Thermochimica Acta, 92 (1985) 807-810
Elsevier Science Publishers B.V., Amsterdam

THERMAL PROPERTIES OF THIO- AND SELENOCYANATOCOPPER(II) COMPLEXES WITH SOME N-DONOR LIGANDS

M. Kabešová, M. Dunaj-Jurčo* and G. Ondrejovič
Department of Inorganic Chemistry, Slovak Technical University,
812 37 Bratislava, Czechoslovakia

ABSTRACT

The thermal decomposition of $CuL_2(NCS)_2$, $CuL_2(NCSe)_2$ and $CuL_2(NCS)(NCSe)$ where L = 2,2′-bipyridine or 1,10-phenanthroline showed that the phenanthroline complexes are thermally more stable than bipyridine complexes. The different course of the thermal decomposition curves of individual complexes is a consequence of a difference in reduction properties between NCS and NCSe ligands.

INTRODUCTION

The thermal properties of Cu(II) compounds of the type $CuL_2(NCS)_2$, $CuL_2(NCS)(NCSe)$ and $CuL_2(NCSe)_2$, where L is 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen), respectively were[1,2,3] studied. In compounds with phenanthroline the Cu(II) central atom exhibits differently distorted pseudooctahedral coordination polyhedra differing in the values of their interatomic distances. The compounds with bipyridine show differently distorted trigonal-bipyramidal; coordination polyhedra around the Cu(II) central atom mutually differ in their bond angles.

MEASURING METHOD

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

RESULTS AND DISCUSSION

The compound of $[Cu(bipy)_2(NCSe)]NCSe$ was prepared in two isomeric forms, the differences between them lying in the degree of distortion of the Cu(II)-coordination polyhedra.

The thermal decomposition of the compounds with bipy may be expressed by the following decomposition schemes:

Proceedings of ICTA 85, Bratislava

$$[\text{Cu(bipy)}_2\text{(NCS)}]\text{NCS} \xrightarrow[\text{130 up to 230 }^{o}\text{C}]{\text{-bipy}} \text{Cu(bipy)(NCS)}_2 \longrightarrow$$

$$\xrightarrow[\text{230 up to 330 }^{o}\text{C}]{\text{-bipy, -S}} \text{CuS(CN)}_2 \xrightarrow[\text{330 up to 500 }^{o}\text{C}]{\text{-2(CN), -0,5S}} \text{CuS}_{0,5}$$

$$[\text{Cu(bipy)}_2\text{(NCS)}]\text{NCSe} \xrightarrow[\text{130 up to 310 }^{o}\text{C}]{\text{-2bipy}} \text{Cu(NCS)(NCSe)} \xrightarrow{\text{-0,5(NCS)}}$$

$$\xrightarrow[\text{310 up to 440 }^{o}\text{C}]{\text{-0,5(NCSe)}} \text{Cu(NCS)}_{0,5}\text{(NCSe)}_{0,5}$$

$$\alpha\text{-}[\text{Cu(bipy)}_2\text{(NCSe)}]\text{NCSe} \xrightarrow[\text{130 up to 300 }^{o}\text{C}]{\text{-2bipy, -0,5(CN)}} \text{Cu(NCSe)Se(CN)}_{0,5} \rightarrow$$

$$\xrightarrow[\text{300 up to 460 }^{o}\text{C}]{\text{-(SeCN), -0,5Se}} \text{Cu(NCSe)}_{0,5} \xrightarrow[\text{460 up to 557 }^{o}\text{C}]{\text{-0,5(NCSe)}} \text{Cu}$$

$$\beta\text{-}[\text{Cu(bipy)}_2\text{(NCSe)}]\text{NCSe} \xrightarrow[\text{130 up to 300 }^{o}\text{C}]{\text{-2bipy, 0,5(CN)}} \text{Cu(NCSe)Se(CN)}_{0,5} \rightarrow$$

$$\xrightarrow[\text{330 up to 550 }^{o}\text{C}]{\text{-(NCSe), -0,5Se}} \text{Cu(NCSe)}_{0,5}$$

The different distortion degree of the coordination polyhedra of complexes with bipy does not become evident in the decomposition temperature, its values for all these complexes being in the interval of 120 to 130 ^{o}C. The decomposition sets in by the release of bipyridine molecules from the pentacoordinate cation $[\text{Cu(bipy)}_2\text{NCX}]^+$, even though one of the two pseudohalogenide groups is found in the structure in a non-coordinated form. For the thiocyanate complex the first bipy ligand releases in a separate step under the formation of Cu(bipy)(NCS)_2, being stable up to ≈ 300 ^{o}C. The release of the other bipy molecule is overlapped by polymerization and reduction reactions of the thiocyanate ligands. For the thermal decomposition of the other complexes no analogous decomposition step was observed indicating an unstability of the analogous investigated compound for the case that one or two selenocyanate groups are coordinated to the Cu(II)-atom.

The different course of thermal decomposition of the bipy compounds under investigation is a consequence of different reduction properties of the selenocyanate and thiocyanate ligands. This is evident from the decomposition scheme of $[\text{Cu(bipy)}_2\text{(NCSe)}]\text{NCSe}$

complex, where already in the first decomposition step at the release of bipy molecules also the decomposition of selenocyanate ligands takes place.

A comparison of the thermal decomposition courses of the α - and β-$[Cu(bipy)_2(NCSe)]NCSe$ isomers compounds, differing from each other by the distortion degree of the pentacoordinate polyhedra of Cu(II) shows that up to 300 °C intermediates of the same stoichiometric composition, however of different physico-chemical properties are formed.

The thermal decomposition of the complexes with phen may be expressed by means of the following schemes:

$$[Cu(phen)_2(NCS)_2] \xrightarrow[260\text{ up to }300\ ^{\circ}C]{-0,5(NCS),\ -0,25phen} Cu(phen)_{1,75}(NCS)_{1,5} \longrightarrow$$

$$\xrightarrow[300\text{ up to }390\ ^{\circ}C]{-0,25(NCS),\ -0,75phen} Cu(phen)(NCS)_{1,25}$$

$$[Cu(phen)_2(NCS)(NCSe)] \xrightarrow[200\text{ up to }230\ ^{\circ}C]{-0,5(NCSe)} Cu(phen)_2(NCS)(NCSe)_{0,5}$$

$$\longrightarrow \quad \xrightarrow[230\text{ up to }420\ ^{\circ}C]{-(phen)} Cu(phen)(NCS)(NCSe)_{0,5}$$

$$[Cu(phen)_2(NCSe)_2] \xrightarrow[200\text{ up to }230\ ^{\circ}C]{-0,25(NCSe)} Cu(phen)_2(NCSe)_{1,75} \longrightarrow$$

$$\xrightarrow[230\text{ up to }370\ ^{\circ}C]{-0,25(NCSe),\ -phen} Cu(phen)(NCSe)_{1,5} \longrightarrow$$

$$\xrightarrow[370\text{ up to }470\ ^{\circ}C]{-0,25phen} Cu(phen)_{0,75}(NCSe)_{1,75}$$

Compounds with phen showed a greater thermal stability than those with bipy. The thermal decomposition begins by the reduction reactions of the pseudohalogenide ligands. In accordance with the conception of more expressive reduction properties of the selenocyanate ligand, the decomposition temperature of complexes $[Cu(phen)_2(NCS)(NCSe)]$ and $[Cu(phen)_2(NCSe)_2]$ is compared with $[Cu(phen)_2(NCS)_2]$ complex. The knowledge about more expressive reduction properties of the selenocyanate ligand in comparison with the thiocyanate ligand is also in good agreement with the experimentally obtained information about the maxima positions of the charge transfer (CT) absorption bands in electronic spectra.

Table: Charge transfer bands in electronic spectra of thiocyanato-, selenocyanato- and mixed thiocyanato-selenocyanato complexes of copper(II) with 2,2′-bipyridine and 1,10-phenanthroline

Complex	Charge transfer band[4] $[\nu_{max}/cm^{-1}]$
$[Cu(bipy)_2(NCS)]NCS$	24 680
$[Cu(bipy)_2(NCS)]NCSe$	24 600
$[Cu(bipy)_2(NCSe)]NCSe$	22 280
$[Cu(phen)_2(NCS)_2]$	25 880
$[Cu(phen)_2(NCS)(NCSe)]$	25 250
$[Cu(phen)_2(NCSe)_2]$	23 420

CONCLUSION

Phenanthroline complexes are termically more stable than bipyridine complexes. Their decomposition sets in by reduction reactions of the pseudohalogenide ligands. On the other hand the bipyridine complexes start to decompose by the release of the ligand molecules L. Different reduction properties of the selenocyanate and thiocyanate ligands, which manifestate themselves in the different values of charge transfer energy / $E(NCS) > E(NCSe)$/, cause different thermal decomposition course of thio- and selenocyanato complexes.

REFERENCES

1. A.Sedov,M.Kabešová,M.Dunaj-Jurčo,J.Gažo and J.Garaj, Chem.zvesti,37,43(1983).
2. A.Sedov,M.Kabešová,M.Dunaj-Jurčo,J.Gažo and J.Garaj, Coord.Khim.,Vol.8,8,1062(1982).
3. A.Sedov,J.Kožíšek,M.Kabešová,M.Dunaj-Jurčo,J.Gažo and J.Garaj, Inorg.Chim.Acta,75,1(1983).
4. M.Kabešová,J.Kohout and J.Gažo, Mh.Chem.107,641(1976).