# Infrared Absorption Spectral Studies of the Complexes with Substituted 2-Thioureas. I. Bis(1-phenyl-2-thiourea)copper(I) Chloride

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Several co-ordinated complexes in which the ligands are urea and 2-thiourea have been reported. Quagliano and his co-workers[1] have established that, among the urea complexes, some are co-ordinated through one of the nitrogen atoms, and the others, through the oxygen atom of the urea molecule. They have then extended these studies to 2-thiourea and 1-methyl-2-thiourea complexes,[2,3] and have concluded that although the co-ordination takes place either through the sulphur atom or one of the nitrogen atoms when 1-methyl-2-thiourea is a ligand, the sulphur atom is exclusively involved in the co-ordination in the 2-thiourea complexes. Rivest[4] came to a similar conclusion from his studies of the co-ordinate complexes of titanium(IV) chloride with alkyl and aryl substituted 2-thioureas. More recently Berni and others[5] have studied the properties of the metal ion complexes of ethylene urea (2-imidazolidinone).

The present investigations were undertaken in order to examine the influence of substituents such as alkyl, aryl and acyl[6] groups on the relative donor abilities towards co-ordination of either the sulphur or the nitrogen atom of the 2-thiourea.

Cuprous salts form many complexes with ligands such as 1-phenyl- and 1-acetyl-2-thioureas in different mole-ratios.[7] This note will present the results of the infrared absorption studies of $CuCl\cdot 2C_6H_5NHCSNH_2$.

## Experimental

**Preparation of the Compound**—Eastman-Kodak white-label 1-phenyl-2-thiourea was used without further purification. The $CuCl_2\cdot 2H_2O$ used was of the reagent grade. Bis(1-phenyl-2-thiourea)copper(I) chloride was prepared according to the method of Banerjee and Sukthankar[7]; it was recrystallised from acetone and dried in a vacuum desiccator for a constant analysis.

**Absorption Measurements**—The spectra were obtained with a Perkin-Elmer recording infrared spectrophotometer, model 21. A sodium chloride prism was used over the complete infrared region to be reported on. As a routine, polystyrene film was used for the wave number calibration. The spectra were taken using the KBr disc technique and were checked using Nujol and fluorolube mulls. The spectra obtained are illustrated in Fig. 1, while the experimental results, along with the corresponding assignments of the frequencies, are given in Table I.

## Results and Discussion

As a necessary prerequisite, the assignments required for this analysis were made on a comparative basis, mainly with 2-thiourea and 1-methyl-2-thiourea,[2,3] since there are no adequate published assignment data on 1-phenyl-2-thiourea.[8] For phenyl-ring and ring-hydrogen vibrations, the assignments of Randle and Whiffen[9] were used.

The absence in the 2500—2600 $cm^{-1}$ region of the absorption band characteristic of the SH group in the spectra of the complex and the ligand (1-phenyl-2-thiourea) indicates that the ligand is in its thiocarbonyl resonance form.

The formation of $S\rightarrow M$ bonds is expected to result in an increased double-bond character for the carbon-to-nitrogen bond and a lowering of it for the carbon-to-sulphur bond.

A comparison of the spectrum of 1-phenyl-2-thiourea with that of the copper(I) complex shows that the general spectral profile of the complex in the 3 $\mu$ region is almost unchanged. These bands, which can be assigned to N–H absorptions, are neither shifted to significantly lower frequencies not split into groups with a decrease in intensity, on the formation of the complex. This indicates the absence of nitrogen-to-metal bonds; therefore, the bonding must be between sulphur and the metal atoms. The broadening of these bands can be attributed to a considerable amount of hydrogen bonding, perhaps a $Cl\cdots H\text{–}N$ type of hydrogen bonding, in the complex.[10]

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[10] W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, **17**, 530 (1961).

TABLE I. INFRARED FREQUENCIES (cm$^{-1}$) AND ASSIGNMENTS FOR 1-PHENYL-2-THIOUREA AND BIS(1-PHENYL-2-THIOUREA)COPPER(I) CHLORIDE

| $C_6H_5NHCSNH_2$ | $CuCl \cdot 2C_6H_5NHCSNH_2$ | Assignment |
|---|---|---|
| 3440 s | 3450 ms | NH stretching |
| 3280 s | 3285 s | |
| 3180 vs | 3180 s | |
| 3025 mw | ~3040 sh | CH sym. stretching |
| 1614 vs | 1616 vs | $NH_2$ bending |
| 1593 ms | 1596 s | CC stretching |
| | 1546 sh | |
| 1527—1522 s, b | 1536 vs | NH deformation + CN antisym. stretching |
| 1490 m | | CC stretching |
| 1465 m | 1498 s | NCN stretching + CC stretching |
| 1451 s | 1452 s | CC stretching |
| | 1420 mw | |
| 1316 ms | 1321 ms | CC stretching |
| 1295 m | 1298 m | CN antisym. stretching + NH deformation |
| 1274 m | 1265—1260 m, b | |
| 1259 m | 1253 sh | CH in-plane deformation + X sensitive* |
| 1231 m | 1243—1233 m, b | |
| 1168 vw | 1173 vw | CH in-plane deformation |
| 1153 vw | 1155 vw | CH in-plane deformation |
| 1073 mw | 1081 sh | CH in-plane deformation |
| 1062 m | 1066 mw | CS stretching + CN sym. stretching + $NH_2$ rocking |
| 1025 vw | 1027 vw | CH in-plane deformation |
| 998 vw | 1004 vw | Ring breathing |
| 918 vw | 910 vw | CH out-of-plane deformation |
| 855 vw | 853 vw | CH out-of-plane deformation |
| 811 mw | 795 mw | CS stretching + CN sym. stretching and X sensitive* |
| 750 ms | 747 ms | CH out-of-plane deformation and NH out-of-plane bending |
| ~ 707 sh | | Ring out-of-plane deformation |
| 693 ms | 692 ms | Ring out-of-plane deformation |

* In monosubstituted benzenes ($C_6H_5X$) there are six fundamental frequencies, out of the possible thirty, sensitive to the mass and the nature of X, the substituent ($-NHCSNH_2$ in the present case). These are classified as X sensitive. The two bands observed here are mainly CX stretching vibrations with some contribution from one of the ring breathing vibrations and CX in-plane deformation vibration.[9]

Abbreviations : s = strong ; m = medium ; w = weak ; sh = shoulder ; b = broad ; v = very.

The strong broad band at 1522—1527 cm$^{-1}$ can be explained as an "hydrid" band due to N–H deformation and C–N antisymmetric stretching vibrations. On co-ordination, this band is shifted to a higher frequency, indicating the increased double-bond character of the C–N bond and, hence, co-ordination through the sulphur atom. Similar behaviour was observed in complexing in the case of 2-thiourea and 1-methyl-2-thiourea.[2,3]

The N–C–N stretching band at 1465 cm$^{-1}$ in the 1-phenyl-2-thiourea corresponds to the 1470 cm$^{-1}$ band of 2-thiourea. The frequency of this band is increased by about 33 cm$^{-1}$ on complexing, again indicating an increased double-bond character of the carbon-to-nitrogen bond.* A similar shift has been observed by Kutzelnigg and Mecke[10] in the $CuCl \cdot 4CH_3CSNH_2$ complex.

A marked difference in the spectrum of the free ligand and its metal complex appears in at about 1100 cm$^{-1}$. A sharp absorption band at 1062 cm$^{-1}$ of 1-phenyl-2-thiourea, corresponding to the 1083 cm$^{-1}$ and 972 cm$^{-1}$ bands of 2-thiourea and 1-methyl-2-thiourea[2,3] respectively, is very much broadened and weakened. The contribution of the C=S vibration and, hence, the intensity of this band is decreased on co-ordination through the sulphur atom. The symmetric N–C–N stretching

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* It seems likely that this band corresponds to the "thioureide" band assigned by Randall and others[11] between 1613—1471 cm$^{-1}$, by Ettlinger,[12] at 1508 cm$^{-1}$ and by Mann,[13] at 1495 cm$^{-1}$.

[11] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York (1949).

[12] M. G. Ettlinger, *J. Am. Chem. Soc.*, **72**, 4699 (1950).

[13] J. Mann, *Trans. Inst. Rubber Ind.*, **27**, 232 (1951).

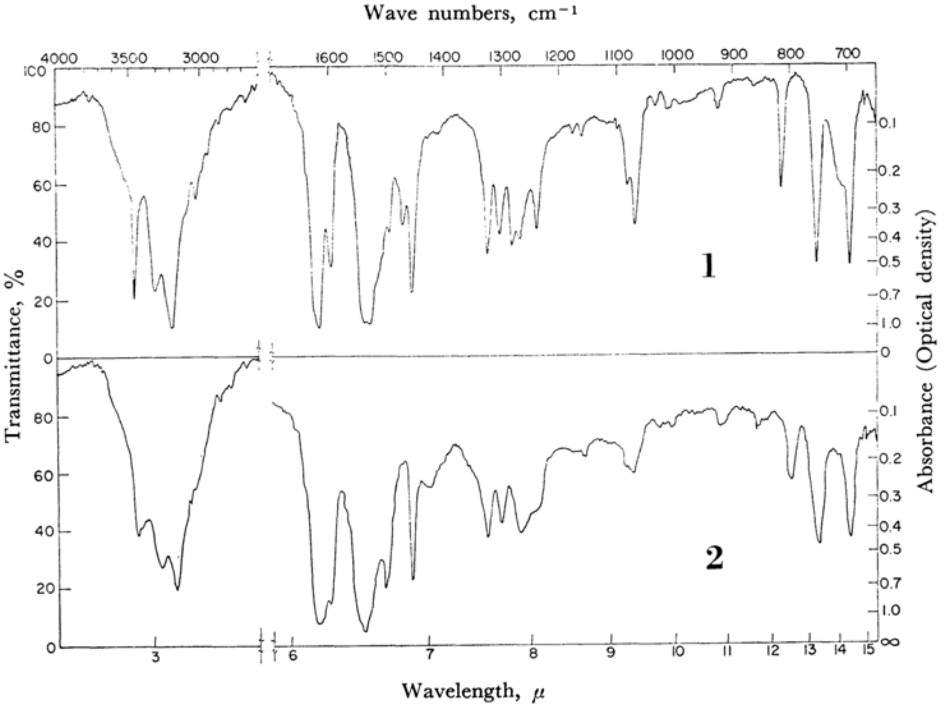

Fig. 1. Infrared spectra in KBr disk.
1. 1-phenyl-2-thiourea 2. Bis(1-phenyl-2-thiourea)copper(I) chloride

vibration can not contribute much to this band, as has been shown for the spectra of urea and 2-thiourea; this explains the overall decrease in intensity. A similar weakening or complete disappearance of a band was observed in co-ordination through sulphur in the case of 2-thiourea and 1-methyl-2-thiourea.[2,3]

The band at 811 cm$^{-1}$ of 1-phenyl-2-thiourea is considered to correspond to the 731 cm$^{-1}$ and 774 cm$^{-1}$ bands in 2-thiourea and 1-methyl-2-thiourea respectively,[2,3] bands arising mainly from the C=S stretching vibration, though with a little contribution from the symmetric C–N stretching vibration. The lowering of this frequency by about 16 cm$^{-1}$ can be attributed to the reduced double-bond character of the carbon-to-sulphur bond.

The above-mentioned three bands could also be identified as "–N–C=S" I, III and IV bands respectively, according to Rao.[14] However in the region to which he assigned the "–N–C=S"–II band, no definite conclusions could be drawn, mainly because of the other overlapping regions.

No significant changes have been observed in the remaining bands of the spectra of the ligand on complexing; this is not unexpected, as these could be identified as arising from the presence of the phenyl ring and from the ring hydrogen vibrations.[9]

The co-ordination of 1-phenyl-2-thiourea to copper(I) shifts certain infrared absorption frequencies, notably at about 1450, 1100 and 800 cm$^{-1}$; these shifts can be correlated with the changes in the double-bond character of the C–S and C–N bonds. Such a situation suggests a considerable covalent character of the sulphur-copper bonds, indicating a ligation through the sulphur atom in a complex.

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[14] C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press., New York and London (1963), p. 303.