

## IR SPECTRA OF COPPER(I) THIOCYANATE COMPLEXES

M.A.S.GOHER

Department of Chemistry, Faculty of Sciences,  
Alexandria University, Egypt

Received July 2nd, 1976

Eleven copper(I) complexes of the type  $L.CuSCN$  have been prepared ( $L =$  pyridine, 2- and 4-picolines, 2,4-, 2,5- and 2,6-lutidines, *s*-collidine, methyl- and ethyl nicotinate, methyl and ethyl isonicotinate), which are diamagnetic and stable on air. Only those derived from ligands with electron attracting substituents (*i.e.* the nicotinates) show  $M-L$  bands. Based on the infra-red IR absorption spectra these complexes are assumed to be binuclear dimers or polynuclear chains with bridging thiocyanate group, which increases the coordination number to three.

The linear thiocyanate group can coordinate either through the sulfur or nitrogen atoms or both. Livingstone<sup>1</sup> has pointed out that the thiocyanate group generally coordinates to class "a" metals<sup>2</sup> through nitrogen and to class "b" metals<sup>3</sup> through sulfur. From the X-ray data<sup>4,5</sup>, the first transition series elements are known to be N-bonded. Criteria for establishing the mode of bonding of the thiocyanate ligand in various complexes of the transition metals by IR spectroscopy have been worked out, based on the frequency range found for the three vibrational modes of the thiocyanate group (in  $cm^{-1}$ ): 2200–2000 for  $\nu_{CN}$  (ref.<sup>6,7</sup>), 860–690 for  $\nu_{CS}$  (ref.<sup>8,9</sup>) and 500–410 for the degenerated  $\delta_{SCN}$  (ref.<sup>10-12</sup>). Absorptions in the 720–690  $cm^{-1}$  region have been accepted as indicating  $M-SCN$  bonding while those about 860–760  $cm^{-1}$  indicate  $M-NCS$  bonding. The S-bonded ligands exhibit a very sharp, well-developed CN stretching peak above 2100  $cm^{-1}$  whereas N-bonded ligands give relatively broad, more intense peaks around or below 2100  $cm^{-1}$ . In addition the weak and medium bands between 440–410  $cm^{-1}$  and 490–460  $cm^{-1}$  also indicate  $M-SCN$  and  $M-NCS$  bonding, respectively.

Recently, we have been interested in the study of copper(I) complexes with some pyridine derivatives<sup>13-15</sup> of the type  $L_nCuX$  prepared by reduction of copper(II) sulfate or chloride in presence of the ligand  $L$  (pyridine derivative) by ascorbic acid followed by addition of the desired anion  $X^-$  (*i.e.*  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $CN^-$ ,  $SCN^-$ ). As an extension of that work and since only few examples of copper(I) thiocyanate complexes have been reported<sup>16,7</sup>, we tried to prepare the thiocyanate complexes with such pyridine derivative ligands. In this paper the isolated  $L.CuSCN$  complexes are described and their structures are considered on the basis of IR spectroscopy.

## EXPERIMENTAL

The liquid ligands were purified by GLC. The other chemicals were analytical grade and commercially available.

Magnetic measurements were made by the Faraday method at room temperature using an apparatus described elsewhere<sup>18</sup>. X-ray powder patterns were taken on a Mikrometa 2 (Chirana, Prague) instrument,  $\varnothing = 53.3$  mm, with  $\text{CuK}\alpha$  radiation. Reflectance spectra of the solids were measured on a VSU-1 (Zeiss, Jena) instrument with  $\text{MgO}$  as a standard and diluent. IR spectra in the  $4000\text{--}400\text{ cm}^{-1}$  region were measured on a Zeiss (Jena) spectrometer UR-20. The solid samples were measured as Nujol mulls and KBr pellets and the liquid pyridine derivatives as capillary film.

Micro-analysis of C, H, N were carried out on a Perkin-Elmer 240 elemental analyzer. Copper was determined gravimetrically as  $\text{CuSCN}$  or by titration against disodium ADTA after degradation and oxidation of the complexes with boiling mixtures of concentrated  $\text{H}_2\text{SO}_4$  and 30%  $\text{H}_2\text{O}_2$ .

#### Preparation of the Complexes

The complexes were prepared according to the published<sup>13</sup> method. In the case of methyl nicotinate the complex was prepared as follows. After precipitation of the yellow perchlorate  $(\text{Men})_3 \cdot \text{CuClO}_4$  according to the general method, a solution of potassium thiocyanate was added at vigorous stirring until the canary yellow disappeared and a faint yellow powder was obtained. The IR spectrum of this powder showed that it is completely free from traces of perchlorate ion. All complexes were filtered off at the pump and washed several times with water, ethanol, and then dried.

### RESULTS

The isolated complexes are characterised in Table I. In Table II the vibrational frequencies of the thiocyanate group in the complexes are collected. Location of the thiocyanate bands in the regions  $\nu_{\text{SC}}$  and  $\delta_{(\text{SCN})}$  absorption was accomplished by comparison of the spectra of the complexes  $\text{L}_n\text{CuSCN}$  with those of the free pyridine derivatives and their copper(I) halide complexes  $\text{L}_n\text{CuX}$  ( $\text{X} = \text{halogen}$ ).

All the isolated complexes are diamagnetic, sufficiently stable on air, and insoluble in acetone, water and alcohols. In chloroform the yellow complexes dissociate into  $\text{CuSCN}$  and free nicotinate.

The chemical individuality of the prepared complexes was proved by comparison of their X-ray powder patterns with that of simple  $\text{CuSCN}$ .

### DISCUSSION

It is seen from Table I that copper(I) thiocyanate complexes derived from ligands with electron attracting substituents are yellow colored or nearly so. Their color is certainly due to  $\text{Cu}(d^{10}) \rightarrow \text{L}(\pi^*)^{19}$  charge transfer transition, which appeared at  $420\text{--}400$  nm. The complexes derived from the other ligands are white and did not show  $\text{M} \rightarrow \text{L}$  charge transfer bands. This is reasonable since the electron attracting groups cause a shift of the electron density from the pyridine ring to the substituent which decreases the electron density on the nitrogen atom. This effect enhances the  $\text{M} \rightarrow \text{L}$  charge transfer transitions. In case of the ligands with electron releasing substituents the reverse effect can be anticipated and thus the  $\text{M} \rightarrow \text{L}$  transitions are not observed.

Complexes I–XI are insoluble in most of the organic solvents and similarly to the copper(I) ion, having  $d^{10}$  configuration, did not show  $d-d$  transitions. Therefore, the structure of the complexes can not be derived from their electronic spectra. The most valuable information about the ligand coordination can be obtained from IR spectra of the solids.

The IR spectra of the complexes showed that all ligands are coordinated to Cu through the nitrogen atoms<sup>13,20,21</sup>. Since detailed analyses of the ligand spectra

TABLE I  
Analytical Data for (L)Cu(SCN) Complexes

L <sup>a</sup>	Calculated/Found, wt. %				Color of powder
	Cu	C	H	N	
py	31.40	35.40	2.58	13.90	white
	31.66	35.91	2.51	13.95	
2-pic	29.17	39.99	3.19	13.12	white
	29.60	39.14	3.28	13.03	
4-pic	29.20	39.43	3.24	12.90	white
	29.60	39.14	3.28	13.04	
2,4-lut	27.95	42.40	3.90	12.62	white
	27.68	42.26	3.96	12.22	
2,5-lut	27.46	42.11	3.94	12.38	white
	27.68	42.26	3.96	12.22	
2,6-lut	27.38	42.09	3.93	12.42	white
	27.68	42.26	3.96	12.22	
s-coll	27.00	46.25	4.75	11.98	white
	27.21	46.73	4.72	11.93	
Men	24.42	37.12	2.72	10.65	pale yellow
	24.56	37.15	2.70	10.81	
Mein	24.36	37.50	2.80	10.62	yellow
	24.56	37.15	2.70	10.81	
Etn	23.40	39.32	3.45	10.34	yellow
	23.30	39.44	3.33	10.26	
Etin	23.16	39.72	3.49	10.38	deep yellow
	23.30	39.44	3.33	10.22	

<sup>a</sup> py pyridine, pic picoline, lut lutidine, s-coll *sym.* collidine, Men methyl nicotinate, Etn ethyl nicotinate, Mein methyl isonicotinate, Etin ethyl isonicotinate.

have been examined for related compounds<sup>22</sup>, these general spectral properties are not concerned here.

Table II shows that complexes *I–XI* exhibit at least two CN stretching bands in the region 2170–1080 cm<sup>-1</sup>. The higher frequency band is sharp and well developed, splitted in some cases, and the other is of medium intensity. The higher frequency absorption may be due to S-bonding thiocyanate group, and the lower due to N-bonded group. The structure of the complex [(P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>.CuSCN] has been examined by X-ray analysis<sup>23</sup>. It exists as a dimer in which the thiocyanate group bridges the two copper atoms. This complex showed two CN stretching bands at 2112 cm<sup>-1</sup> and 2080 cm<sup>-1</sup> attributed to S- and N-bonding thiocyanate group, respectively. Tramer<sup>7</sup> and others<sup>24</sup> have pointed out that an increase of  $\nu(\text{C}\equiv\text{N})$  within 50–70 cm<sup>-1</sup> relative to free SCN<sup>-</sup> indicates a S-bonding. For N-bonded thiocyanate this increase is only 30–40 cm<sup>-1</sup>. A large increase of 70–170 cm<sup>-1</sup> is diagnostic for bridging groups. The free thiocyanate ion shows  $\nu(\text{C}\equiv\text{N})$  band at 2053 cm<sup>-1</sup>. In line with this correlation and with Table II, one could postulate bridging thiocyanate groups in our copper(I) complexes.

For  $\nu_{\text{SC}}$  which is most diagnostic of S- or N-bonding, the frequency range is 765 to 750 cm<sup>-1</sup> for the copper(I) thiocyanate complexes, which is a little wider than previously reported for S-bonded compounds<sup>8</sup>. For those copper(I) complexes where  $\nu(\text{S}-\text{C})$  could not be located in the 770–720 cm<sup>-1</sup> region due to strong absorption

TABLE II  
Positions (cm<sup>-1</sup>) and Intensities<sup>a</sup> of the Thiocyanate Bands in LCu(SCN)

Complex	L	$\nu(\text{C}\equiv\text{N})$		$\nu(\text{S}-\text{C})$	$\delta(\text{SCN})$
		Nujol	KBr		
<i>I</i>	py	2 136 vs	2 125 vs	2 080 w	480 w 445 m
<i>II</i>	2-pic	2 170 m	2 120 vs 2 165 w	2 120 vs 2 080 m	760 wm 470 w 440 m
<i>III</i>	4-pic	2 170 m	2 135 vs 2 170 w	2 130 vs 2 080 w	755 m 450 m
<i>IV</i>	2,4-lut	2 170 w	2 135 vs 2 170 w	2 120 vs 2 080 w	760 wm 450 w
<i>V</i>	2,5-lut	2 125 vs	2 165 w 2 120 vs	2 080 w	760 m 440 w
<i>VI</i>	2,6-lut	2 160 w	2 135 vs 2 160 w	2 130 vs 2 080 vs	760 m 430 w
<i>VII</i>	s-coll	2 170 w	2 125 vs 2 170 m	2 125 vs 2 085 m	765 m 460 w
<i>VIII</i>	Men	2 140 vs	2 140 vs 2 080 wm	750 m	460 w 410 w
<i>IX</i>	Mein	2 132 vs	2 130 vs 2 085 m		442 w
<i>X</i>	Etn	2 125 vs	2 130 vs 2 080 ms		445 w
<i>XI</i>	Etin	2 125 vs	2 180, 2 130 vs,	2 080 ms	445 w

<sup>a</sup> Abbreviations: w weak, s strong, m medium, v very.

by the organic ligands, the absence of bands between  $860-770\text{ cm}^{-1}$  still argued against N-bonding.

For the bonding mode of the thiocyanate group, all the complexes showed a weak to medium band in  $450-410\text{ cm}^{-1}$  region which is slightly higher than reported for other S-bonded thiocyanate complexes<sup>12</sup>. Compounds *I*, *II*, *VIII* showed another band above  $460\text{ cm}^{-1}$ . It may be due to the ligand absorption in this region, as the other complexes did not show a similar band.

The appearance of two bands (around  $450-410\text{ cm}^{-1}$  and above  $460\text{ cm}^{-1}$ ) for some of the prepared complexes, indicates bridging thiocyanate groups. This assignment indicating bridging thiocyanate ligands, would accord with insolubility of our compounds. The properties of the compounds suggests that their structure is made up of chains as could be inferred from the band positions.

Our results thus complement the published conclusions<sup>24</sup> that for study of solids the position of  $\delta_{(\text{SCN})}$  is of greatest use for diagnostic purposes in distinguishing between S- and N-bonded thiocyanate groups. However, the positions of  $\nu_{(\text{CN})}$  and  $\nu_{(\text{CS})}$  also are sensitive to the mode of bonding.

From the discussion, one can conclude that our copper(I) complexes are bridged thiocyanate compounds of a chain type and furthermore copper atom is attached to the sulfur atom more strongly than the nitrogen. Copper(I) ion therefore belongs to class "b" elements<sup>3</sup>. With such polymeric chain structures, copper(I) ion presumably has coordination number three and approximately a trigonal structure.

*The autor expresses his gratitude to Dr M. Drátovský, Department of Inorganic Chemistry, Charles University, Prague, for helpful discussions.*

#### REFERENCES

1. Livingstone S. E.: *Quart. Rev., Chem. Soc.*, *19*, 386 (1965).
2. Ahrland S., Chatt J., Davis N. R.: *Quart. Rev., Chem. Soc.* *12*, 265 (1958).
3. Craig D. P., Nyholm R. S.: *Chelating Agents and Metal Chelates*, p. 58. Academic Press, New York 1964.
4. Brown B. W., Lingafelter E. C.: *Acta Cryst.* *16*, 753 (1963).
5. Porai-Koshits M. A., Tishchenko G. N.: *Soviet Cryst.* *4*, 216 (1959).
6. Mitchell P. C. H., Williams R. J. P.: *J. Chem. Soc.* *1960*, 1912.
7. Tramer A.: *J. Chim. Phys.* *59*, 232 (1962).
8. Turco A., Pecile C.: *Nature* *191*, 66 (1961).
9. Lewis J., Nyholm R. S., Smith P. N.: *J. Chem. Soc.* *1961*, 4590.
10. Sabatini A., Bertini I.: *Inorg. Chem.* *4*, 959 (1965).
11. Clark R. J. H., Williams C. S.: *Spectrochim. Acta* *22*, 1081 (1966).
12. Aslam M., Assai W. H. S.: *Inorg. Nucl. Chem. Lett.* *7*, 96 (1971).
13. Goher M. A. S., Drátovský M.: *This Journal* *40*, 26 (1975).
14. Goher M. A. S., Drátovský M.: *Naturwissenschaften* *62*, 96 (1975).
15. Goher M. A. S., Drátovský M.: *Naturwissenschaften* *63*, 89 (1976).
16. Toeniskoetter R. H., Solomon S.: *Inorg. Chem.* *7*, 617 (1968).

17. Chauhan S. S., Sinha P. C., *J. Indian Chem. Soc.* *40*, 799 (1963), *45*, 1180 (1968).
18. Vilim F.: *Česk. Čas. Fyz.* *4*, 416 (1965).
19. Williams R. J. P.: *J. Chem. Soc.* *1955*, 137.
20. Gill N. S., Nuttall R. H., Scaife D. E., Sharp R. W. A.: *J. Inorg. Nucl. Chem.* *18*, 79 (1961).
21. Gill N. S., Kingdon H. J.: *Aust. J. Chem.* *19*, 2197 (1966).
22. Goldstein M., Mooney E. F., Anderson A., Gebbis H. A.: *Spectrochim. Acta* *21*, 105 (1965).
23. Gaughan A. P., Ziolo R. F., Dori Z.: *Inorg. Chim. Acta* *4*, 640 (1970).
24. Contreras G., Schmidh R.: *J. Inorg. Nucl. Chem.* *32*, 127 (1970).