the hybridization towards sp<sup>2</sup> results in bending in the ∠S-C-N angle, which may lead even to an  $\eta$  (sideways) coordination mode.[6] Monomeric structures containing a three-coordinated copper(I) ion and Ncoordinated ligands are very scarce in the solid state, however. [7]

### 2 Methodology

All calculations have been carried out using the Gaussian 94 package [8] of programs. All geometries have been fully optimized and all stationary points on the hypersurface have been characterized by harmonic frequency analysis. The hybrid exchange-correlation Becke 3-Lee-Yang-Parr functional (Becke3LYP) [9, 10] was used together with the LANL2DZ basis.

Bader analyses have been performed by the AIMPAC series of program [11] using the wavefunction as imput, as described in "Atoms in Molecules Theory" [12, 13].

## 3 Results and Discussion

The seven posible isomers (str. 1–7) for the treecoordinated tris-thiocyanate of copper(I) dianion (see Figures 1 and 2) [14] have been characterized at the DFT (B3LYP/LANL2DZ) level of theory. The relative energies are listed in the table. As we observed from the table, the relative stability of the isomers favored the N-bonding coordination against S-bonding one.

**3.1** Bader analysis The Laplacian of the charge density ( $\nabla^2(\rho(\mathbf{r}))$ ) was calculated in order to evaluate the electronic properties for the seven isomers (str. 1–7). The results showed the predominance of the ionic behaviour of the thiocyanate groups when the interaction occurs between copper and nitrogen (see Figure 4).

**3.2** *Hydrogen bonding* We also studied the effect that the solvent produces to the gas-phase relative stabilities of structures 2 and 3(the S- and N-bonded ones). We modelized mainly three systems: the first one with only two amonia molecules (above and below the main molecular symmetry plane), the second one also include three HF molecules, and the third one included two oxonium and three water molecules (see Figures 5 and 6) [14].

As we can see in the Table, the differences in the relative energies of 2 and 3 reduce drastically. This is clearly in accordance with the S-bonded isomer 1 observed in the solid state (Fig. 3) [14]

Table : Relative Energy (kcal/mol)					
	$E_r$	$NH_4$	HF	$H_2O$	
1	28.28				
2	26.80	17.58	13.44	4.86	
3	0.00	0.00	0.00	0.00	
4	8.47				
5	19.44				
6	17.69				
7	17.90				

#### 4 Conclusions

From all the above we can draw the following conclusions:

 The structures of seven different copper(I) thiocyanate complexes (S and/or N bonded) were optimized by DFT methods. The resulting geometry of the isomer 1 is in agreement with the corresponding crystallographic data.

- All the theoretical results yielded planar geometries with slight bending of the ∠SCN angle (c.a. 175°) for the S-bonded thiocyanate anions.
- In the gas phase N-bonding is preferred to S-bonding.
- Additional structures with solvent molecules were modelized to study the hydrogen bonding properties. As we increase the solvent effect the S-bonded structures became more stable in comparison to the N-bonded.
- According to the Bader analyses, the thiocyanate anion prefers the canonical form of <sup>-</sup>N=C=S when the anion is N-bonded.

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- [14] the blue and yellow colours refer to nitrogen and sulfur atoms, respectively



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