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THERMAL PROPERTIES OF THIOCYANATOCOPPER(II) COMPLEXES WITH SOME MONODENTATE N-DONOR LIGANDS

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ABSTRACT

The thermal decomposition of $CuL_2(NCS)_2$, where L = NH_3, pyridine and its methyl- and halogenoderivates showed that variability in the chemical properties of ligands L manifestates itself in the different extent of the chemical change of NCS ligands.

INTRODUCTION

The thermal decomposition of a series of thiocyanatocopper(II) complexes with monodentate N-donor ligands $CuL_2(NCS)_2$, where L = NH_3, pyridine (py), 2-, 3-, 4-picoline (pic), 2,4-, 2,5-, 2,6-, 3,4-, 3,5-lutidine (lut), 3-chloropyridine (3-Clpy), 3-bromopyridine (3-Brpy), 3-iodopyridine (3-Ipy), 4-chloropyridine (4-Clpy), and 4-bromopyridine (4-Brpy) was studied.[1,2,3] The thermal properties of these pseudooctahedral complexes can be significantly affected by different basicity, π-bonding properties and also by inductive effect of substituents on pyridine ring of monodentate N-donor ligands.

MEASURING METHODS

The thermal decomposition was carried out on a derivatograph MOM, Budapest, in inert nitrogen atmosphere.

RESULTS AND DISCUSSION

The thermal decomposition of $CuL_2(NCS)_2$ complexes showed that various chemical properties of ligands L manifestate themselves not only in different decomposition temperatures of the complex, but also in different chemical changes of the coordinated thiocyanate ligands.

The $CuL_2(NCS)_2$ complexes may be divided by their decomposition temperature into two groups. The first group involving

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complexes with L = py, 3- and 4-pic, 3,4- and 3,5-lut, 3-Clpy, 3-Brpy and 3-Ipy has a decomposition temperature of 100 - 110 °C. The other group comprises the complexes for which ligand L contains a substituent in position 2. Their decomposition temperature decreased to 70 - 80 °C. The decreased thermal stability of the second group complexes is in good agreement with the smaller strenght of Cu-N(L) bonds due to spheric effects of ligands L.

The complexes $CuL_2(NCS)_2$ may be divided by the course of their thermal decomposition into four groups.

The complexes of the first group decompose according to scheme 1 or 2 under the formation of an intermediate of the composition of CuNCS.L.

Scheme 1: $CuL_2(NCS)_2 \xrightarrow{-L} CuNCS.NCS.L \xrightarrow{-(NCS)} CuNCS.L$

Scheme 2: $CuL_2(NCS)_2 \xrightarrow{-(NCS)} CuNCS.L_2 \xrightarrow{-L} CuNCS.L$

Scheme 1 is followed by the thermal decomposition of complexes with L = NH_3, while for complexes with L = 4-Clpy, 4-Brpy the decomposition course follows scheme 2.

The intermediate formed for complexes of the second group shows the composition of CuNCS.NCS and is obtained by thermal decomposition according to scheme 3 and 4.

Scheme 3: $CuL_2(NCS)_2 \xrightarrow{-L,-L} CuNCS.NCS$

Scheme 4: $CuL_2(NCS)_2 \xrightarrow{-2L} CuNCS.NCS$

Scheme 3 is obeyed by thermal decomposition of complexes with L = 3-Clpy, while complexes with L = 3-Brpy, 3-Ipy decompose according to scheme 4.

The third group of complexes with L = py, 3,5-lut yields the decomposition intermediate of 2 $CuNCS.S(NC)_2$ by scheme 5:

Scheme 5: $2\ CuL_2(NCS)_2 \xrightarrow{-(4\ L+S)} 2\ CuNCS.S(CN)_2$

To the fourth group belong the complexes with L = 2-pic, 3-pic, 4-pic, 2,4-lut, 2,5-lut, 2,6-lut and 3,4-lut. They decompose yelding the intermediates of nonstoichiometric composition, since the polymerization and decomposition reaction of the thiocyanate ligand are accompanied by the release of molecules of ligand L. The fourth group of complexes can be divided in to three subgroups according to a physico-chemical properties of the intermediates of thermal decomposition. Subgroup 1 is formed by intermediates of complexes with L = 4-pic, 3,4-lut, 2,4-lut;

Subgroup 2 cover intermediates of complexes with L = 3-pic, 3,5-lut, 2,5-lut;
Subgroup 3 include intermediates of complexes with L = 2-pic, 2,6-lut.

This division shows that the position of the methylsubstituent on the pyridine ring individually effects the course of thermal decomposition of $CuL_2(NCS)_2$ complexes with picoline ligands. The results is consistent with the information given above about the different influence of 4- and 3-halogen-substituted pyridine ligands.

It is interesting that the deepest thermal decomposition of thiocyanate ligands connected with the greatest loss of sulphur atoms was observed just for complexes with L = 4-pic. The study of thermal properties of complexes with lutidine ligands proves the exceptibility of the influence of position 4 on the pyridine ring upon the thermal decomposition course. Its determining effect on the chemical change of thiocyanate ligands was proved also for the case that on the pyridine ring there is another methylsubstituent in position 3 or 2.

CONCLUSION

Chemical changes of the ligand L caused by the variability of substituents and their position at pyridine ring in $CuL_2(NCS)_2$ complexes are manifestated:

- in the modification of their thermal decomposition course demonstrated by different degree in the chemical change of the coordinated NCS-ligands. Their deepest decomposition is connected with the greatest sulphur decrease and can be observed at 4-picoline complex,

- in the fact that only the methylsubstituent at the 2-position of the pyridine ligand L influences the thermal stability of the above complexes.

REFERENCES

1. **M.Kabešová,T.Šramko,J.Gažo,E.K.Žumadilov and V.I.Nefedov, J.Therm.Anal.13,55(1978).**
2. **M.Kabešová,I.Vargová,T.Šramko and J.Gažo,J.Therm.Anal.13,65 (1978).**
3. **R.Gireth,Diploma work,Faculty of Chemical Technology,Slovak Technical University,Bratislava,1980.**