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# Thermal properties of solid complexes with biologically important heterocyclic ligands

## Part III. Thermal decomposition and infrared spectra of thiocyanato Mg(II) complexes with 2-hydroxypyridine, quinoline, and quinoxaline

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**Abstract** The thermal decomposition of the complexes $Mg(SCN)_2(2\text{-}OHpy)_4{\cdot}H_2O$(I), $Mg(SCN)_2(quin)_4{\cdot}2H_2O$(II) and $Mg(SCN)(quinox)_4{\cdot}5H_2O$(III) (2-OHpy–2-hydroxypyridine, quin–quinoline, quinox–quinoxaline) has been investigated in static air atmosphere at 20–1000 °C by means of thermogravimetry (TG), differential thermal analysis (DTA), and infrared (IR) spectroscopy. The composition of the complexes had been identified by means of elemental analysis and complexometric titration. The possible scheme of destruction of the complexes is suggested. The final product of the thermal decomposition was MgS. IR data suggest that heterocyclic ligands were coordinated to Mg(II) through the nitrogen atom of their heterocyclic ring. Thiocyanate group is also coordinated through the nitrogen atom.

**Keywords** Thermal decomposition · Mg(II) complexes · 2-hydroxypyridine · Quinoline · Quinoxaline · TG · DTA · IR

## Introduction

The relationship between the thermolyses and structures of metal complexes and the influence of the natures of the ligands on the process of thermal decomposition are very important. Therefore, many authors have studied thermal properties of many coordination compounds with heterocyclic ligands [1, 2] since these compounds play an important role in many biological systems. The authors have studied the thermal behavior of Mg(II) complexes with pyridine and quinoline derivates to improve the understanding of drug-metal ion interactions. This study is a continuation of previous studies on the stereochemistry [3] and thermal properties [4–11] of Mg(II) complexes with N-donor ligands. This article deals with the preparation of thiocyanato Mg(II) complexes with 2-hydroxypyridine, quinoline and quinoxaline (Fig. 1) together with the thermal and IR spectral analyses of these complexes.

## Experimental

### Synthesis of Mg(II) complexes

Compounds **I** and **III** were prepared by dissolving 20.30 g (0.1 mol) $MgCl_2{\cdot}6H_2O$ in ethanol and gradually adding 19.40 g (0.2 mol) KSCN. KCl was filtered off from the solution and then, 32.22 g (0.4 mol) 2-hydroxypyridine or 52.06 g (0.4 mol) quinoxaline was added, respectively, to filtrate. The resulting solutions were reduced in volume at

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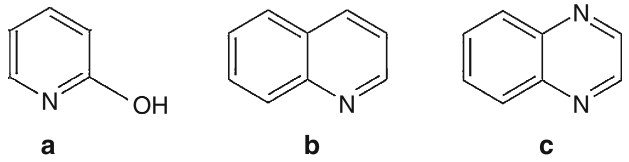


**Fig. 1** Structures of 2-hydroxypyridine (**a**), Quinoline (**b**), and Quinoxaline (**c**)

room temperature and the complexes which formed, were filtered off, washed with ether and dried at room temperature.

The complex **II** was prepared by treating $Mg(SCN)_2\cdot 5H_2O$ 2.305 g (0.01 mol) in ethanol with quinoline (2.46 mL, 0.02 mol). The solution was left to stand at room temperature. The fine microcrystals thus precipitated were filtered off, washed with cold ethanol and finally dried at room temperature.

### Measurements

Elemental analyses (C, H, and N) were carried out on a Carlo Erba 1106 Analyser and the content of Mg(II) was determined by complexometric titration.

Thermal decomposition was studied on a Derivatograph OD 102 (MOM Budapest) in air atmosphere using a ceramic crucible with a sample mass of 100 mg from room temperature to 900 °C. A heating rate of 10 °C $min^{-1}$ was chosen for all measurements.

The infrared (IR) spectra were obtained on a Philips analytical PU 9800 FTIR spectrometer using KBr pallet in the range 400–4000 $cm^{-1}$.

## Results and discussion

### Analysis of compound

The content of carbon, hydrogen, and nitrogen was determined by elemental analysis and the content of magnesium was estimated by complexometric titration. The analysis confirms (Table 1) the theoretical expectation of the studied complexes I–III.

### Thermal behavior of the compounds

The thermal decomposition data of the compounds I–III are summarized in Table 2. The complexes I–III are relatively thermally stable. Thermal decomposition of these compounds started with the dehydration process and followed by the elimination of the ligands. The final solid product was always identified as MgS.

**Table 1** Elemental analysis and complexometric titration data of the complexes I–III

| Complex | Theoretical/% | | | | Experimental/% | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Mg | C | H | N | Mg |
| $Mg(SCN)_2(2\text{-}OHpy)_4\cdot H_2O$ (I) | 49.03 | 4.11 | 15.59 | 4.51 | 50.30 | 4.02 | 15.74 | 4.55 |
| $Mg(SCN)_2(quin)_2\cdot 2H_2O$ (II) | 55.20 | 4.17 | 12.88 | 5.59 | 52.71 | 4.32 | 16.80 | 5.57 |
| $Mg(SCN)_2(quinox)_4\cdot 5H_2O$ (III) | 54.37 | 4.56 | 18.65 | 3.23 | 55.45 | 4.53 | 17.71 | 3.19 |

**Table 2** Thermal decomposition data

| Complex | DTA | | TG | | |
|---|---|---|---|---|---|
| | $T_{peaks}$/°C | $T_{range}$/°C | Mass loss/% found/calc. | Lost component | Residue |
| I | 120 | 108–205 | 3.00/3.34 | $H_2O$ | |
| | 286 | 205–430 | 53.00/52.94 | 3(2-OHpy) | |
| | 484 | 430–575 | 18.00/17.64 | 1(2-OHpy) | |
| | 682 | 575–795 | 16.00/15.61 | SCN,CN | MgS |
| II | 132 | 107–170 | 9.00/8.29 | $2H_2O$ | |
| | 209 | 170–344 | 60.00/59.41 | 2(quin) | |
| | 419 | 344–460 | 12.00/13.36 | SCN | |
| | 501 | 460 | 6.00/5.98 | CN | MgS |
| III | 128 | 105–177 | 12.00/11.99 | $5H_2O$ | |
| | 211 | 177–301 | 70.00/69.31 | 4(quinox) | |
| | 413 | 301–549 | 8.00/7.73 | SCN | |
| | 590 | 549–730 | 4.00/3.46 | CN | MgS |

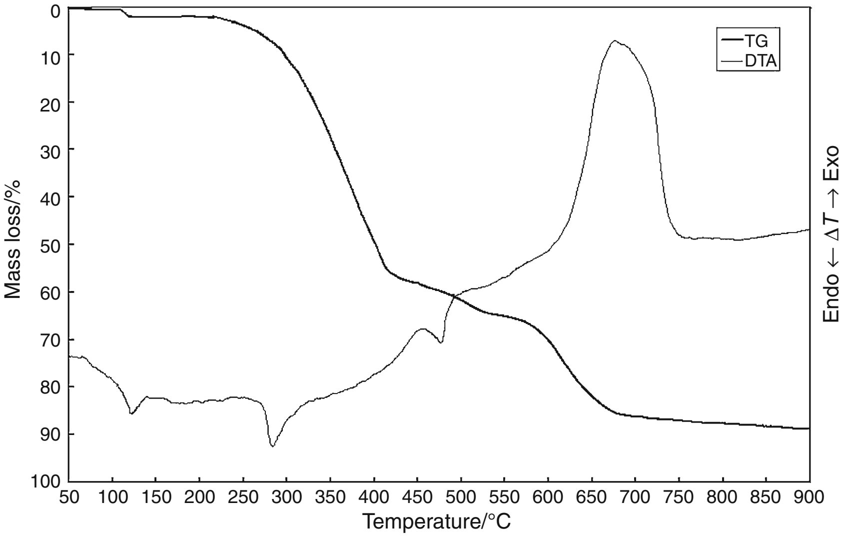


**Fig. 2** TG and DTA curves of $Mg(SCN)_2(2\text{-}OHpy)_4 \cdot H_2O$ (I)

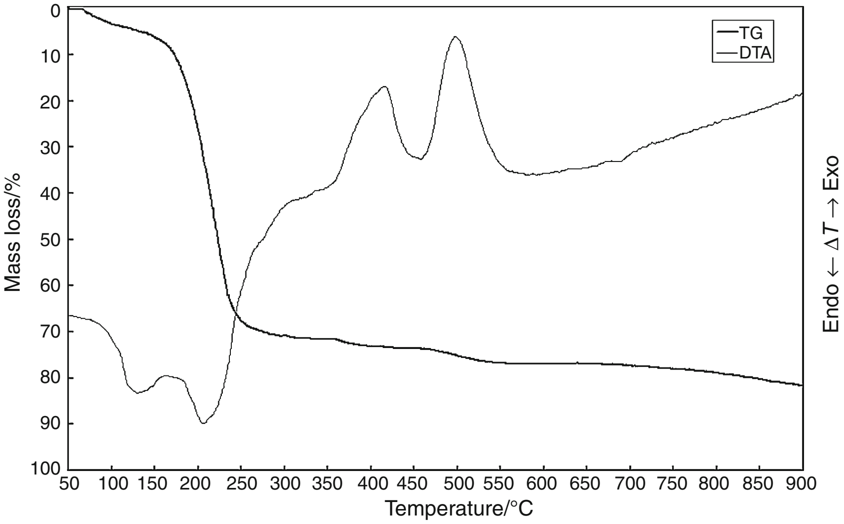


**Fig. 3** TG and DTA curves of $Mg(SCN)_2(quin)_2 \cdot 2H_2O$ (II)

The TG and DTA curves for $Mg(SCN)_2$ (2-OHpy)$_4$ $H_2O$ (I) are shown in Fig. 2. The TG and DTA curves of that complex indicate that it is thermally stable up to 108 °C, where the dehydration process commences. This is followed by two mass loss steps between 205–430 °C and 430–575 °C. Based on the mass loss values (Table 2), these two steps were attributed to the formation of two intermediate decomposition products, i.e., $Mg(NCS)_2$(2-OHpy) and $Mg(NCS)_2$, while the final solid product is concluded to be MgS. The thermal decomposition scheme is:

$$Mg(SCN)_2(2\text{-}OHpy)_4 \cdot H_2O \xrightarrow{108-205^\circ C} Mg(SCN)_2(2\text{-}OHpy)_4 \quad (1)$$

$$Mg(SCN)_2(2\text{-}OHpy)_4 \xrightarrow{205-430^\circ C} Mg(SCN)_2(2\text{-}OHpy) \quad (2)$$

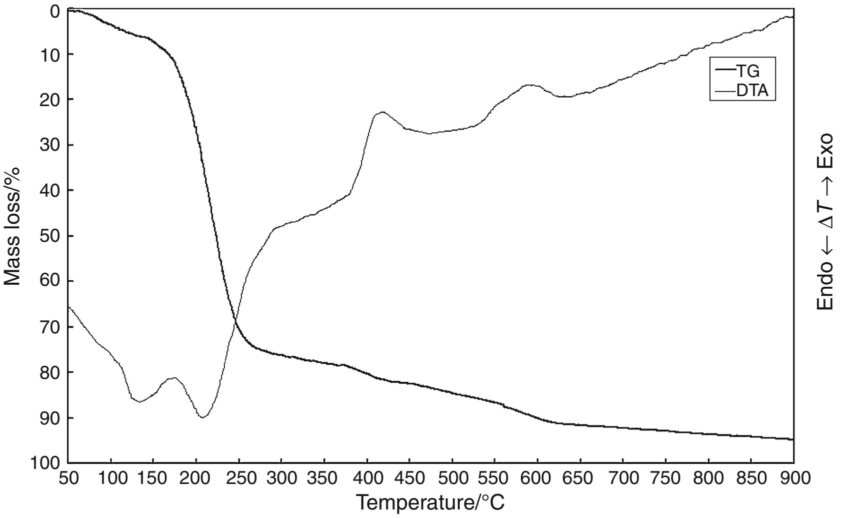
$$Mg(SCN)_2(2\text{-}OHpy) \xrightarrow{430-575^\circ C} Mg(SCN)_2 \quad (3)$$

$$Mg(SCN)_2 \xrightarrow{575-795^\circ C} MgS \quad (4)$$

The DTA curve of complex I (Fig. 2) displays three endothermic peaks maximized at 120, 286, and 484 °C corresponding to the loss of 1 mol $H_2O$, 3 mol 2-OHpy, and 1 mol 2-OHpy, respectively, and one exothermic peak maximalized at 682 °C corresponding to the decomposition reaction of $Mg(SCN)_2$ with simultaneous formation of MgS.

As summarized in Table 2, the TG curve for the complex $Mg(SCN)_2(quin)_2 \cdot 2H_2O$(II) indicate that mass loss starts observable at ~107 °C (in the temperature range 50–900 °C) and four mass loss steps were observed. The first step between 107 and 170 °C is accompanied by 9% mass loss and corresponds to the release of 2 molecules $H_2O$. The second step took place between 170 and 344 °C

**Fig. 4** TG and DTA curves of $Mg(SCN)_2(quinox)_4 \cdot 5H_2O$ (III)



is accompanied by 60% mass loss and corresponds to the release of 2 molecules quin. The third step between 344 and 460 °C, and fourth step between 460 and 695 °C correspond to the decomposition of $Mg(SCN)_2$ and Mg·SCN to MgS as final decomposition product. The most probable thermal decomposition scheme is given below:

$$Mg(SCN)_2(quin)_2.2\,H_2O \xrightarrow{107-170^\circ C} Mg(SCN)_2(quin)_2 \tag{5}$$

$$Mg(SCN)_2(quin)_2 \xrightarrow{170-344^\circ C} Mg(SCN)_2 \tag{6}$$

$$Mg(SCN)_2 \xrightarrow{344-460^\circ C} Mg \cdot SCN \tag{7}$$

$$Mg \cdot SCN \xrightarrow{460-695^\circ C} MgS \tag{8}$$

The DTA curve for the complex II (Fig. 3) shows two endothermic peaks at 132 and 209 °C corresponding to the loss of 2 molecules $H_2O$ and 2 molecules quin, respectively, and two exothermic peaks with maxima at 419 and 501 °C, corresponding to decomposition reactions of $Mg(SCN)_2$ and Mg·SCN with simultaneous formation of MgS.

The TG and DTA curves of $Mg(SCN)_2(quinox)_4 \cdot 5H_2O$(III) are shown in Fig. 4. The TG curve of that complex indicates that it is thermally stable up to 105 °C, where the dehydration process commences. This is followed by three mass loss steps between 105–177, 177–301, and 301–549 °C. Based on the mass loss values (Table 2), these three steps were attributed to the formation of three decomposition products, i.e., $Mg(SCN)_2(quinox)_4$, $Mg(SCN)_2$, and Mg·SCN, while the final solid product is concluded to be MgS. The most probable thermal decomposition scheme is:

$$Mg(SCN)(quinox)_4.5H_2O \xrightarrow{105-177^\circ C} Mg(SCN)_2(quinox)_4 \tag{9}$$

$$Mg(SCN)_2(quinox)_4 \xrightarrow{177-301^\circ C} Mg(SCN)_2 \tag{10}$$

$$Mg(SCN)_2 \xrightarrow{301-549^\circ C} Mg.SCN \tag{11}$$

$$Mg.SCN \xrightarrow{549-730^\circ C} MgS \tag{12}$$

The DTA curve of complex III (Fig. 4) displays two endothermic peaks maximized at 128 and 211 °C corresponding to the loss of 5 molecules $H_2O$ and 4 molecules quinox, respectively, and two exothermic peaks maximized at 413 and 590 °C, corresponding to the decomposition reactions of $Mg(SCN)_2$ and Mg·SCN with simultaneous formation of MgS.

## IR spectra

The most important infrared spectral data of studied complexes are reported in Table 3. The absorption bands which occur in the range 3500–3200 $cm^{-1}$ (symmetric and antisymmetric OH stretching) and 1630–1590 $cm^{-1}$ (HOH bending) confirm the presence of water in the complexes I–III [4, 10].

The stretching vibration $\nu$(C–H) in the pyridine ring appeared at 1590 $cm^{-1}$. Upon complex formation the peak shifts to higher frequencies. The shifts in complexes I–III (in the range 1600–1620 $cm^{-1}$) may suggest that the bond formation of the metal with the N of pyridine ring increases the dipolar contribution of $C{=}N^+$ in the heterocyclic ring [11].

The thiocyanate groups as a ligand can principally occur as a monofunctional, bonded through nitrogen or sulfur, as a bifunctional or trifunctional ligand in the function of a bridge. At coordination of the SCN group, the changes of the C–N and C–S stretching vibrations are studied in the first place. According to the literature data [12], the main

**Table 3** Some IR spectral data (450–2600 $cm^{-1}$) of complexes I–III

| Assignment | Complex | | |
|---|---|---|---|
| | I | II | III |
| ν(CN) NCS | 2081 | 2083 | 2083 |
| ν(CS) NCS | 767 | 764 | 766 |
| ν(CN) py ring | 1615 | 1612 | 1614 |
| ν(CC) | 951 | 959 | 959 |
| ν(CH) ring | 858 | 864 | 866 |
| γ(CCC) | 767 | 764 | 766 |
| ν (OH) | 3258 | 3244 | 3234 |
| δ (HOH) | 1633 | 1632 | 1630 |

criterion of the M-NCS or M-SCN bondings is the band position corresponding to the C–S stretching vibration: the region from 770 to 860 $cm^{-1}$ is assigned to the M-SCN bonding, from 690 to 730 $cm^{-1}$ to the M-NCS bonding. The C–N stretching vibrations, observed in the region 2080–2110 $cm^{-1}$ indicate M-NCS bonding, in the region 2110–2130 $cm^{-1}$ M-SCN bonding. The ν(C–S) and ν(C–N) vibrations for studied complexes (Table 3) confirm the coordination of SCN group to Mg(II) through nitrogen atom.

## Conclusions

All of the studied complexes I–III are hydrated, stable in air and soluble in water, ethanol, methanol, and dimethylsulfoxide. In complex I, loss of *N*-heterocyclic ligands occurs (on the TG curve) in the two steps and in complexes II and III in one step. The thermal stability of the complexes can be ordered in the sequence I > II > III (but the differences are minimum). The results reveal that MgS is left as residue at the end of the thermal degradation experiments of the compounds I–III. The preliminary study has shown that the complexes do have biological activities.

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