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On the bonding isomerism in three-co-ordinated copper(I) thiocyanates

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Density functional theory (DFT) and *ab initio* MP2 methods have been applied to characterize the structural features of seven different bonding isomers of copper(I) thiocyanate dianion complexes (S- and/or N-bonded). The DFT calculations were carried out by means of the hybrid Becke 3LYP functional, using the 6-311+G* basis set. The *ab initio* calculations were done at the MP2/6-311+G* theoretical level. The results indicate that in the gas phase N-bonding is preferred to S-bonding. The Atoms in Molecules theory was also employed to study the electronic properties in these isomers. The co-ordination bond between the copper(I) cation and the donor atoms is strongly polarized, almost ionic. The charge depletion around the copper(I) cation is in accordance with sp^2 hybridization. Moreover, the canonical form for the non-co-ordinated as well as S-co-ordinated thiocyanates is mainly $^-$S–C≡N, whereas the N-bonded thiocyanates have also $^-$N=C=S contribution.

1 Introduction

Three-co-ordination in metal complexes is relatively uncommon. It has been suggested that steric hindrance of the co-ordinating ligand itself is the main factor in limiting the co-ordination number to three.[1] Surprisingly, there are two structural reports of discrete three-co-ordinated complexes containing a transition metal and thiocyanate anion as ligand,[2,3] despite of the lack of steric hindrance. Generally, structural studies on mononuclear copper(I) complexes containing merely monodentate S-donor ligands are scarce[4–9] owing to the pronounced tendency of copper(I) ions to form polynuclear complexes with sulfur containing ligands.[7,10–18] The available structural information on copper(I) thiocyanate systems is limited to polymeric copper thiocyanate itself[19,20] and the pyridinium salt of the polyanion $[Cu(SCN)_3^-]_\infty$,[21] broken to give single and double stranded polymeric chains[2,23] in which the anion still bridges the metal nuclei.

There is a basic question connected with the possible co-ordination of a thiocyanate anion to copper(I) cation: is the ligand S- or N-co-ordinated? The hard–soft acid–base (HSAB) principle simply states that hard acids prefer to co-ordinate to hard bases and soft acids to soft bases.[24,25] Since the copper(I) cation is classified as a soft Lewis acid, its co-ordination to sulfur of the thiocyanate anion would be 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^2 results in bending in the S–C–N angle, which may lead even to an η (sideways) co-ordination mode.[26] There are various factors influencing the co-ordination of thiocyanate anion.[27,28] These are the electronic and steric effects of ancillary ligands as well as solvent and counter ion effects.

The N- and S-bonding in copper(I) complexes is also of importance in photosynthesis. Plastocyanin is a water-soluble protein that receives electrons from a cytochrome complex. The redox center of plastocyanin consists of a copper ion co-ordinated to the side chains of a cysteine, a methionine, and two histidine residues.[30,31] Thiocyanate anion is also a strong protein-stabilizing and structure-destabilizing agent owing to its interactions with the protein involved.[32]

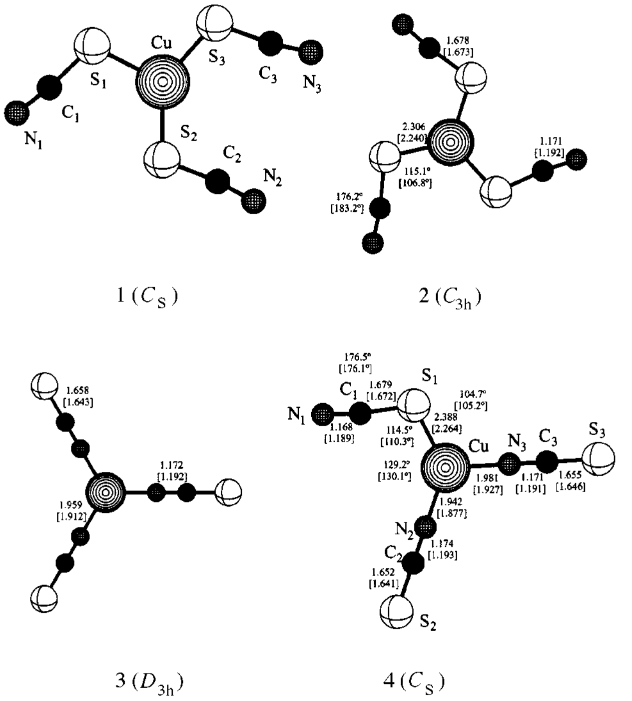
Density Functional Theory (DFT)[33,34] has generated a lot of interest, and it can potentially be applied to larger systems than any accurate *ab initio* method currently in use. Moreover, DFT methods also include electron correlation and they have been applied successfully for the study of transition metal complexes.[35–42]

The aim of the present work is to study the competition between sulfur and nitrogen of a thiocyanate anion in co-ordination with a copper(I) ion, and to characterize the unusual three-co-ordination mode for these complexes. To achieve this, the energetics, structure and harmonic vibrations of the seven different copper(I) thiocyanate dianion complexes (S and/or N bonded) have been investigated using quantum chemical methods. We employed both B3LYP and MP2 methods to compare their applicability to copper(I) complexes.

Although the HSAB principle and simple valence bond models are able to give a *qualitative* picture of the bonding in many cases, we use here the Atoms in Molecules (AIM) theory to produce a detailed quantitative description for the bonding properties. It has been used in the electronic description of many types of compounds.[43–46]

2 Methods of calculation

All calculations have been carried out using the GAUSSIAN 94 package[47] of programs. The standard grids have been used for the integration of the DFT electron density. All geometries have been fully optimized at the B3LYP/6-311+G* and MP2(full)/6-311+G* levels, and all stationary points on the hypersurface have been characterized as true minima by harmonic frequency analysis at the B3LYP/3-21+G*//B3LYP/3-21+G* level. Bader analyses have been performed by the AIMPAC series of programs[48] using the wavefunction at B3LYP and MP2 levels as input, as described in AIM theory.[49,50] An overview of the AIM theory can be obtained elsewhere.[46]



1 (C_S) 2 (C_{3h})

3 (D_{3h}) 4 (C_S)

Fig. 1 Copper(I) trithiocyanate anion structures **1**–**4**, with the corresponding geometrical parameters (B3LYP and in parentheses MP2 values, all in Å and °).

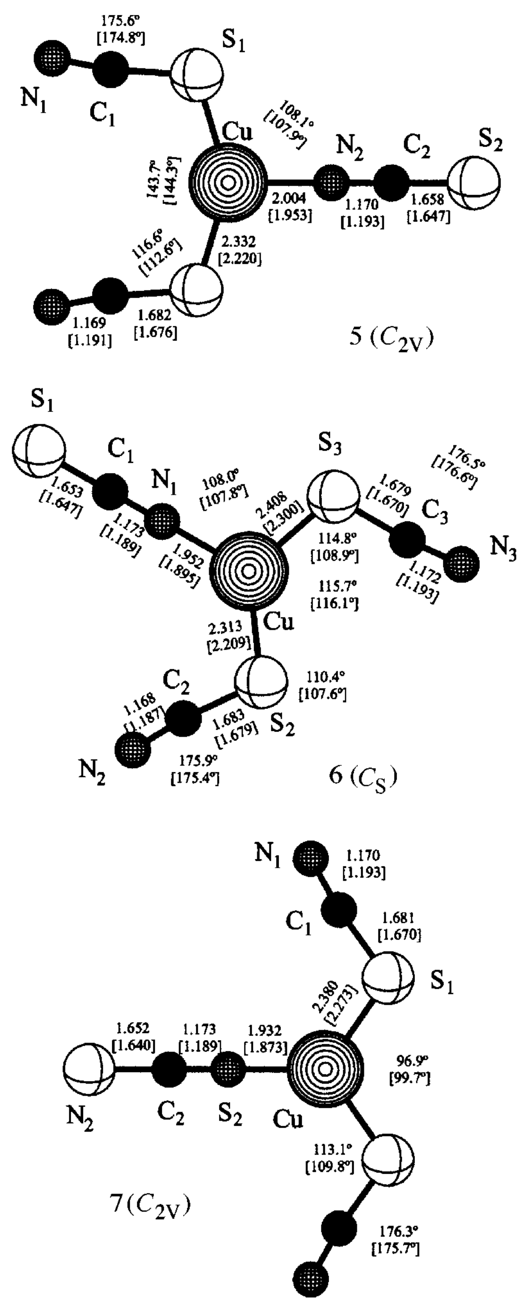
3 Results and discussion

A Geometries and energetics

To gain an insight into the geometries in N- and S-bonded copper(I) compounds displaying three-co-ordination we carried out a survey on the structures in CSDS (Cambridge Structural Database).[51,52] The search was restricted to the discrete monomeric complexes with three identical ligands. In total 10 N-co-ordinated and 14 S-co-ordinated complex units were found. It is noteworthy that no mixed monomeric complexes exist. The maximum out-of-the-plane deviations for the central copper cation in the N- and S-co-ordinated complexes were 0.205 and 0.249 Å, respectively. However, in most of the complexes the deviation was very small. This can be seen in the average values for the deviations, which were for the N- and S-bonded complexes 0.05(6) and 0.07(7) Å, respectively. Three N-bonded complexes displayed zero deviation, whereas no such planarities were found for the S-bonded moieties. The complexes are characterized by significant variation in the bond lengths and in the bond angles around the central copper(I) cation. The ranges for the Cu–S and Cu–N bond lengths are 2.213–2.338 and 1.934–2.096 Å, respectively. The wide variation is even more pronounced in the ranges for the S–Cu–S and N–Cu–N angles, which are 108.9–139.4 and 106.1–141.5°, respectively. However, there was one N-bonded and two S-bonded complex units, where a threefold rotation symmetry axis could be found.

Based upon the results discussed above we constructed seven possible bonding isomers assuming planarity for the moieties. The results of the optimizations for the copper(I) trithiocyanate at the different theoretical levels are listed in Table 1, for structure **1**, and in Figs. 1 and 2 for structures **2**–**7**. All of the structures **1**–**7** display at least a symmetry plane (C_s); **2** and **3** had an even higher symmetry of C_{3h} and D_{3h}, respectively.

There are some basic features that are characteristic for the optimized structures. In the S-bonded isomers the C–S–Cu angle is always bent, whereas in the N-bonded complexes the corresponding C–N–Cu angle is always 180°. Moreover, there is always a slight bending involved for the S–C–N angle in the former isomers, whereas the angle is always linear in the latter ones.



5 (C_{2V})

6 (C_S)

7 (C_{2V})

Fig. 2 Copper(I) trithiocyanate anion structures **5**–**7**, with the corresponding geometrical parameters (B3LYP and in parentheses MP2 values, all in Å and °).

In general, the MP2 level of theory seems to give more reliable geometrical parameters, when the experimental structure and the optimized structure **1** are compared (see Table 1). Usually the B3LYP method tends to give too long Cu–S bond lengths. The biggest deviations between the experimental and calculated structures occur at the parameters concerning one of the thiocyanate groups (with the subscript 2 in our notation). However, all of the experimental parameters (including the thermal displacement values) are anomalous. Obviously there must be either a disorder in the structure or the anomalies are mathematical artefacts due to the modest quality of the diffraction data [the crystallographic $R(F)$ value was 0.079].[3]

As stated in the Introduction, there are only two reports concerning discrete trithiocyanate complexes of copper. Both of the papers describe the structure determination for bis[6-amino-5-(2-ethylphenylazonium)-1,3-dimethyluracil] tris(thiocyanato-*S*)cuprate(I).[2,3] In the former report the single-crystal structure determination was carried out at room temperature and in the latter at 193 K. In the subsequent discussion we

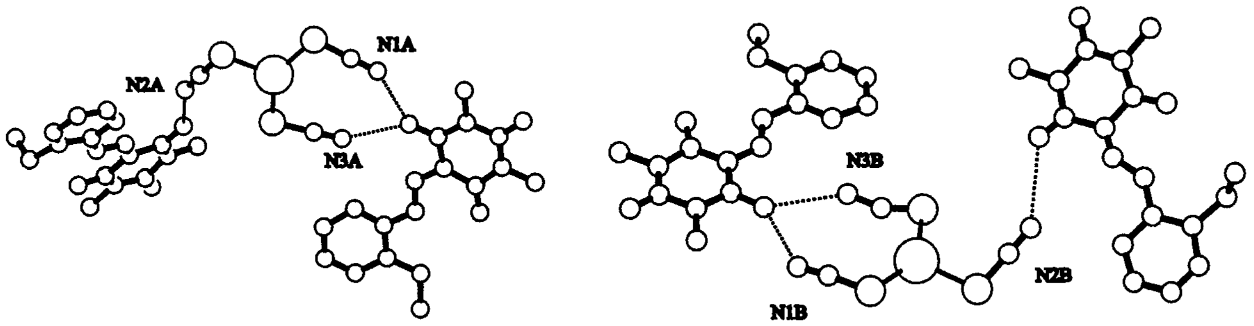


Fig. 3 A perspective view of the two crystallographically independent complex units in bis[6-amino-5-(2-ethylphenylazonium)-1,3-dimethyluracil] tris(thiocyanato-*S*)cuprate(I). The input co-ordinates are taken from ref. 3 . The short contacts between the anions and cations are depicted by dashed lines. The hydrogen atoms are omitted for clarity. The orientation for each complex unit is chosen to give the best possible illustration of the short contacts for each nitrogen atom of the thiocyanate groups.

Table 1 Geometrical parameters (Å and °) for thiocyanate ion and for the structure **1**, at different theoretical levels

	B3LYP	MP2	Exptl. I	Exptl. II
Thiocyanate ion ($C_{\infty v}$)				
S–C	1.669	1.657	1.689 ± 0.013[a]	1.63[b]
C–N	1.175	1.195	1.149 ± 0.014[a]	1.15[b]
Structure **1** (C_s)[c]				
Cu–S(1)	2.438	2.312	2.264	2.316
Cu–S(2)	2.303	2.205	2.228	2.271
Cu–S(3)	2.340	2.240	2.227	2.253
S(1)–C(1)	1.680	1.671	1.62	1.63
S(2)–C(2)	1.682	1.679	1.69	1.41
S(3)–C(3)	1.678	1.673	1.65	1.64
C(1)–N(1)	1.172	1.191	1.12	1.16
C(2)–N(2)	1.172	1.189	1.16	1.30
C(3)–N(3)	1.172	1.188	1.18	1.15
S(1)–Cu–S(2)	115.3	115.4	113.1	111.0
S(2)–Cu–S(3)	147.8	144.6	135.7	139.0
S(3)–Cu–S(1)	97.0	100.1	111.1	109.0
Cu–S(1)–C(1)	114.3	108.6	100	104
Cu–S(2)–C(2)	112.9	110.3	102	89
Cu–S(3)–C(3)	115.4	112.6	108	107
S(1)–C(1)–N(1)	176.5	176.3	177	176
S(2)–C(2)–N(2)	175.2	174.5	175	158
S(3)–C(3)–N(3)	175.5	174.5	178	175

[a] X-Ray data from ref. 53 for potassium thiocyanate. [b] X-Ray data from ref. 53 for ammonium thiocyanate. [c] Exptl. I and II data from ref. 3 correspond to two crystallographically independent isomers. The atom numbering is depicted in Fig. 1.

refer to the latter paper only. The experimental and theoretical structural data for this compound are listed in Table 1. Two crystallographically independent three-co-ordinated tri(thiocyanato-*S*)cuprate(I) moieties (Exptl. I and Exptl. II, respectively) were found in the same unit cell (see Fig. 3). The geometrical parameters are reproduced reasonably well by the computational methods, especially at the MP2 level. The average value for the experimental Cu–S bond lengths is 2.254 Å and the corresponding calculated value is 2.253 Å (MP2). There is notably more deviation in the S–Cu–S angles, however. Obviously the angles show a propensity to deform easily, as is seen also in the statistical variation for the angles in the structures found from CSDS. Both anions in the experimental structure present bent SCN groups (*ca.* 176°). Furthermore, both co-ordination moieties in the unit cell display non-planarity with one of the three S–Cu–S–C torsion angles of one SCN group out of the plane constructed through three sulfur atoms, *ca.* 19 and 25°, respectively.

According to a recent review thiocyanate anions are very susceptible to participate in hydrogen bonding.[54] A closer inspection of the experimental structure reveals that there are relatively short intermolecular distances between each of the N atoms of the thiocyanate anions and the amino groups of the cations. These interactions are seen for both of the crystallographically independent complex units (Fig. 3). There are bifurcated contacts with one of the amino groups to two of the thiocyanate groups to form an almost coplanar system. The third thiocyanate group is bent towards an amino group of the other cation. It is readily seen that the isomer formation of this compound is governed by the ratio of two cations to one anion. Accordingly, the existence of structure **2** is highly improbable in the solid state.

We checked the torsional barrier of one of these SCN groups (structures **1** and **2**). The values for the barrier were very small (*ca.* 1.6 kcal mol^{-1}, at the B3LYP/LANL2DZ level), indicating an almost free rotation around the S(2)–Cu–S(1)–N(1) angle. Therefore, the intermolecular interactions are very likely playing a marked role in defining the conformations in the solid state.

It is also very interesting that the solid state structure corresponds to the isomer with the least favourable energy. We suggest that hydrogen bonding must play an important role here. On the other hand, the energy differences are small, especially at the MP2 level (<7 kcal mol^{-1}). There are several examples of how the co-ordination mode varies depending on the solvent. So, in the series of $ML_2(CNS)_2$ complexes (where M = Pd^{II} or Pt^{II}, CNS = the thiocyanate ligand without any reference to the co-ordination mode and L = PPh_3, $AsPh_3$ or $SbPh_3$) the only co-ordination mode is the S-bonding, when a solvent with a high relative permittivity is used. However, when solvents like C_6H_6 or $CHCl_3$ with lower values are applied, the complexes display either a mixture of S- and N-bonding or even N-bonding alone.[55] In another example, $[Co(CN)_5(CNS)]^{3-}$ exists in an equilibrium of the S-bonded (70%) and N-bonded (30%) isomers in an aqueous solution. Yet the N-bonded isomer is more stable, if the solvent is CH_2Cl_2, $PhNO_2$, 2-furaldehyde or Me_2CO.[56] Accordingly, it seems that a M–SCN fragment will form stronger hydrogen bonds than a M–NCS moiety. Indeed, thiocyanic acid displays a structure where the proton is attached to the nitrogen atom.[56] Therefore, we suggest that the seemingly reversed order of the stability may well be explained by hydrogen bonding. A similar suggestion was recently made by Fukushima *et al.*[57] who discussed the effect of solvents on a series of thiocyanate complexes of Zn^{II}, Cd^{II} and Hg^{II}. The theoretical S–C and C–N bond lengths at both levels (*ca.* 1.675 and 1.18 Å, respectively) are within the experimental values 1.64(4) and 1.14(5) Å, respectively.† With respect to the other geometrical parameters for structure **1**, the agreement for bond angles is poorer. The largest deviation for the Cu–S–C angles is *ca.* 14°. As will be discussed later on, the bonds between the central copper(I) ion and the ligands are very

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† Experimental values obtained for 68 fragments found from CSDS. Each fragment contained a transition metal and a monoco-ordinated thiocyanate group.

Table 2 Relative energies E_r/kcal mol^{-1} and dipole moments μ/D for structures **1**–**7** at different theoretical levels, taking the calculated total energies of **3** at each level as reference

Level of theory	**1** (C_s)		**2** [$C(3)_h$]		**3** (D_{3h})		**4** (C_s)		**5** [$C(2)_v$]		**6** (C_s)		**7** [$C(2)_v$]	
	E_r	μ	E_r	μ	E_r	μ	E_r	μ	E_r	μ	E_r	μ	E_r	μ
B3LYP	18.83	3.40	17.45	—[a]	0.00[b]	—[a]	5.39	2.35	12.85	3.97	10.99	1.80	11.43	2.60
MP2	6.83	3.86	3.81	—[a]	0.00[c]	—[a]	1.42	1.97	4.84	3.29	2.57	1.81	3.58	3.34

[a] Dipole moment equal to zero by symmetry. [b] Calculated total energy −3114.0036052 au. [c] Calculated total energy −3111.2932200 au.

Table 3 Charge density $\rho(r)$ (e/a_0^3), Laplacian of the charge density $\nabla^2\rho(r)$ (e/a_0^5), ellipticity ε and local energy density $E_d(r)$ (hartree/a_0^3) for BCPs for structures **1**, **2**, **3** and **5**

Structure (bond)	$\rho(r)$		$\nabla^2\rho(r)$		ε		$E_d(r)$	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
1 Cu–S(1)	0.068	0.053	0.170	0.120	0.018	0.011	−0.020	−0.014
Cu–S(2)	0.083	0.068	0.219	0.170	0.010	0.021	−0.026	−0.019
Cu–S(3)	0.077	0.063	0.202	0.154	0.004	0.024	−0.024	−0.018
S(1)–C(1)	0.204	0.205	−0.053	−0.163	0.131	0.106	−0.241	−0.237
S(2)–C(2)	0.203	0.204	−0.089	−0.198	0.163	0.135	−0.240	−0.235
S(3)–C(3)	0.203	0.204	−0.082	−0.190	0.158	0.130	−0.241	−0.236
C(1)–N(1)	0.433	0.458	−0.390	−0.395	0.004	0.006	−0.755	−0.807
C(2)–N(2)	0.434	0.459	−0.371	−0.372	0.006	0.008	−0.757	−0.811
C(3)–N(3)	0.434	0.459	−0.371	−0.374	0.006	0.008	−0.757	−0.810
2 Cu–S	0.077	0.067	0.205	0.172	0.022	0.003	−0.024	−0.019
S–C	0.203	0.205	−0.065	−0.167	0.147	0.123	−0.240	−0.238
C–N	0.433	0.459	−0.388	−0.392	0.004	0.007	−0.755	−0.808
3 Cu–N	0.098	0.087	0.511	0.440	0.061	0.048	−0.020	−0.015
N–C	0.425	0.450	−0.289	−0.336	0.022	0.019	−0.732	−0.784
C–S	0.207	0.208	0.111	−0.018	0.004	0.003	−0.243	−0.243
5 Cu–S(1)	0.080	0.064	0.213	0.157	0.010	0.016	−0.025	−0.018
Cu–N(2)	0.088	0.079	0.448	0.382	0.048	0.033	−0.017	−0.013
C(1)–N(1)	0.434	0.459	−0.369	−0.377	0.006	0.007	−0.758	−0.810
N(2)–C(2)	0.425	0.451	−0.301	−0.346	0.013	0.010	−0.733	−0.785
S(1)–C(1)	0.203	0.204	−0.088	−0.191	0.155	0.122	−0.240	−0.236
C(2)–S(2)	0.207	0.209	0.105	−0.014	0.004	0.002	−0.243	−0.243
HSCN S–C	0.208	0.207	−0.073	−0.451	0.599	0.309	−0.252	−0.214
C–N	0.452	0.469	−0.045	−0.120	0.048	0.018	−0.809	−0.839
S–H	0.210	0.203	−0.582	−0.519	0.099	0.086	−0.177	−0.164
SCN$^-$ S–C	0.205	0.206	0.292	−0.104	0.000	0.000	−0.232	−0.239
C–N	0.443	0.455	−0.446	−0.451	0.000	0.000	−0.782	−0.799
SCNH S–C	0.222	0.226	0.749	0.373	0.000	0.000	−0.239	−0.260
C–N	0.413	0.422	−0.146	−0.220	0.000	0.000	−0.695	−0.705
N–H	0.325	0.328	−2.059	−1.854	0.000	0.000	−0.548	−0.502
SCNLi S–C	0.219	0.221	0.611	0.226	0.000	0.000	−0.240	−0.258
C–N	0.435	0.443	−0.681	−0.644	0.000	0.000	−0.758	−0.760
N–Li	0.050	0.054	0.388	0.392	0.000	0.000	0.012	0.011

polarized. Therefore, the orientation of the ligands is very likely dependent on the intermolecular interactions. Structures **2** and **3** are the S- and N-bonded ones with $C(3)_h$ and D_{3h} symmetries, respectively. The Cu–S bond lengths are shorter than for structure **1**, independent of the level of theory. The S–C bond length for structure **3** becomes shorter (*ca.* 0.03 Å) than for structure **2** and the thiocyanate ion.

Structure **4** presents two N- and one S-bonding to the copper(I) cation. The most characteristic structural feature is the increase for the S–Cu bond length (*ca.* 0.08 Å) at the B3LYP and N–S–Cu angle (4°) at the MP2 level compared with structure **2**. Moreover, a decrease in the N–Cu distance (*ca.* 0.03 Å) is also observed compared with structure **3**.

Structures **5**–**7** are the three remaining isomers with two S and one N bonded to copper. Structure **6** shows two significantly different Cu–S bond lengths (the difference is *ca.* 0.1 Å at both levels), while **5** and **7** present Cu–S distances with intermediate values *ca.* 2.33 and 2.38 Å at the B3LYP and 2.22 and 2.27 Å at the MP2 levels.

The energy values for the structures **1**–**7** are listed in Table 2, together with the respective dipole moments. At both theoretical levels, **3**, the purely N-bonded isomer, was the most stable structure, whereas **1** and **2** with three S bonded to copper had the highest energy (in the range 3.8–6.9 kcal mol^{-1} at MP2 level). However, structures **5**–**7**, with two S and one N bonds, present similar energies (in the range 2.5–4.9 kcal mol^{-1} at the MP2 level). The remaining mixed complex (structure **4**) has one S and two N bonded to copper, and is closer in energy to structure **3** (*ca.* 1.4 kcal mol^{-1}). The same trend was observed at the B3LYP level but with an increase in the relative barriers by *ca.* 4–14 kcal mol^{-1}. Based upon the discussion above, the theoretical results favour N- to S-bonding in the isolated isomers.

B Bonding nature

Since a copper(I) cation has a $d^{10}s^0$ electron configuration there are no empty d orbitals available to form covalent bonds with either sulfur or nitrogen atoms. Instead, the s and p orbitals are conceivable. In terms of the valence-bond approach, the planar three-co-ordination can be described as a result of sp^2 hybridization. To get an insight into the interactions between the central copper(I) cation and a ligand we made use of the AIM theory.[49,50]

The bond critical points (BCPs) on the charge density $\rho(r)$ for the structures **1**, **2**, **3** and **5** have been calculated, and the numerical values are listed in the Table 3. The different BCPs are further characterized by their values of charge density $\rho(r)$, Laplacian of charge density $\nabla^2\rho(r)$, ellipticity ε and local elec-

Table 4 AIM Summary of the critical points (3,+3) for Cu and (3,−3) for S, C and N, in $-\nabla^2\rho(r)$ for the structures **1**, **2**, **3** and **5** at the B3LYP theoretical level indicating the values of $\rho(r)$, its Laplacian and its relative orientation

Structure	Central atom (type)	Bond	$\rho(r)$ (e/a_0^3)	$\nabla^2\rho(r)$ (e/a_0^5)	Orientation[a]	NECP[b]
1	Cu (3,+3)	Cu–S(1)	1.61	19.01	Plane 0.883 au	3
	Cu (3,+3)	Cu	1.65	18.37	Vertical 0.877 au	2
	S(1) (3,−3)	S(1)–C(1)	0.29	−0.86	Plane 2.264 au	
	S(1) (3,−3)	S(1)–	0.18	−0.53	Out of plane 1.296 au	2
	S(1) (3,−3)	S(1)–Cu	0.20	−0.64	Plane 1.294 au	
	C(1) (3,−3)	C(1)–N(1)	0.51	−1.74	Linear 1.468 au	
	N(1) (3,−3)	N(1)–	0.54	−2.29	Linear 0.737 au	
2	Cu (3,+3)	Cu–S	1.61	19.02	Plane 0.883 au	3
	Cu (3,+3)	Cu	1.65	18.36	Vertical 0.877 au	2
	S (3,−3)	S–C	0.29	−0.86	Plane 2.266 au	
	S (3,−3)	S–Cu	0.20	−0.64	Plane 1.294 au	
	S (3,−3)	S	0.18	−0.53	Out of plane 1.296 au	2
	C (3,−3)	C–N	0.51	−1.74	Linear 1.467 au	
	N (3,−3)	N–	0.54	−2.28	Linear 0.737 au	
3	Cu (3,+3)	Cu–N	1.61	19.29	Plane 0.883 au	3
	Cu (3,+3)	Cu	1.64	18.23	Vertical 0.875 au	2
	N (3,−3)	N–Cu	0.53	−2.06	Linear 0.747 au	
	N (3,−3)	N–C	0.51	−1.68	Linear 0.828 au	
	C (3,−3)	C–S	0.30	−0.90	Linear 0.920 au	
	S (3,−3)	S–	0.18	−0.51	Plane 1.300 au	2
5	Cu (3,+3)	Cu–S(1)	1.62	18.97	Plane 0.881 au	2
	Cu (3,+3)	Cu–N(2)	1.61	19.55	Plane 0.878 au	1
	Cu (3,+3)	Cu	1.64	18.30	Vertical 0.877 au	2
	S(1) (3,−3)	S(1)–C(1)	0.29	−0.86	Plane 2.263 au	
	S(1) (3,−3)	S(1)–Cu	0.20	−0.63	Plane 1.294 au	
	S(1) (3,−3)	S(1)	0.18	−0.53	Out of plane 1.296 au	2
	S(2) (3,−3)	S(2)	0.18	−0.51	Plane 1.300 au	2
	N(1) (3,−3)	N(1)–	0.54	−2.30	Linear 0.737 au	
	N(2) (3,−3)	N(2)–Cu	0.53	−2.02	Linear 0.748 au	
	N(2) (3,−3)	N(2)–C(2)	0.51	−1.69	Linear 0.828 au	
	C(1) (3,−3)	C(1)–N(1)	0.51	−1.75	Linear 1.465 au	
	C(2) (3,−3)	C(2)–N(2)	0.51	−1.69	Linear 1.448 au	

[a] Refers to a position of a critical point and its distance (in atomic units) from a central atom. “Plane” refers to a molecular plane. “Vertical” means a perpendicular direction from a molecular plane with a central atom as starting point. An “out-of-plane” critical point is situated at a non-perpendicular position at a given distance from a central atom. A “linear” position refers to a critical point pointing away from a central atom along a given bond. [b] Number of equivalent critical points.

tronic energy density $E_d(r)$, all in atomic units. Three BCPs are found in the surroundings of the copper atom, located nearby the ligand atoms in every structure (see Table 3). These BCPs display similar overall characteristics. They present small $\rho(r)$ values (0.05–0.10 e/a_0^3), and medium and positive values of $\nabla^2\rho(r)$ (*ca.* 0.1–0.5 e/a_0^5), which is expected for a closed shell bonding interaction (ionic). However, the BCPs present significant differences depending on their bonding mode (see Table 3).

Table 4 gives a summary of the critical points (3,+3) for Cu and (3,−3) for S, C and N in $\nabla^2\rho(r)$ for the structures **1**, **2**, **3** and **5**. Each point is characterized by its $\rho(r)$ value, its Laplacian and its relative orientation. The copper atoms have five (3,+3) critical points (minimum of charge concentration), three of them in the molecular plane and directed towards the ligands and two in the axial positions, compatible with the sp^2 hybridization and with the non-hybridized p$_z$ orbital of the copper(I) ion. The charge concentration maxima (3,−3) corresponding to the ligand atoms bonded to copper are directed towards the copper charge depletion.

The nature of the bonds to S and N is characterized by the number and orientation of the charge concentration maxima of the ligand atoms bonded to copper. The sulfur atoms present four critical points (3,−3). Two of them are on the molecular plane and directed towards copper and carbon, respectively (although the second one is closer to C than S). The remaining two are out of the co-ordination plane completing a distorted tetrahedron around sulfur. These latter critical points correspond to the electron lone pairs of sulfur. The orientation of the four critical points on sulfur restrains direct linear interaction between sulfur and copper.

As for the bonding at N, there are two (3,−3) charge concentration maxima in a linear direction, one towards Cu and the other one towards C forming a straight line Cu–BCP–N–BCP–C, also compatible with a larger charge concentration towards the copper (see Table 4). Furthermore, the S-bonded compounds have extra charge concentration in the axial positions over and below the molecular plane. In structure **5** the charge ‡ for the central copper atom is 0.72, which means that the co-ordination bonds between the donor atoms and the acceptor are almost ionic. The charges for the co-ordinated and non-co-ordinated sulfur atoms are −0.09 and −0.07, respectively. The corresponding values for nitrogen are −1.24 and −1.10. These values show clearly that the co-ordination has only a very marginal effect on the charge distribution in the ligands. Moreover, it seems that the bond between copper and a donor atom is essentially electrostatic. Structures **1**–**7** have thiocyanate anions N- or S-bonded to copper. The electronic properties of the thiocyanate anion can be described with the help of two canonical forms $^-$N=C=S and $^-$S–C≡N. From the electronic characteristics calculated and presented in Tables 3 and 4, the latter canonical form is the main one in both N- and S-bonded ligands. This is compatible with the existence of only one maxima concentration on the nitrogen atom in a linear disposition, irrespective of the co-ordination mode.

The electronic properties of the S–C BCPs in the N-bonded complexes show small deviations compatible with some double bond character (see Table 3). This is in accord with the calculated S–C bond length (*ca.* 1.67 Å for S-bonded and 1.64 Å for the N-bonded complexes).

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‡ Bader atomic charges were calculated with the PROAIM program within the AIMPAC series of programs, see ref. 48.

Table 5 Comparison of the most important vibrational frequencies for the thiocyanate ion and structures **1**–**7** at the B3LYP/3-21+G*//B3LYP/3-21+G* level

	1 (C_s)		**2** [$C(3)_h$]		**3** (D_{3h})		**4** (C_s)	
No.	Frequency[a]	Intensity[b]	Frequency[a]	Intensity[b]	Frequency[a]	Intensity[b]	Frequency[a]	Intensity[b]
1	27(A″)	1	40(E′)	6	22(E′)	2	24(A′)	4
2	39(A′)	9	40(E′)	6	22(E′)	2	32(A′)	3
3	40(A′)	3	41(A″)	13	39(A_2'')	5	43(A″)	8
4	45(A″)	11	42(E″)	0	89(A_2')	0	57(A″)	0
5	66(A″)	0	42(E″)	0	116(E″)	0	78(A′)	11
6	73(A′)	19	75(A′)	0	116(E″)	0	129(A′)	4
7	98(A′)	8	89(A″)	4	132(E′)	9	131(A″)	0
8	102(A″)	4	104(E′)	15	132(E′)	9	139(A′)	19
9	109(A′)	12	104(E′)	15	197(A_1')	0	194(A′)	0
10	193(A′)	15	205(A′)	0	228(A_2'')	9	210(A″)	6
11	209(A′)	1	241(E′)	16	252(E′)	31	217(A′)	17
12	271(A′)	16	241(E′)	16	252(E′)	31	288(A′)	35
13	495(A′)	1	500(E″)	0	514(A_2')	0	497(A′)	0
14	497(A″)	1	500(E″)	0	518(E′)	3	501(A″)	2
15	503(A″)	1	500(A″)	7	518(E′)	3	511(A′)	0
16	508(A″)	5	501(A′)	0	531(E″)	0	515(A′)	6
17	511(A′)	1	505(E′)	2	531(E″)	0	533(A″)	1
18	513(A′)	2	505(E′)	2	540(A_2'')	5	544(A″)	3
19	720(A′)	5	720(E′)	9	798(E′)	62	724(A′)	6
20	723(A′)	11	720(E′)	9	798(E′)	62	803(A′)	46
21	729(A′)	4	721(A′)	0	805(A_1')	0	813(A′)	34
22	2116(A′)	579	2119(E′)	559	2135(E′)	753	2115(A′)	467
23	2123(A′)	80	2119(E′)	559	2135(E′)	753	2137(A′)	814
24	2130(A′)	468	2122(A′)	0	2147(A_1')	0	2145(A′)	220

	5 [$C(2)_v$]		**6** (C_s)		**7** [$C(2)_v$]		Thiocyanate ion ($C_{\infty v}$)[c]	
	Frequency[a]	Intensity[b]	Frequency[a]	Intensity[b]	Frequency[a]	Intensity[b]	Frequency[a]	Description
1	27(A′)	7	29(A′)	4	27(A′)	1	735	ν_{SC}
2	39(A′)	1	30(A′)	6	33(A″)	8	465	δ_{SCN}
3	43(A″)	0	44(A″)	7	38(A′)	9	2058	ν_{CN}
4	44(A″)	9	50(A″)	4	66(A″)	0		
5	74(A″)	2	78(A″)	1	68(A′)	24		
6	79(A′)	15	78(A′)	7	70(A″)	4		
7	106(A′)	8	100(A′)	17	99(A′)	0		
8	135(A′)	3	142(A′)	10	135(A′)	20		
9	161(A″)	5	176(A′)	4	184(A″)	4		
10	202(A′)	0	192(A′)	8	200(A′)	0		
11	231(A′)	35	218(A′)	11	202(A′)	9		
12	248(A′)	18	287(A′)	26	289(A′)	29		
13	497(A″)	4	498(A′)	1	492(A′)	1		
14	499(A″)	0	502(A″)	2	505(A′)	0		
15	504(A′)	0	508(A″)	2	506(A″)	0		
16	505(A′)	1	510(A′)	0	508(A″)	5		
17	513(A′)	4	515(A′)	4	515(A′)	3		
18	528(A″)	1	534(A″)	2	543(A″)	2		
19	722(A′)	9	719(A′)	6	722(A′)	14		
20	722(A′)	1	725(A′)	7	727(A′)	1		
21	800(A′)	32	812(A′)	36	819(A′)	33		
22	2120(A′)	98	2114(A′)	526	2117(A′)	804		
23	2127(A′)	949	2122(A′)	337	2121(A′)	2		
24	2137(A′)	287	2142(A′)	496	2145(A′)	557		

[a] Wavenumber in cm^{-1} and symmetry in parentheses. [b] Intensity in kM mol^{-1}. [c] Experimental data from refs. 58 and 59.

All of the above considerations are in accordance with a small contribution of the $^{-}N{=}C{=}S$ canonical form.

It is also possible to draw some conclusions from Table 4 about the stability of the S- or N-bonded isomers in the presence of a polar solvent (hydrogen bonding). For the structure **3** the absolute maximum of non-bonding concentration [$\rho(r) = 0.5\ e/a_0^3$ and $\nabla^2\rho(r) = -2.1\ e/a_0^5$] of the ligand (corresponding to the nitrogen lone electron pair) is oriented towards the charge concentration minimum of Cu producing a strong electrostatic stabilization. Moreover, the extra negative charge is located on the sulfur atoms (large and polarizable ones), in two small charge concentration maxima [$\rho(r) = 0.18$ and $\nabla^2\rho(r) = -0.51\ e/a_0^5$] on the molecular plane. This results in a more dispersed charge concentration which is also more stable under apolar conditions with less propensity for forming strong hydrogen bonds. On the other hand, the S-bonded structures present the absolute charge concentration maxima (corresponding to the non-bonding lone electron pair on the N) in only one linear CP [$\rho(r) = 0.5\ e/a_0^3$ and $\nabla^2\rho(r) = -2.3\ e/a_0^5$], which favours the formation of stable hydrogen bonds.

C Vibrational spectra

The vibrational spectrum affords another window into what is happening to the electronic structure on complexation. Values for the ν_{SC} and ν_{CN} stretching and δ_{SCN} bending modes of the thiocyanate anion alone and within the copper(I) complexes, are listed in Table 5. Kivekäs *et al.*[3] reported two experimental IR bands at 2107 and 2093 cm^{-1} for bis[6-amino-5-(2-ethylphenylazonium)-1,3-dimethyluracil] tri(thiocyanato-*S*)cuprate(I). As noted before, their structure resembles the structure **1**. There are two calculated strong bands for this structure at 2130 and 2116 cm^{-1}. The difference between the calculated and observed frequencies may well be due to hydrogen bonding in the solid state. Hydrogen bonding is known to cause shifting to lower wavenumbers.[60] In their earlier paper, Kivekäs *et al.* suggested that the origin of the two bands is in the interaction between the central copper(I) cation and a neighbouring carbon atom of a thiocyanate group. However, we claim that the existence of two strong bands is due to two different orientations of the thiocyanate groups. The thiocyanate anions S(2)–C(2)–N(2) and S(3)–C(3)–N(3) are mutually similar in contrast to the remaining S(1)–C(1)–N(1) (see Fig. 1). Indeed, when the thiocyanate anions are identical, as required by symmetry, there is only one C–N stretching band, as for structures **2** and **3**. However, the proposed interaction between a copper(I) cation and a neighbouring carbon atom cannot be totally ruled out.

4 Conclusion

The structures of seven different copper(I) thiocyanate complexes (S and/or N bonded) were optimized by MP2 and B3LYP methods. The resulting geometry of structure **1** is in agreement with the corresponding crystallographic data at both levels of theory (including polarization functions on carbon, nitrogen and sulfur atoms). All the theoretical results yielded planar geometries with slight bending of the S–C–N angle (*ca.* 175°) for the S-bonded thiocyanate anions. The results also indicate that in the gas phase N-bonding is preferred to S-bonding.

The existence of the pure S-bonded isomer in the solid state may be explained by preferred hydrogen bonding to the N atoms.

The existence of hydrogen bonding in the solid state is also supported by the comparison of the observed and calculated ν_{CN} frequencies. The charge densities at the BCPs fall merely into three categories representing the Cu–X, S–C and C–N bonds. The ranges for these bonds are 0.05–0.09, 0.20–0.21 and 0.43–0.46 e/a_0^3, respectively.

In the S-bonded isomers there is a formal co-ordinate bond between copper and sulfur. However, the bond is strongly polarized and almost of ionic nature. This suggests easy deformations in the bond lengths and angles around a copper(I) cation. These deformations manifest themselves in the wide ranges of the experimental parameters obtained from CSDS. According to the AIM analyses, the thiocyanate anion prefers the canonical form of $^{-}$S–C≡N in both S- and N-bonded forms, however when it is N-bonded some $^{-}$N=C=S contribution is expected. The charge density depletion around the central copper(I) cation is in accordance with sp^2 hybridization.

Finally, we note that the geometrical parameters are better reproduced by MP2 than B3LYP methods. Furthermore, the AIM theory is a convenient tool to analyse quantitatively the electronic properties in metal complexes.

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