# Thermal behaviour of copper(II), nickel(II), cobalt(II) and palladium(II) complexes of $N,N$-dimethyl-$N$'-benzoylthiourea

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$N,N$-dimethyl-$N'$-benzoylthiourea (DMBT) complexes of Ni(II), Cu(II), Co(II) and Pd(II) were synthesised. The thermal decomposition of these metal complexes was investigated by TG, DTG and DTA. A GC-MS combined system was used to identify the products during pyrolytic decomposition. The pyrolytic end-products were identified by X-ray powder diffraction. The thermoanalytical data of these complexes are presented in this communication. The kinetic analysis of the thermogravimetric data was performed by using the Coats-Redfern and Horowitz-Metzger methods. All the metal complexes except Cu(II) complex undergo decomposition in three stages and NiS, CoS, Pd, and Cu remained as end-products of the complexes.

**Key Words:** Complexes, $N,N$-dimethyl-$N'$-benzoylthiourea, Thermal behaviour, Thermal decomposition kinetics.

## Introduction

The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions, and some $N$-substituted-$N'$-carbonyl thiourea have been used in commercial fungicides[1,2]. $N,N$-dialkyl-$N'$-benzoylthioureas have been found to be useful ligands for the potential determination of traces of the transition metals by means of normal phase chromatography[3]. More significantly, these reagents have been shown to selectively extract several of the platinum group metals in the form of remarkably stable neutral metal chelates[4].

In previous studies, $N,N$-dialkyl-$N'$-benzoylthioureas derivatives having such properties and their metal complexes were synthesised and their thermal behaviours examined[5−8]. The thermal properties and decomposition kinetics of $N,N$-dimethyl-$N'$-benzoylthiourea complexes have not been studied previously. In this study, the thermal properties and decomposition kinetics of the metal complexes of Ni(II), Cu(II), Co(II) and Pd(II) were investigated. In the decomposition kinetic study, the integral method employing the

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Coats-Redfern equation and the approximation method using the Horowitz-Metzger equation were used for the calculation of kinetics parameters such as the reaction order, $n$, the activation energy, $E^*$, entropies, $\Delta s^*$, and the pre-exponential factor, $A$, from a nonisothermal kinetic study[9,10].

## Experimental

The ligand and metal complexes were prepared using a previously described method[11,12]. Metal solutions of Co(II), Ni(II), Cu(II) and Pd(II) ions were prepared from analytical purity reagents of $CoCl_2.6H_2O$, $NiCl_2$, $CuCl_2.2H_2O$ and $PdCl_2$ (60% Merck) salts. Metal complexes were obtained from the reactions of metal solutions with the alcoholic ligand solutions and solid complexes were filtered out from the liquid phase. Pd(II) complex was purified by recrystallisation from $Me_2CO/EtOH$.

### Apparatus

The DTA and TG curves were obtained with Shimadzu DT-40 model simultaneously with DTA and TG apparatus. The heating rate and other characteristics are given below: heating rate-10 $K.min^{-1}$, atmosphere-nitrogen, flow rate of furnace atmosphere-60 $mL.min^{-1}$, crucible-Platinum, sample size-5 to 8 mg, reference substance-$\alpha$-$Al_2O_3$.

A GC-MS system, Finnigan, Mat Magnum model, was used to identify pyrolysis products evolved during heating. Microanalyses were performed using a Carlo Erba MOD 11016 instrument. Infrared spectra were recorded in the region 4000-400 $cm^{-1}$ on a Mattson Satellite model spectrophotometer, using KBr pellets. X-ray powder diffraction analyses of the final residues were performed with a Siemens F model diffractometer. The X-ray generator was a Phillips PW-1010 model and ranging from 20 to 40 kV and 6 to 50 mA while using fine focus Cu-$K_\alpha$ radiation ($\lambda$=1.5406 Å).

## Results and Discussion
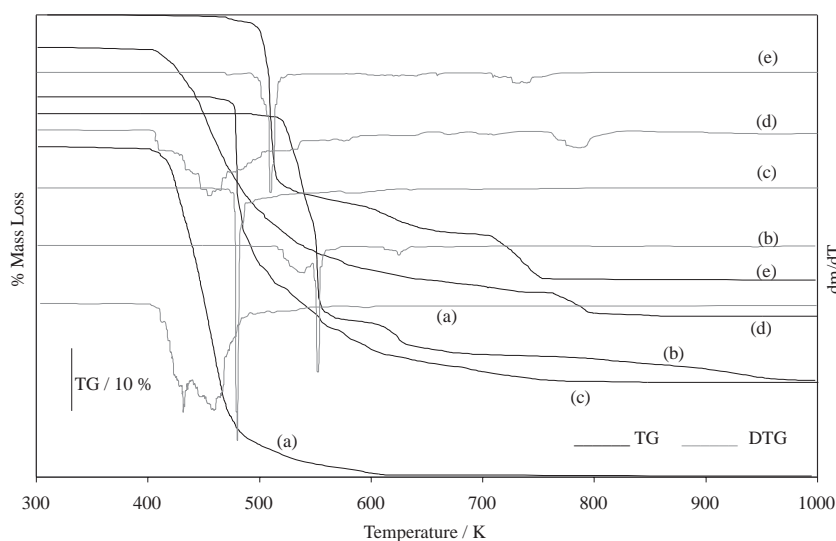
### Thermal Behaviour

Ni(II), Cu(II), Co(II) and Pd(II) complexes of N,N-dimethyl-N'-benzoylthiourea were studied by thermogravimetric analysis from ambient temperature to 1273 K in nitrogen atmosphere. The TG curves were redrawn as % mass loss *vs.* temperature (TG) curves and also as the rate of loss of mass *vs.* temperature (DTG) curves. Typical TG, DTG and DTA curves are presented in Figs. 1 and 2, and the temperature ranges and percentage mass losses of the decomposition reaction are given in Table 1, together with evolved moiety and the theoretical percentage mass losses.

The overall loss of mass from the TG curves is 87% for $Cu(DMBT)_2$, 81% for $Ni(DMBT)_2$, 81% for $Co(DMBT)_2$ and 81% for $Pd(DMBT)_2$. All the complexes show three-stage mass loss except Cu(II) complex in their TG/DTG curves. The first mass loss corresponds to the formation of their respective dimethylbenzamides (DMB). While the second and third mass loss is due to the decomposition of the thiocyanates. The end-products were confirmed with XRD data.

**Table 1.** Thermoanalytical results for the investigated compounds.

| Sample | Stage | TG results temperature range (K) | DTA results temperature peak (K) | Weight loss (%) | | Evolved moiety* |
|--------|-------|------|------|-------|------------|--------|
| | | | | Found | Calculated | |
| DMBT | I | 402-438 | 412 | 28.3 | 28.4 | HNCS |
| | II | 438-614 | 458 | 71.7 | 71.6 | DMB |
| Co(DMBT)$_2$ | I | 404-548 | 409, 458 | 61.4 | 63.0 | 2DMB |
| | II | 548-860 | 646, 791 | 19.7 | 17.8 | SCN + CN |
| | Residue | >860 | - | 18.9 | 19.2 | CoS |
| Ni(DMBT)$_2$ | I | 495-593 | 519, 553, 571 | 63.0 | 63.0 | 2DMB |
| | II | 593-731 | 621, 686 | 10.4 | 12.3 | SCN |
| | III | 731-988 | 786 | 7.4 | 5.5 | CN |
| | Residue | >988 | - | 19.2 | 19.2 | NiS |
| Cu(DMBT)$_2$ | I | 456-538 | 481, 488, 501 | 62.3 | 62.4 | 2DMB |
| | II | 538-879 | 606, 739 | 24.2 | 24.3 | 2SCN |
| | Residue | >879 | - | 13.5 | 13.3 | Cu |
| Pd(DMBT)$_2$ | I | 407-570 | 519 | 56.5 | 57.3 | 2DMB |
| | II | 570-676 | 642 | 12.0 | 11.1 | SCN |
| | III | 676-803 | 710, 770 | 12.0 | 11.1 | SCN |
| | Residue | >803 | - | 19.5 | 20.5 | Pd |

* DMB: Dimethylbenzamide.



**Figure 1.** TG/DTG curves of (a) DMBT, (b) Ni(DMBT)$_2$, (c) Cu(DMBT)$_2$, (d) Co(DMBT)$_2$ and (e) Pd(DMBT)$_2$ complexes in nitrogen atmosphere.

## DMBT ($C_{10}H_{12}N_2OS$)

DMBT melts at 411-412 K with simultaneous decomposition. The first mass loss was observed at 411 K in the TG profile. The DTA/TG/DTG profiles of ligand are shown in Figs. 1 and 2. From the TG curve, it appears that the sample decomposes in two stages over the temperature range 402-614 K. The first

decomposition occurs between 402 and 438 K with a mass loss of 28% and the second decomposition starts at 438 K and ends at 614 K with a 72% mass loss. From the corresponding DTA profile, two endothermic peaks are noted. The first maximum is at 412 K and the second at 458 K.
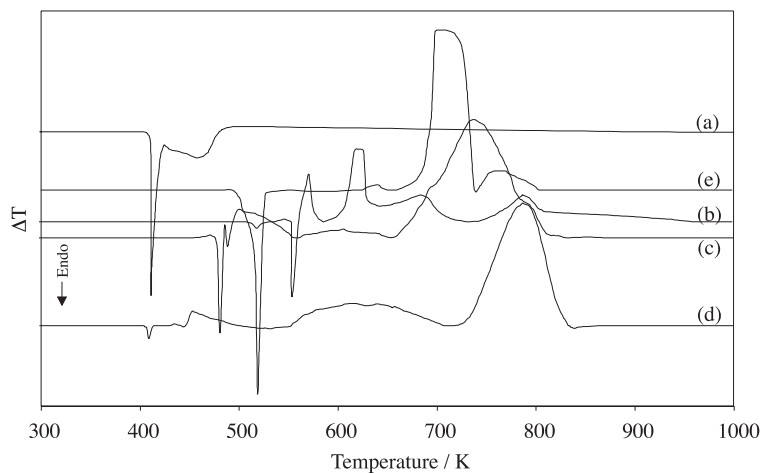


**Figure 2.** DTA curves of (a) DMBT, (b) Ni(DMBT)$_2$, (c) Cu(DMBT)$_2$, (d) Co(DMBT)$_2$ and (e) Pd(DMBT)$_2$ complexes in nitrogen atmosphere.

## Ni(II) complex $(C_{20}H_{22}N_4O_2S_2 \cdot Ni)$

The TG of this complex reveals a mass loss in the temperature range 495-593 K corresponding to the formation of Ni(SCN)$_2$. The next decomposition step occurs in the temperature range 593-731 K and corresponds to the thermal decomposition of Ni(SCN)$_2$ to NiSCN. The last decomposition step occurs in the temperature range 731-988 K and corresponds to the formation of NiS. Two endothermic peaks and four exothermic peaks were observed in the DTA analysis. The maximas of these peaks are found to be 519, 553, 571, 621, 686, and 786 K, respectively. The first peak corresponds to the melting of the complex. The first exothermic effect corresponds to the dimerisation of dimethylbenzamid group.

## Cu(II) complex $(C_{20}H_{22}N_4O_2S_2 \cdot Cu)$

The complex is thermally stable up to 456 K. The mass loss at the first stage in the temperature range 456-538 K corresponds to the decomposition of the complex to Cu(SCN)$_2$. The mass loss at the second stage in the temperature range 538-879 K due to the decomposition of Cu(SCN)$_2$ to metallic copper. The DTA profile shows two endothermic and three exothermic effects. The first, at 481 K, corresponds to the melting of the complexes, while the second, at 488 K, corresponds to the decomposition of the complexes to Cu(SCN)$_2$. The first exothermic effect corresponds to the dimerisation of the dimethylbenzamid group. The maximas of all peaks are found to be 481, 488, 501, 606, and 739 K, respectively.

## Co(II) complex $(C_{20}H_{22}N_4O_2S_2 \cdot Co)$

The TG curve indicates that the mass change begins at 404 K and continues up to 860 K. The mass loss corresponds to the formation of Co(SCN)$_2$. Beyond 548 K continuous mass loss in the TG curve is

observed up to 860 K, which corresponds to the decomposition of $Co(SCN)_2$ to CoS. The DTA curve shows one endothermic and three exothermic effects, at 409, 458, 646 and 791 K. While the endothermic peak corresponds to the melting of the complex, the first exothermic peak corresponds to its decomposition to $Co(SCN)_2$ and the latter exothermic peak corresponds to the dimerisation of the dimethylbenzamid group.

## Pd(II) complex $(C_{20}H_{22}N_4O_2S_2 \cdot Pd)$

The TG curve shows an initial mass loss in the temperature range 407-570 K corresponding to the decomposition of the complex to $Pd(SCN)_2$. This is followed by another mass loss in the temperature range 570-676 K due to the thermal decomposition of $Pd(SCN)_2$ to PdSCN. The mass loss at the last stage in the temperature range 676-803 K is due to the decomposition of PdSCN to metallic palladium. The DTA curve shows one endothermic and three exothermic effects at 519, 642, 710, and 770 K, respectively. The melting point was observed at 519 K. The first exothermic peak corresponds to the decomposition of the complexes to $Pd(SCN)_2$ at 642 K, while the second, at 710 K, corresponds to the decomposition of $Pd(SCN)_2$ to PdSCN, and the third exothermic peak, at 770 K, corresponds to the dimerisation of dimethylbenzamid and also corresponds to the decomposition of PdSCN to Pd.

The decomposition steps for the ligand are in agreement with those described by Özpozan et al.[5] The theoretical mechanism is confirmed by the GC-MS data and mass data in Figs. 3 and 4. The peaks observed at 148, 105 and 77 m/z are responsible for the evolved radical moiety. DMBT complexes of Ni(II), Cu(II), Co(II) and Pd(II) have a similar thermal decomposition mechanism, which is expected since they both have a square-planar structure. These complexes do not contain any water molecule and there is no detectable change in TG curves up to 373 K. The absence of dehydration peaks in the DTG curves and the absence of hydroxyl bands in the IR spectra indicate all of the complexes are anhydrous (Fig. 5). The stages of decomposition for all of the complexes are in agreement with those described by Özpozan et al.[5−7] and Merdivan et al.[8] and are confirmed by GC-MS data ($C_6H_5$-CO-NH-CS-N($CH_3$)$_2$(207 m/z), $C_6H_5$-CO-N($CH_3$)$_2$ (148 m/z), $C_6H_5$-CO (105 m/z), N($CH_3$)$_2$(44 m/z)), TG data and X-ray powder diffraction data (Compound, ASTM File: CoS, 25-1081; NiS, 2-1280, Pd, 5-681; Cu, 4-836)[13]. The GC-MS chromatogram and the mass spectra of DMBT and Pd(DMBT)$_2$ at different retention times are given in Figs. 3 and 4, respectively, as an example.

## Decomposition kinetics

Two methods are mentioned in the literature related to decomposition kinetics studies, Coats-Redfern[9] and Horowitz-Metzger[10], and we used these two methods in our study. From the TG curves, the order, $n$, activation energy, $E^*$, entropies, $\Delta S^*$, and pre-exponential factor, $A$, of the thermal decomposition were elucidated by well-known methods.

The linearisation curves of the Coats-Redfern and Horowitz-Metzger methods are shown in Figs. 6 and 7, respectively. Kinetic parameters for the first stages, calculated by employing the Coats-Redfern and Horowitz-Metzger equations, are summarised in Table 2, together with the radii of metal ions. The results show that the values obtained by various methods are comparable.
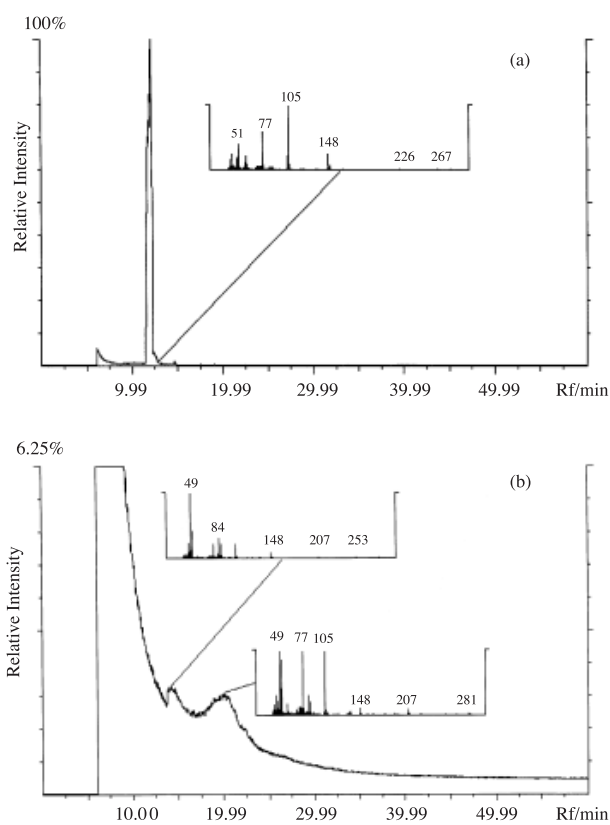
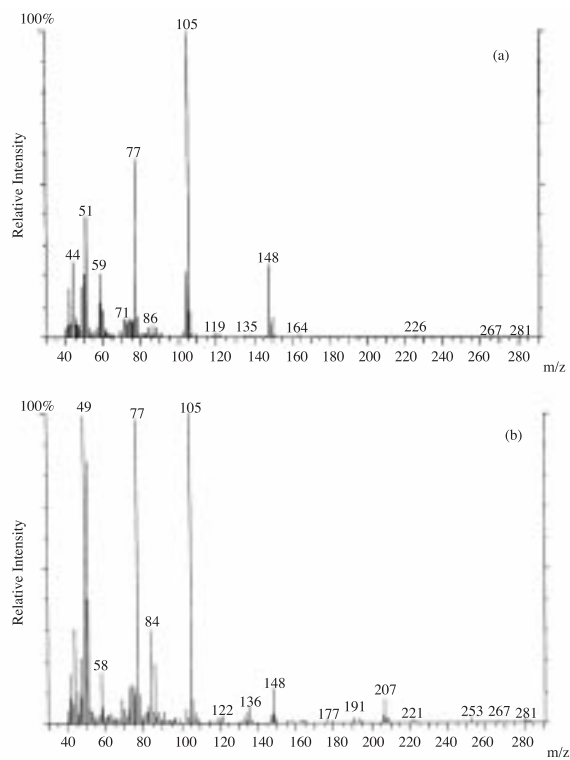**Figure 3.** GC-MS chromatogram of (a) DMBT and (b) Pd(DMBT)$_2$.



**Figure 4.** Mass spectrum of (a) DMBT (Rf=12.91) and (b) Pd(DMBT)$_2$ (Rf=19.99).

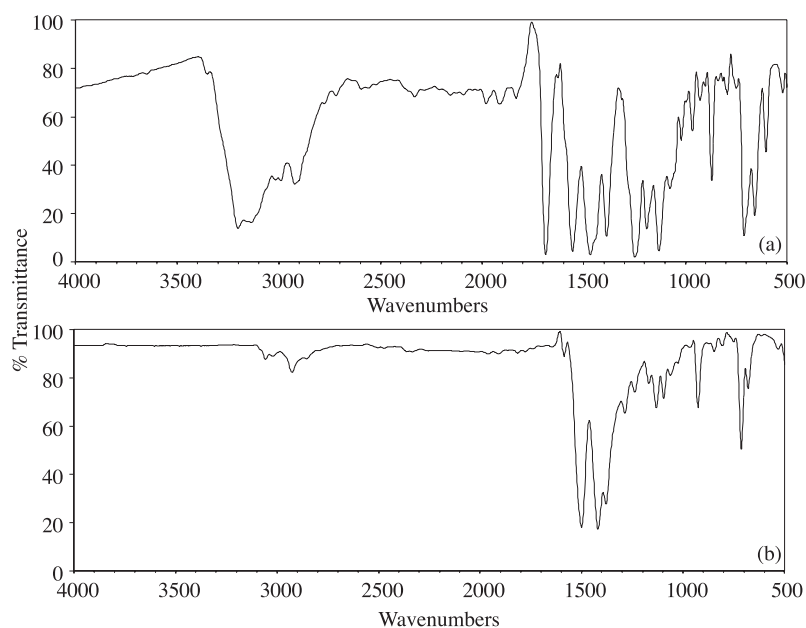**Figure 5.** IR spectra of (a) *N,N*-dimethyl-*N′*-benzoylthiourea and (b) Cu(DMBT)$_2$ complex.

**Table 2.** Kinetic data on the investigated compounds for stage I

| Compounds | Radius of metal ion /pm | Reaction order ($n$) | Parameters * | From Coats-Redfern eqn. | From Horowitz-Metzger eqn. |
|---|---|---|---|---|---|
| Cu(DMBT)$_2$ | 70 | 0.947 | $E^*$ | 43.3 | 44.6 |
|  |  |  | $A$ | 177.6 | 237.2 |
|  |  |  | $\Delta S^*$ | -205.9 | -203.5 |
|  |  |  | $r$ | 0.9922 | 0.9942 |
| Ni(DMBT)$_2$ | 72 | 0.890 | $E^*$ | 40.4 | 40.4 |
|  |  |  | $A$ | 39.9 | 17.0 |
|  |  |  | $\Delta S^*$ | -219.4 | -226.5 |
|  |  |  | $r$ | 0.9802 | 0.9852 |
| Co(DMBT)$_2$ | 74 | 0.951 | $E^*$ | 37.7 | 39.2 |
|  |  |  | $A$ | 36.4 | 63.5 |
|  |  |  | $\Delta S^*$ | -219.0 | -214.4 |
|  |  |  | $r$ | 0.9978 | 0.9989 |
| Pd(DMBT)$_2$ | 86 | 0.683 | $E^*$ | 16.0 | 23.4 |
|  |  |  | $A$ | $8.0 \times 10^{-2}$ | $42.9 \times 10^{-2}$ |
|  |  |  | $\Delta S^*$ | -270.5 | -256.4 |
|  |  |  | $r$ | 0.9865 | 0.9959 |

* Unit of parameters: $E^*$ in kJ mole$^{-1}$, $A$ in s$^{-1}$, $\Delta S^*$ in J mole$^{-1}$K$^{-1}$, $r$-correlation coefficient of the linear plot

The kinetic data obtained with the two methods are in harmony with each other. The activation energy of Co(II), Ni(II), Cu(II) and Pd(II) complexes is expected increase in relation with decrease in their radius[14]. All the complexes have the same square-planar geometry and similar decomposition steps. The smaller size of the ions permits a closer approach of the ligand. Hence the $E^*$ value in the first stages for the Cu(II) complex is higher than for the other complexes[15−18].
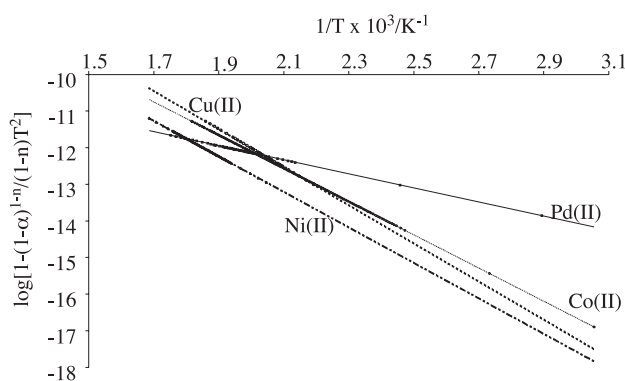
**Figure 6.** Linearisation curves of the first decomposition steps of the Coats-Redfern method for Co(II)-, Ni(II)-, Cu(II)-, Pd(II)-*N*,*N*-dimethyl-*N*′-benzoylthiourea complexes.
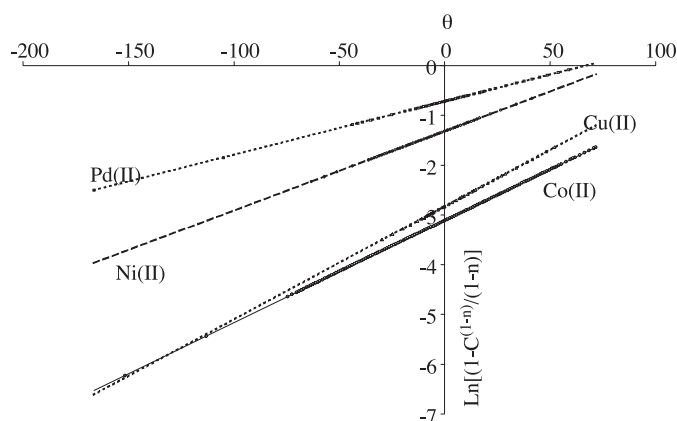


**Figure 7.** Linearisation curves of the first decomposition steps of the Horowitz-Metzger method for Co(II)-, Ni(II)-, Cu(II)-, Pd(II)-*N*,*N*-dimethyl-*N*′-benzoylthiourea complexes.

The $E^*$ values calculated with the method of Coats-Redfern for the first stages of the complexes are given below:

$E^*_{Cu} = 43.3$ kj mole$^{-1}$ $>$ $E^*_{Ni} = 40.4$ kj mole$^{-1}$ $>$ $E^*_{Co} = 37.7$ kj mole$^{-1}$ $>$ $E^*_{Pd} = 16.0$ kj mole$^{-1}$

$r_{Cu(II)} = 70$ pm $<$ $r_{Ni(II)} = 72$ pm $<$ $r_{Co(II)} = 74$ pm $<$ $r_{Pd(II)} = 86$ pm

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