



## Mode of Bonding and Isomerism in Mixed Cu(II) Thiocyanate Diamine Ligand Complexes

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### ABSTRACT

The reactions of excess thiocyanate with Cu(II) ions in the presence of the chelate ligand 1,3-diaminopropane (dp) were reinvestigated. The reaction in ethanol yielded successively brown, violet and blue complexes. The above order of isolation corresponds to their respective decreasing molecular masses and increasing solubilities. The use of vibrational (infra-red) and electronic (ultra-violet/visible) spectra in elucidating the structure and mode of coordination of the thiocyanate groups was discussed. The possibility of linkage isomerism and intermolecular H-bonding were also examined. The infra-red spectrum of the brown complex [Cu<sub>2</sub>(dp)(SCN)<sub>4</sub>] showed bands in the  $\nu_{CN}$  region strongly suggesting a dimeric species. Further evidence for the dimeric structure was provided by the insolubility of the complex in most of the common solvents but it dissolved readily in pyridine which is a donor solvent capable to cleave catenating bridges in polymeric species.

### المستخلص

أجريت هذه الدراسة لمتابعة تفاعلات أيون النحاس (II) مع 1,3-ثنائي أمينو بروبييل (dp) في وجود المترابطة المخالبية ثيوسيانات في وسط من مذيب الإيثانول ليؤدي لترسيب ثلاثة معقدات بالألوان بني، بنفسجي، ثم أزرق على التوالي ويقابل هذا الترتيب التناقص في الأوزان الصيغية والزيادة في الإذابة. وتم استخدام طيف الإهتزاز (الأشعة تحت الحمراء) وطيف الانتقالات الإلكترونية (الأشعة فوق البنفسجية/المرئية) في تحديد بنية المعقدات تحت الدراسة وتحديد تناسق ارتباط مجموعة الثيوسيانات كما تم اختبار احتمال وجود الأيسوميرية الترابطية والرابعة الهيدروجينية البينية في المعقدات. وقد أظهر طيف الأشعة تحت الحمراء للمعقد البني أدلة قوية على البنية الثنائية لهذا المعقد وهو ما توضح أيضاً من عدم ذوبانية المعقد في معظم المذيبات بينما ذاب بسهولة في البيريدين المعروف كمذيب مانح يتميز بمقدرته على كسر الروابط الجسرية في المركبات متعددة المركز.

**KEYWORDS:** SCN<sup>-</sup> complexes; UV-charge transfer bands, intermolecular H-bonding, Symmetry, Jahn- Teller distortion.

### INTRODUCTION

The environment in which Cu(II) ions are characteristically found, tetragonally distorted octahedra and square planer, (D<sub>4h</sub>) contain less number of symmetry operations

compared to the cubic groups (Oh and Td). Because of the relatively lower symmetry of the D<sub>4h</sub> group, detailed interpretations of spectra and magnetic properties are somewhat complicated even though one is dealing with the equivalent of a one electron case. For a

$d^9$  complex (e.g Cu(II) complex) in an octahedral ligand field the energy level diagram is obtained by inverting that of the  $d^1$  complex<sup>(1)</sup>. The inversion applies because the ground state of a  $d^9$  configuration is doubly degenerate ( $t_2g^6 eg^3$ ) and the excited state is triply degenerate ( $t_2g^5 eg^4$ ). Therefore the transition is  ${}^2E_g \rightarrow {}^2T_{2g}$ . In effect the electronic transition causes the motion of a positive hole from the (eg) energy level in the ground state to the ( $t_2g$ ), energy level in the excited state and the appropriate energy diagram (Orgel diagram) results by inverting that for the electronic transition for a  $d^1$  case. Thus for Cu (II) ( $d^9$ ) one is effectively dealing with a simple system, theoretically, as it can be considered as a single positive hole in an otherwise filled  $d^{10}$  configuration (this phenomenon is referred to as the hole formalism). Virtually all Cu (II) complexes and compounds are blue or green. Exceptions are generally caused by strong uv- charge transfer bands tailing off into the blue end of the visible spectrum causing substances to appear or brown<sup>(1)</sup>. The blue or green colors are due to presence of an absorption band in the 600-900 nm region. Complexes of the thiocyanate ion are known for most of the complex forming metal ions. One aspect of these complexes, which has been of interest, is the mode of bonding of thiocyanate ligand. According to Pearson<sup>(1)</sup>, the nitrogen end of this ligand is a hard base expected with "class a" metal ions while S-bonding is expected with "class b" metal ions. Since many systems (metal ions) are intermediate and the behavior can be influenced by other coordinated ligands or even non-coordinated ions, the bonding in a given case is not always obvious. The thiocyanate ligand has been widely studied by infra-red spectroscopy, which provides

a means of establishing the mode of bonding. In tetrahedral complexes only three vibrational modes are expected for the thiocyanate group in the near infrared region assigned to the C-N and C-S stretches and NCS deformation. Any of the above modes may be split by deviation of the complex from high symmetry or by crystal site symmetry in solid complexes and overtones may occur<sup>(2)</sup>. The position of the C-S stretching frequency is considered diagnostic of the mode of coordination of the thiocyanate ligand<sup>(3)</sup>. Frequencies near  $700\text{ cm}^{-1}$  indicate S-bonding, while those near  $800\text{--}830\text{ cm}^{-1}$  indicate N-bonding. The low intensity of the N-bonding band is also diagnostic, although it is often mistaken for  $\delta_{NCS}$  or difficult to identify in the presence of organic ligands or counter ions. The C-N stretching mode shows a slight down shift below the ion value ( $2053\text{ cm}^{-1}$  in KSCN) in the case of N-bonding, while S-bonding results in an up shift to near  $2100\text{ cm}^{-1}$ <sup>(4)</sup>. A third criterion based on the NCS deformation was proposed by Sabatini and co-workers<sup>(5)</sup>. A single, sharp band near  $480\text{ cm}^{-1}$  indicates N-bonding while S-bonding is suggested by several bands of low intensity near  $420\text{ cm}^{-1}$ . There are many systems of interest to chemists that can be treated by the simple techniques of group theory. For example, one can easily determine the number and symmetries of molecular vibrations associated with any molecule of known point group. Furthermore, a chemist can determine the number of active infra-red and Roman lines depending on the symmetry group of the molecule<sup>(6)</sup>. In this work the preparation of a number of Cu(II) mixed ligand complexes containing diamino and thiocyanato ligands is described. The use of infra-red spectroscopy in elucidating the

mode of coordination of the thiocyanate ligand and accordingly the Cu(II) ion in view of its affinity for S versus N is discussed. The possibility of linkage isomerism in these complexes is also examined. In a recent publication, the possibility of linkage isomerism in thiocyanate complexes has been reported<sup>(7)</sup>.

## **MATERIALS and METHODS**

### **Materials and Equipments**

All preparations and handling of materials were carried out in simple standard equipment and apparatus. All chemicals and reagents used in this work were supplied by the chemistry department of Garyounices University, and were of AR grade, and were used directly without any further purification.

### **Preparation of Complexes**

Cu (dp) (SCN)<sub>4</sub>, Cu (dp)<sub>2</sub> (SCN)<sub>2</sub> and Cu(dp)(SCN)<sub>2</sub> complexes were prepared and isolated as follows: 3gm (0.018 moles) of copper (II) chloride dihydrate CuCl<sub>2</sub>·2H<sub>2</sub>O, were dissolved in 20 ml ethanol, and treated dropwise with 6.6gm (0.09 moles) of excess ammonium thiocyanate, NH<sub>4</sub>SCN, in 30 ml ethanol, at room temperature during which the colour of the solution changed from green to brown. To this mixture, 2.7ml (0.05 moles) of 1,3-diaminopropane, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (dp), dissolved in 10 ml ethanol was added dropwise with constant stirring at room temperature. Addition of the first drops of 1,3- diaminopropane afforded a bluish solution and subsequently the precipitation of a mixture of violet and blue solids with further addition of 1,3-diaminopropane. The reaction mixture

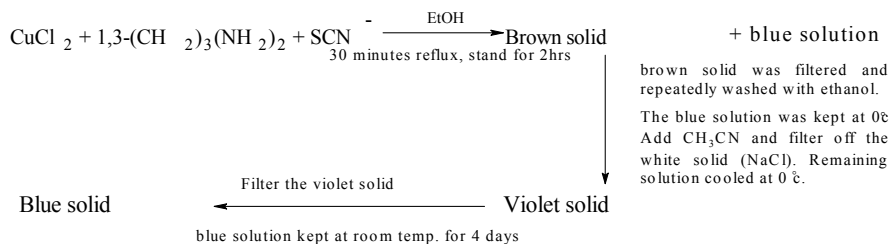
then refluxed for 30 minutes. The reaction mixture was allowed to stand for 2 hours, and subsequently filtered yielding a brown solid and a blue solution. The brown solid was washed repeatedly with ethanol and analysed for C, H, N and Cu. The blue solution was kept at 0°C for 24 hours resulting in a mixture of white, violet and blue solids. The white solid, tested to be NaCl was filtered off by dissolving the violet and blue solids in CH<sub>3</sub>CN. Further cooling of this solution resulted in the slow precipitation of a violet crystalline solid. The remaining blue solution was left at room temperature and this resulted in the precipitation of a blue crystalline solid over a period of 4 days.

### **Characterization**

All infrared spectra were made on a Pye Unicam infrared Spectrophotometer Model SP-100. Solid samples were thoroughly grinded in an agate mortar with pure paraffin oil for the region 3800- 625 cm<sup>-1</sup> using NaCl plates. Solution infrared spectra were carried out neat between NaCl plates. Measurements of ultraviolet and visible spectra were carried out using a Pye-Unican Model SP-1700 spectrophotometer. Analysis for Cu, N, and H was carried out by the Chemistry Department, University of Aston in Birmingham, Gosta Green, Birmingham 4, England.

### **RESULTS and DISCUSSION**

Mixtures of Cu(II) chloride, excess thiocyanate and (dp) in ethanol yielded three complexes in successive crops. The schematic diagram, below, summarizes the successive separation of the three complexes.



Scheme 1. Schematic diagram for the separation of the three products from the reaction mixture of Cu(II) chloride with excess thiocyanate and 1,3-diaminopropane in ethanol.

On the basis of elemental analysis, table (1), the brown solid is formulated as Cu<sub>2</sub>(dp)(SCN)<sub>4</sub>. The infrared spectrum of this complex, (Fig.1), showed bands in the ν<sub>CN</sub> region at 2010cm<sup>-1</sup> (s,sh) and 2080cm<sup>-1</sup> (v.s) and 2120cm<sup>-1</sup> (w.s) and 2180cm<sup>-1</sup>(v.s) strongly suggesting a dimeric species. Similar results have been reported by C. P. Panntone and co-workers<sup>(8)</sup>. The bands at 765 cm<sup>-1</sup> and 735 cm<sup>-1</sup> in the ν<sub>CS</sub> region strongly suggest S-bonding of the thiocyanate groups<sup>(9)</sup>. The band at 690 cm<sup>-1</sup> is due to coordinated 1,3-diaminopropane. Further evidence for dimeric structure is provided by the insolubility of the brown solid in most of the common solvents; dissolving quite readily in pyridine which is recognized as a donor solvent capable to cleave catenating bridges in

polymeric species. On the basis of this dimeric structure, linkage isomers involving either S- or N-bonding in the bridge positions are not ruled out. On the basis of the infrared spectrum and the solubility in pyridine, two different dimeric structures are possible for the brown solid.

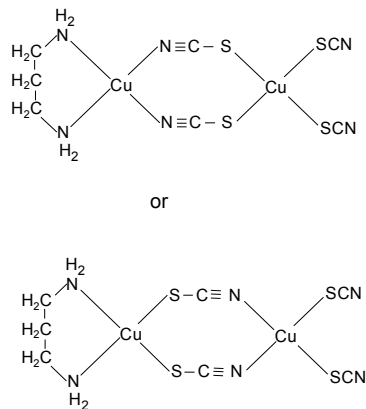


Table 1: Analytical data for the Brown solid

Percentage %	Cu	H	C N
Found	28.8	2.2	16.1 19.0
Calculated for	29.3	2.3	19.4 19.4
			Cu <sub>2</sub> (dp)(SCN) <sub>4</sub>

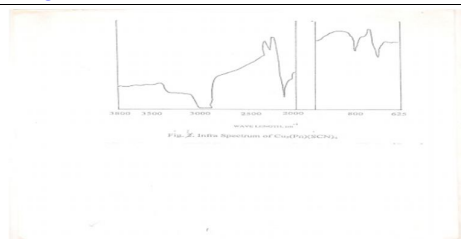


Figure 1: Infrared Spectrum of  $Cu_2(dp)(SCN)_4$

The elemental analysis of the violet solid, (Table2), is consistent with the formulation,  $Cu(dp)_2(SCN)_2$ . Evidence for the mode of bonding of the thiocyanate groups is provided by infrared spectrum, (Figure.2).

Table 2: Analytical data for the Violet complex

Percentage %	Cu	H	C	N
Found	19.2	5.9	28.9	25.4
Calculated for	19.5	6.1	29.3	25.6
			$Cu(dp)_2(SCN)_2$	



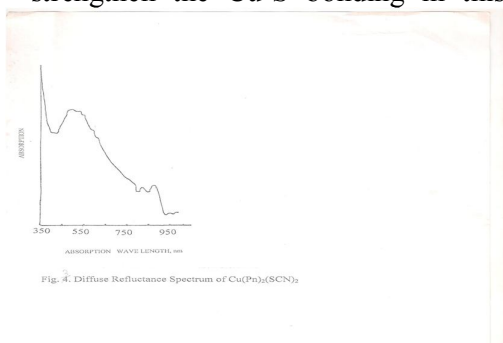
Figure 2: Infrared Spectrum of  $Cu(dp)_2(SCN)_4$

The infrared band near  $700\text{ cm}^{-1}$  in the  $\nu_{CS}$  region indicates S-bonding of the thiocyanate groups. In the  $\nu_{CN}$  region the single sharp band at  $2080\text{ cm}^{-1}$ , confirms S-bonding, appears at a slightly lower frequency. Furthermore, the spectrum of this complex indicates unambiguous evidence for the existence of intermolecular hydrogen bonding involving the amine hydrogens. The N-H stretching frequency is substantially shifted to lower frequency and the absorption band assigned to  $\nu_{NH}$  is appreciably

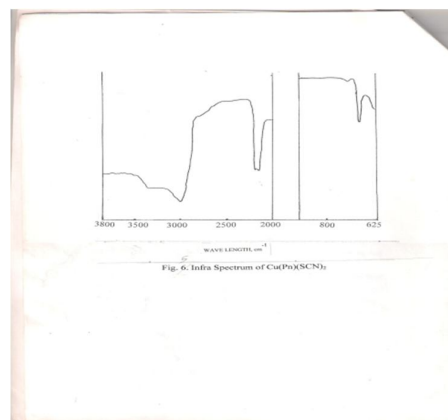
broadened,  $3060\text{-}3300\text{ cm}^{-1}$ . Nozary and co-workers have reported similar results with regard to  $\nu_{OH}$  in free phenols and hydrogen-bonded phenols<sup>(9)</sup>. The presence of intermolecular H-bonding further supports the S-bonding of the thiocyanate groups and accounts for the relatively lower frequency of this band through the interactions of free nitrogens of thiocyanate groups with the hydrogens of the amine groups. The bond order of the  $-C\equiv N$  moiety would consequently decrease

slightly due to H-bonding resulting in shifts to lower frequency (less than  $2100\text{cm}^{-1}$ ) for  $\nu_{\text{CN}}$  of the S-bonded thiocyanate. The bonding of thiocyanate groups in cis positions would be expected to show two infrared active bands in the  $\nu_{\text{CN}}$  region ( $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$ ); whereas trans-axial coordination with  $D_{4h}$  distorted structure would show a single infrared active band in the  $\nu_{\text{CN}}$  region. The symmetric band,  $\nu_{\text{sym}}$ , is infrared inactive, but Raman active. Accordingly,  $\text{Cu}(\text{dp})_2(\text{SCN})_2$  is formulated as trans tetragonally distorted complex. However, the effect of H-bonding is likely to reduce the extent of Jahn-Teller distortion and strengthen the Cu-S bonding in this

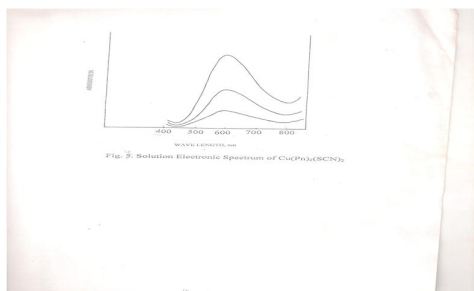
complex. The diffuse reflectance spectrum of this complex, (Figure.3), is compatible with a slightly distorted octahedral structure ( $\lambda_{\text{max}}$ . 500 and 800 nm). In solutions of acetonitrile it is completely ionized conducting as a 1:2 electrolyte ( $\wedge_{\text{M}} = 150 \text{ MHOS}$  in  $10^{-3} \text{ M}$  solution). The profile of the solution spectrum of the absorbing solvated species ( $\lambda_{\text{max}}$ . 600nm;  $\epsilon_{\text{m}}$  86, Figure.4) is different from the solid state spectrum. The similarity of the solution spectra for different dilutions further supports the complete ionization of this complex into the same solvated species, in these solutions.



*Figure3: Diffuse Reflectance Spectrum of  $\text{Cu}(\text{dp})_2(\text{SCN})_2$*



*Figure5: Infrared Spectrum of  $\text{Cu}(\text{dp})(\text{SCN})_2$*



*Figure4: Solution Electronic Spectrum of  $\text{Cu}(\text{dp})_2(\text{SCN})_2$*

The elemental analysis of the blue solid, which slowly deposits from the filtrate of the violet complex, (Table 3), is consistent with the formulation as a monochelate complex  $\text{Cu}(\text{dp})(\text{SCN})_2$ . The solid state infrared spectrum of

this complex in the  $\nu_{\text{CN}}$  and  $\nu_{\text{CS}}$  regions (Figure.5) provides unequivocal evidence for bonding of both thiocyanate groups through the sulphur atoms. Two sharp, strong bands at  $2110$  and  $2140 \text{ cm}^{-1}$ , not only exclude the possibility of a polymeric structure with bridging thiocyanate groups, but lend definitive support for its formulation as a four coordinate monomer<sup>(10)</sup>. An unsymmetrical planar complex with two cis thiocyanate groups would show two infrared active

bands in the  $\nu_{\text{CN}}$  region; namely  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$ . The appearance of two such bands for this complex is therefore suggestive of a square planar structure. The broad band at  $765 \text{ cm}^{-1}$  in the  $\nu_{\text{CS}}$  region indicates S-bonding, while the

band at  $690 \text{ cm}^{-1}$  is assigned to coordinated 1,3-diaminopropane (11,12,13). There is also evidence of H-bonding; presumably intermolecular in this complex.

Table 3: Analytical data for the blue complex

Percentage %	Cu	H	C	N
Found	24.7	3.88	23.4	22.3
Calculated for	24.9	3.94	23.7	22.13

Cu(dp)(SCN)<sub>2</sub>

The diffuse reflectance spectrum of the blue solid (Figure.6)  $\{\lambda_{\text{max}} 550 \text{ nm. (sh), 790 \text{ nm. (sh), and } 970 \text{ nm. (sh)}\}$  was not well resolved due to the tailing off of a charge transfer transition into the visible region. However, the spectrum is typical of Cu(II) ions in an unsymmetrical planar environment. It is also different from the diffuse reflectance spectrum of the violet solid, (Figure.3), implying dissimilar environments in these two complexes. Solution spectra in acetonitrile (Figure.7,  $\lambda_{\text{max}} 604 \text{ nm}$ ) are different from the solid state spectrum due to solvation and ionization of the complex ( $\lambda_{\text{M}} 93 \text{MHOS}$  for  $10^{-3} \text{ M}$  solutions). The similarity of the solution electronic spectra for different dilutions suggests the complete ionization of this complex into the same solvated species, (Figure.7).

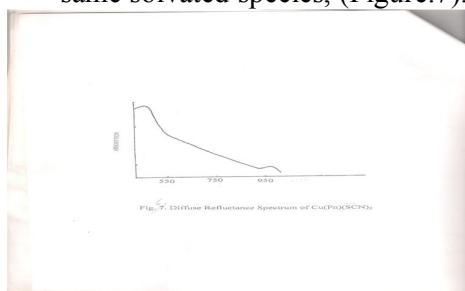


Figure 6: Diffuse Reflectance Spectrum of  $\text{Cu}(\text{db})(\text{SCN})_2$

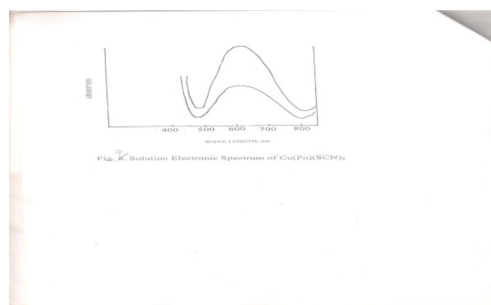


Figure 7: Solution Electronic Spectrum of  $\text{Cu}(\text{dp})(\text{SCN})_2$

## CONCLUSIONS

The reaction of excess thiocyanate ion with Cu(II) chloride in presence of the chelating ligand 1,3- diaminopropane in ethanol yielded successively brown, violet, and blue complexes. The brown complex  $\text{Cu}_2(\text{dp})(\text{SCN})_4$  is a dimer with bridging thiocyanates. The electronic spectra of the solid state and of the pyridine solutions, ion exchange studies of the pyridine solutions and E.S.R measurements are further investigations necessary to characterize this complex unambiguously. The violet complex is formulated as  $\text{Cu}(\text{dp})_2(\text{SCN})_2$  with two S-bond thiocyanates in a tetragonally distorted environment around Cu(II) ion. The existence of intramolecular hydrogen bonding, however, is felt likely to reduce the extent of this distortion. Further studies with similar bidentate chelating ligands is necessary to

interpret meaningfully the effect of hydrogen bonding upon the magnitude of tetragonal distortion in hexa coordinate Cu(II) complexes. The blue complex, Cu(dp)(SCN)<sub>2</sub>, which is separates last from the ethanolic solution is formulated as a four coordinate square planar complex with two S-bond thiocyanates groups.

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