ELSEVIER

Thermochimica Acta 329 (1999) 57–65

thermochimica acta

# Thermal studies of *p*-toluidino-*p*-chlorophenylglyoxime and of some corresponding Ni(II), Cu(II) and Co(II) complexes

Hakan Arslan[a], Nilgün Ozpozan[b,*], Talat Ozpozan[b]

[a]*Department of Chemistry, Nigde University, Nigde, Turkey*
[b]*Department of Chemistry, Erciyes University, Kayseri, Turkey*

Received 26 August 1998; received in revised form 18 December 1998; accepted 22 December 1998

**Abstract**

The thermal behaviour of *p*-toluidino-*p*-chlorophenylglyoxime (*p*T*p*CPG) and its Cu(II), Ni(II), and Co(II) complexes have been studied by DTA and TG. It was found that pyrolytic decomposition undergoes with melting in both ligand and its metal complexes and metal oxides remained as end products of the metal complexes. The ligand decomposes in two stages through two different mechanisms and the metal chelates undergo decomposition in three stages. GC–MS combined system was used to identify the products during pyrolytic decompositions. The pyrolytic end products were identified by X-ray powder diffraction. 

*Keywords:* *p*-Toluidino-*p*-chlorophenylglyoxime; Cu(II)-, Ni(II)- and Co(II)-complexes; Thermal behaviour; Pyrolysis; DTA/TG/DTG

## 1. Introduction

Vic-dioxime metal complexes are important as coordination compounds. The early studies on oxime complexes date from 1905 and have been reviewed by Chakravorty [1] who also studied Ni(II) dimethylglyoximes. Later in 1907, Tschugaeff [2] isolated dimethylglyoxime complexes of Co(III) which played an important role as model compounds in the elucidation of some biological and biochemical mechanisms.

Several studies were concentrated on Co vic-dioxime complexes in later years [3,4]. These were used as model compounds to explain the structure of vitamin $B_{12}$ and coenzyme $B_{12}$, since these macromolecules play important roles in biological mechanisms.

In some recent studies, Pt vic-dioxime complexes have been tested as anti-tumour agents in chemotherapy [5]. These complexes have also been used in the production of semiconductors [6]. Liquid crystal properties of some vic-dioxime complexes have been studied [6] and further applications include column packing material in chromatographic separation of nucleotides and nucleosides after bonding to natural resins as functional groups [7].

In the present study, *p*-toluidino-*p*-chlorophenylglyoxime (*p*T*p*CPG) complexes of Ni(II), Co(II), and Cu(II) are studied by DTA and TG and the mechanisms of thermal decomposition have been determined.

*Corresponding author. Fax: +90-352-4374933; e-mail: ozpozant@erciyes.edu.tr

0040-6031/99/$ – see front matter 
PII: S0040-6031(99)00004-0

## 2. Experimental

The ligand *p*T*p*CPG and the corresponding Ni(II), Co(II), and Cu(II) chelates were synthesized from analytical pure reagents as described in [8].

### 2.1. Instrumentation

A Shimadzu model DT-40 simultaneous TG, DTA thermal analysis system was used over the temperature range 273–1823 K (0–1550°C). The samples were

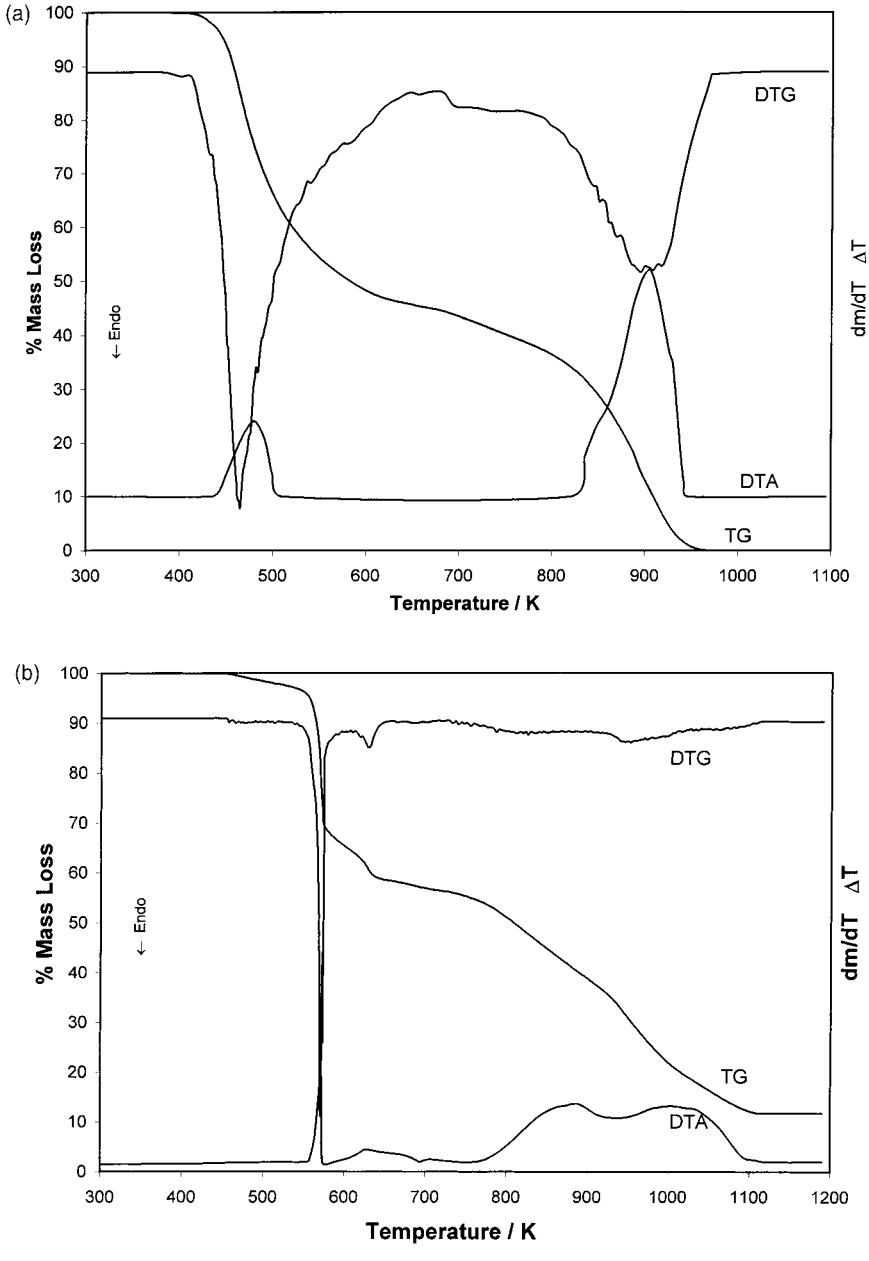



Fig. 1. DTA/TG/DTG diagram of (a) *p*-toluidino-*p*-chlorophenylglyoxime, (b) Ni(II) complex of *p*T*p*CPG, (c) Cu(II) complex of *p*T*p*CPG, (d) Co(II) complex of *p*T*p*CPG.

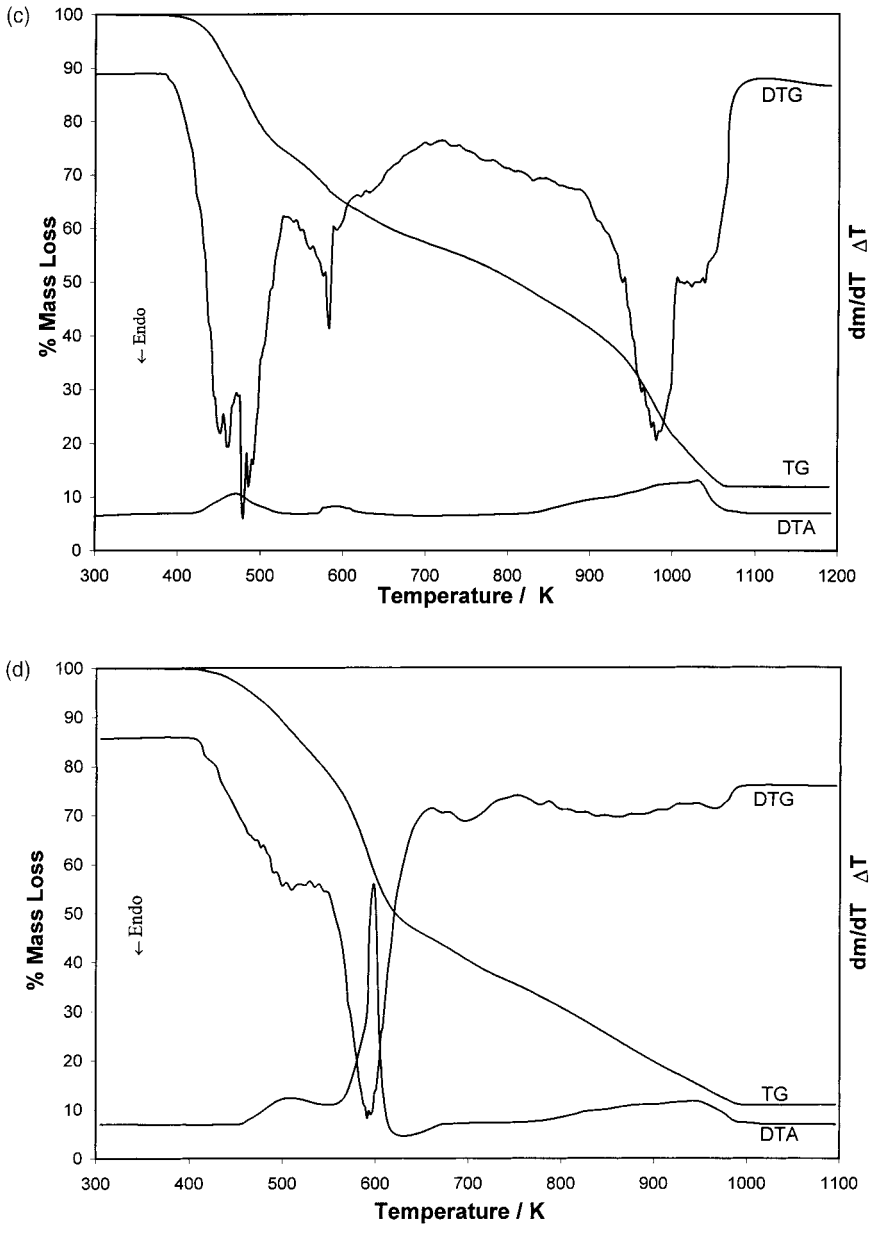



Fig. 1. (*Continued*)

placed in Pt crucibles and $\alpha$-$Al_2O_3$ was used as the reference material. Heating was performed under a $N_2$ atmosphere and a flow rate of 60 ml/min. The sample size was limited to 4–8 mg and the heating rate was adjusted to 10 K/min in all cases.

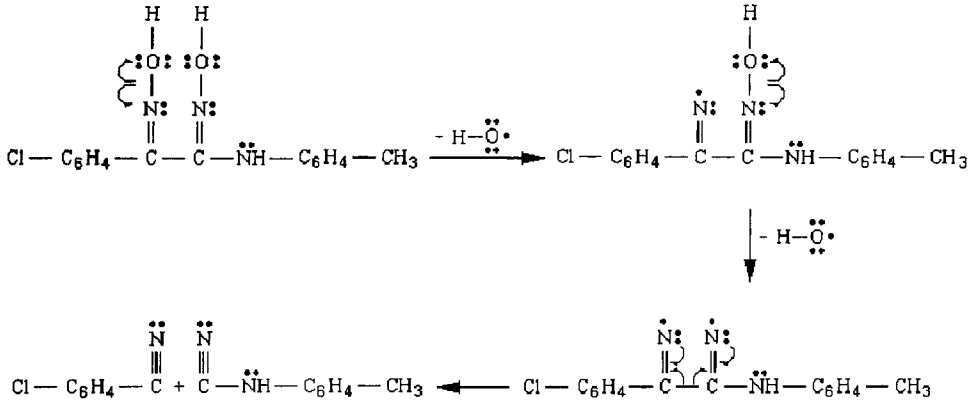
A GC–MS system VG-ZabSpec model DFMS, was used to identify pyrolysis products evolved during heating. The residual end products of heating were identified by X-ray powder diffractometry using a power generator from Phillips (model PW-1010) and a goniometer from Siemens (type F). Melting point determinations were performed with a digital melting point instrument from Electrothermal model 9200.

## 3. Results and discussions

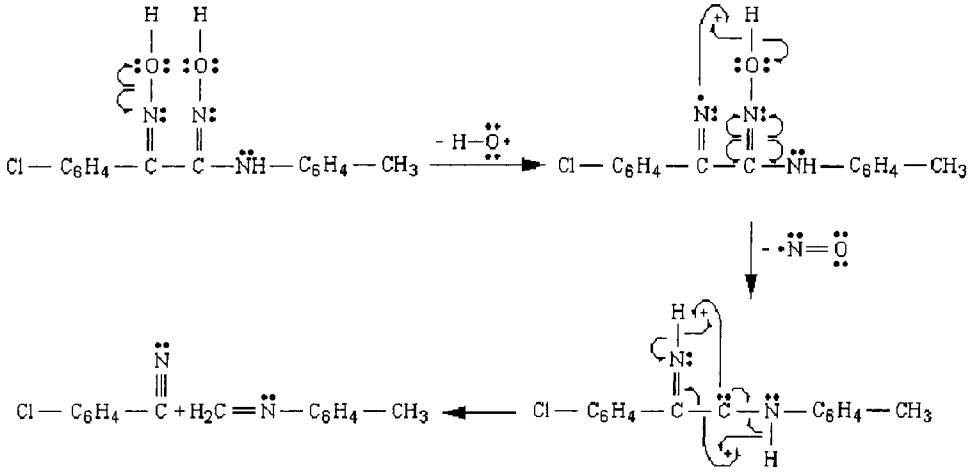
### 3.1. p-Toluidino-p-chlorophenylglyoxime

*p*T*p*CPG melts at 398–399 K with simultaneous decomposition. The first mass loss was observed at 401 K in the TG profile. The DTA/TG/DTG profiles of the ligand are shown in Fig. 1(a). From the TG curve, it appeared that the sample decomposes in two stages over the temperature range 298–973 K. The first decomposition occurs between 298 and 669 K with a mass loss of 55.1% and the second decomposition starts at 669 K, ends at 973 K with a 44.8% mass loss. From the corresponding DTA profile, two exothermic peaks are noted, the first between 434 and 509 K with a maximum at 481 K and the second between 820 and 946 K with a maximum at 903 K.

Two different mechanisms of decomposition for the ligand are possible as shown by Schemes 1 and 2. The theoretical mechanisms given in Schemes 1 and 2 are in agreement with that of Burakevich et al. [9], who studied with phenylglyoxime in 1971. The theoretical mechanisms dealt with in Schemes 1 and 2 are confirmed by the GC–MS data in Fig. 2(a). The peaks observed at 303, 287, 270, 256, 138, 133, 118 m/z are responsible for the evolved radical moiety. The



Scheme 1.



Scheme 2.

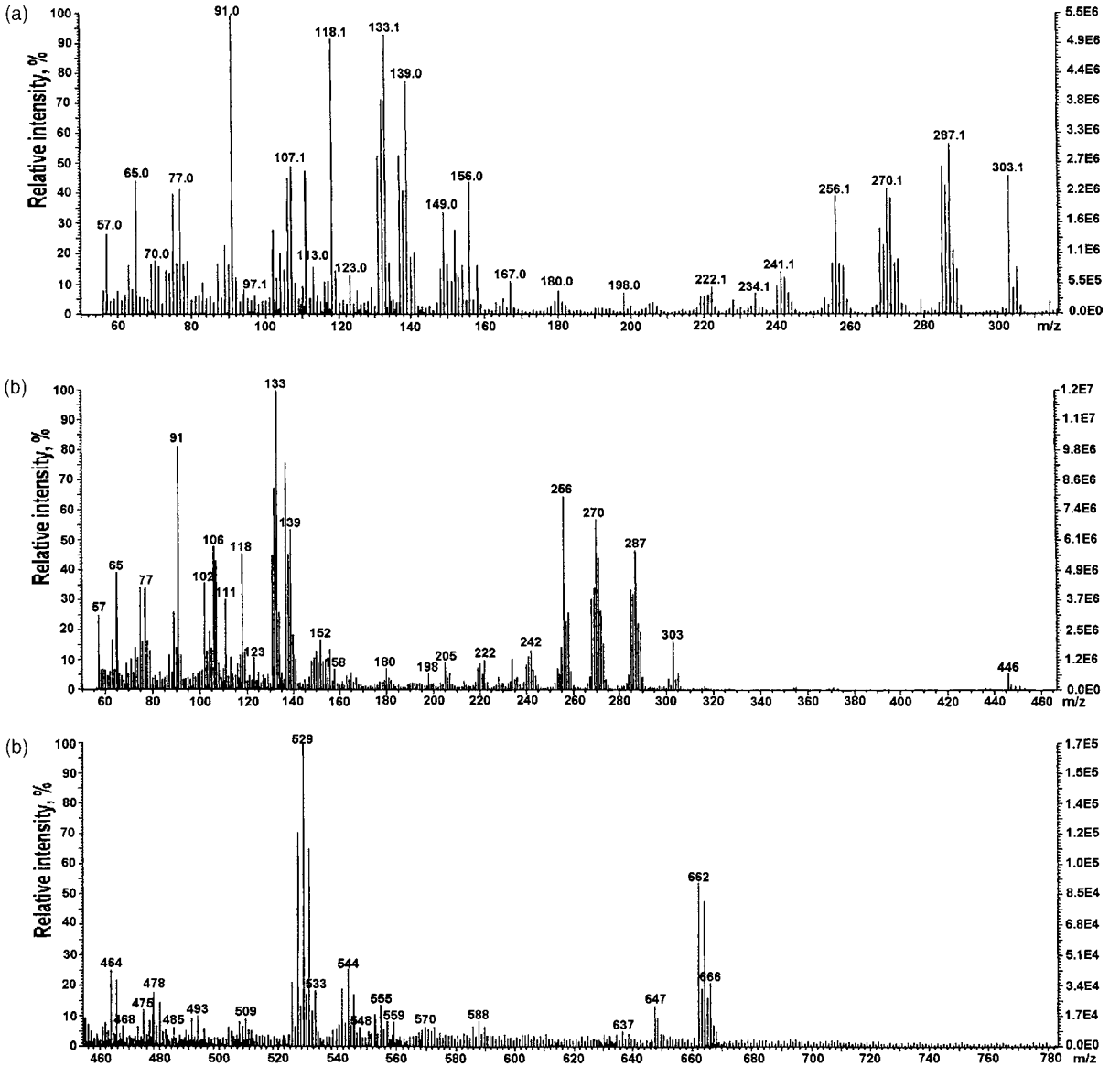
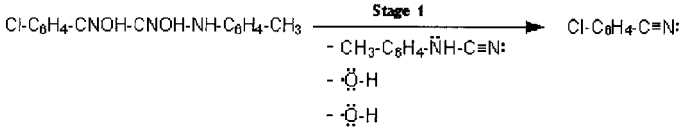


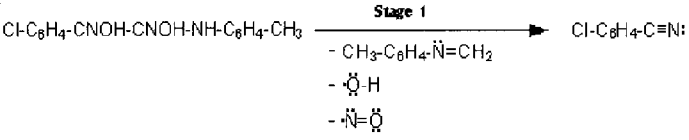

Fig. 2. GC–MS spectrum of (a) *p*-toluidino-*p*-chlorophenylglyoxime, (b) Ni(II) complex of *p*T*p*CPG.

decomposition mechanisms obtained from TG profiles are shown in Schemes 3 and 4. The theoretical and the experimental per cent mass losses obtained from these decomposition stages are in good agreement.

The mechanism of reaction (1) proceeds in two stages, the first of which is apparent in reaction (3). The end-product ($Cl–C_6H_4–C{\equiv}N$:) of this stage undergoes pyrolysis in the second stage. The second decomposition mechanism proceeds in two stages, the first of which is apparent in reaction (4). The end-product ($Cl–C_6H_4–C{\equiv}N$:) of the second stage undergoes pyrolysis in the same way as in the second stage of the first mechanism. The first stages in both suggested mechanisms correspond to a theoretical mass loss of 54.7%. This percentage was found to be 55.1% from TG studies. The second stages in both mechanisms




Scheme 3.



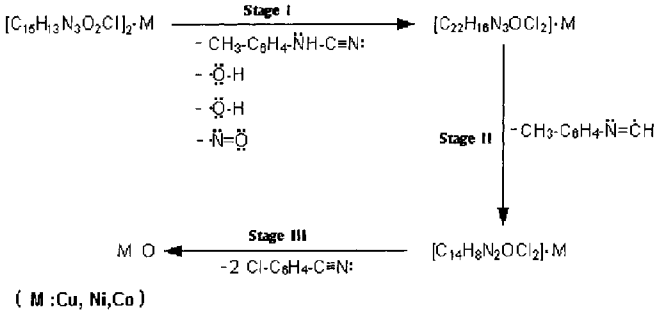

Scheme 4.

correspond to a theoretical mass loss of 45.3% for which the experimentally found value is 44.8% from TG studies. This mass loss corresponds to the mass of $Cl–C_6H_4–C{\equiv}N$: as observed in GC–MS data (Fig. 2(a)). The mass losses found experimentally are very close to the theoretical values.

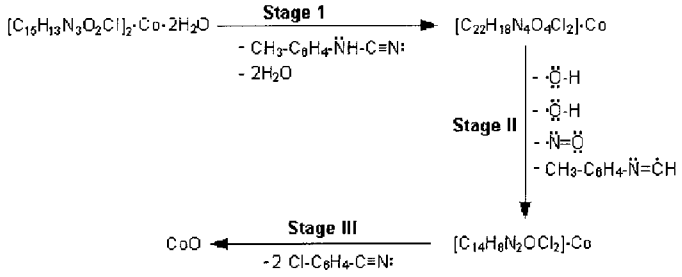
### 3.2. Ni(II) complex

It is noted from the TG analysis that the Ni(II) complex of *p*T*p*CPG looses 88.3% of its original mass between 298 and 1111 K and the 11.7% residue is a greenish-black coloured solid. The DTA/TG/DTG data for the Ni complex is shown in Fig. 1(b). The sample decomposes in three stages. The first decomposition occurs between 298 and 575 K with 30.8% mass loss, the second decomposition occurs between 588 and 693 K with 16.7% mass loss and the third decomposition occurs between 786 and 1111 K with 40.8% mass loss. Three exothermic peaks were observed in the DTA analysis. The first peak occurs between 554 and 573 K with a maximum at 571 K. The second peak occurs between 588 and 693 K with a maximum at 624 K and the third occurs between 783 and 1121 K and is associated with two maxima at 889 and 1006 K.

The theoretical mechanisms given in Schemes 5 and 6 are supported by GC–MS data as shown in Fig. 2(b) and the identification of greenish-black end product of decomposition is obtained by X-ray diffraction (Fig. 3). In both studies, it is concluded that the decomposition of the Ni-complex yields NiO as the decomposition end product in accordance with reaction (5). The theoretical mass of remaining NiO is 11.2% which corresponds to 11.7% from the TG studies. 29.5% theoretical mass loss in the first decomposition corresponds to 30.8% from TG. The same theoretical mass losses in the second and third stages




Scheme 5.




Scheme 6.

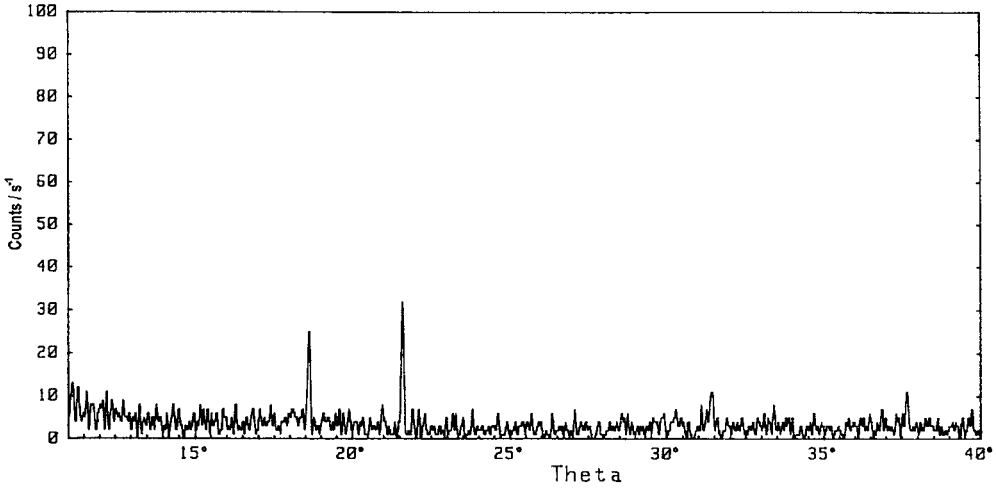



Fig. 3. X-ray powder diffraction pattern of NiO.

were 17.8% and 41.4%. These values were experimentally found to be 16.7% and 40.8% from TG data, respectively.

### 3.3. Cu(II) complex

The TG studies on the Cu(II) complex of *p*T*p*CPG showed that the initial mass loss occurs at 383 K. Decomposition ends with a total of 88.1% mass loss at 1080 K with a black solid residue corresponding to a mass of 11.9%. DTA/TG/DTG diagrams of the Cu(II) complex are shown in Fig. 1(c).

It was observed from the TG curve that the sample decomposes in three stages and it looses 30.34%, 16.55% and 41.13% of its mass in each stage, respectively. The temperature ranges of these decompositions are found to be 298–567, 567–770 and 770–1080 K, respectively.

The DTA curves shows three exothermic peaks. The first peak occurs between 414 and 526 K with a maximum at 470 K. The second occurs between 569 and 628 K with a maximum at 592 K and the third occurs between 825 and 1076 K with a maximum at 1034 K.

Both DTA/TG and X-ray powder diffraction studies showed that the residual black solid was CuO which corresponds to a theoretical mass of 11.9% of the complex. TG curve of the same complex gave an end-product having a mass of 11.9%. Hence the Cu(II) complex decomposes in a similar way to the Ni(II) complex in three stages in accordance with Scheme 5.

The theoretical and experimental mass losses of each stage are as follows; 29.3%, 17.7%, 41.1%, where the corresponding experimental per cent mass losses are found to be 30.3%, 16.6%, 41.1%, respectively.

The TG studies on *p*T*p*CPG chelates of both Ni(II) and Cu(II) showed that these two complexes have similar thermal decomposition mechanisms which is expected since they both have square-planar structure. Since the decomposition of both Ni(II) and Cu(II) complexes undergo the similar thermal decomposition mechanism, only the GC–MS spectrum and X-ray powder diffraction patterns of the Ni(II) complex are included here.

### 3.4. Co(II) complex

It was found from TG analysis that the sample starts losing mass at 408 K and ends at 994 K after losing 89.0% of its mass with a greenish-brown residue which corresponds to 11.0% of the total mass. The DTA/TG/DTG diagrams of the Co(II) complex are shown in Fig. 1(d). The examination of TG curve showed that the sample decomposes in three stages. The sample loses 23.6% of mass between 298 and 557 K, 25.5% of the mass between 557 and 617 K and 39.9% between 617 and 996 K. The DTA study of the complex showed three exothermic peaks. The first peak appeared between 452 and 539 K with a maximum at 506 K. The second appeared between 558 and 614 K with a maximum at 599 K and the third appeared between 614 and 987 K with a maximum at 947 K.

TG analysis showed that the Co(II) complex yields a pyrolysis solid product of mass 11.0% corresponding to the theoretical mass of 10.7% for CoO. As given in Scheme 6, the Co(II) complex decomposes in three stages by losing 24.0%, 26.0% and 39.3% of its mass theoretically during the pyrolysis, respectively. In these pyrolytic reactions, the mass losses derived from TG curve are 23.6%, 25.5% and 39.9%.

It was concluded from TG studies that all the Ni(II), Cu(II) and Co(II) complexes examined were converted to the corresponding oxides. The ligand decomposes in two stages by two different mechanisms, and the complexes decompose in three stages. The oxides yielded at the end of pyrolysis were confirmed by the X-ray powder diffraction data given in the related sources [10].

The critical data and values deduced from the present study were summarized in Table 1.

Table 1
DTA/TG data for the Ni(II), Cu(II) and Co(II) complexes of *p*-toluidino-*p*-chlorophenylglyoxime

| Sample | Stage | Temperature of DTA peak maximum (K) | TG temperature range (K) | Mass loss (%) | | |
|---|---|---|---|---|---|---|
| | | | | TG | Theoretical | RE (%) |
| Ligand | I | 481 | 401–669 | 55.12 | 54.71 | 0.75 |
| (*p*T*p*CPG) | II | 903 | 669–973 | 44.85 | 45.29 | 0.97 |
| Cu(II) | I | 470 | 383–567 | 30.34 | 29.32 | 3.48 |
| complex | II | 592 | 567–770 | 16.65 | 17.66 | 5.72 |
| | III | 1034 | 770–1080 | 41.11 | 41.13 | 0.05 |
| | Last | – | >1080 | 11.90 | 11.89 | 0.08 |
| Ni(II) | I | 571 | 453–575 | 30.77 | 29.54 | 4.16 |
| complex | II | 624 | 575–786 | 16.68 | 17.79 | 6.24 |
| | III | 889–1006 | 786–1111 | 40.81 | 41.42 | 1.47 |
| | Last | – | >1111 | 11.74 | 11.25 | 4.36 |
| Co(II) | I | 506 | 408–557 | 23.56 | 24.01 | 0.09 |
| complex | II | 599 | 557–617 | 25.51 | 26.01 | 1.92 |
| | III | 947 | 617–996 | 39.93 | 39.28 | 1.65 |
| | Last | – | >996 | 11.00 | 10.70 | 2.80 |
| Average | | | | | | 2.41 |

%RE: % relative error.

## References

[1] A. Chakravorty, Coordination Chem. Rev. 13 (1974) 1.
[2] L. Tschugaeff, Ber. Deutsch. Chem. Ges. 40 (1907) 3498.
[3] G.N. Schrauzer, R.J. Windgassen, J. Am. Chem. Soc. 89 (1967) 143–147.
[4] N. Tan, O. Bekaroglu, Synth. React. Inorg. Met. Org. Chem. 13 (1983) 667–682.
[5] Metal complexes may be better anticancer drugs, Chem. Eng. News, 19 April (1982) p. 36.
[6] M.A. Deveci, Ph.D. Thesis, Selçuk University, Konya-TR, 1994.
[7] M. Ersoz, S. Yildiz, E. Pehlivan, J. Chromatogr. Sci. 31 (1993) 65.
[8] A.I. Pekacar, E. Ozcan, Synth. React. Inorg. Met. Org. Chem. 25(6) (1995) 859–868.
[9] J.V. Burakevich, A.M. Lore, G.P. Volpp, J. Org. Chem. 36(1) (1971) 1.
[10] ASTM (1981), Index (Inorganic) to the powder Diffraction File (4-805), 81 ed., The Joint Committee on Powder Diffraction Standard.