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SYNTHESIS, CHARACTERIZATION OF COMPLEXES OF N-BENZOYL-N'-2-NITRO-4-METHOXYPHENYL-THIOUREA WITH Cu, Ni, Pt, Pd, Cd AND Hg

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Abstract

A series of coordination complexes with the compositions CuL, NiL·2H_2O, ML_2Cl_2 (*M*=Pt(II), Hg(II)) and $M(L–H)_2$ (*M*=Pd(II)), Cd(II)), where *L*=N-benzoyl-N'-2-nitro-4-methoxyphenylthiourea, were synthesized and characterized by conductance, EPR, IR and electronic spectral studies and thermogravimetric analysis. The IR and electronic spectra suggest coordination through the thiocarbonyl S and carbonyl O in the Pd(II) and Cd(II) complexes, and S bonding for the Pt(II) and Hg(II) complexes. The Cu(II) and Ni(II) complexes have polymeric structures in which the ligand is coordinated via the N, O and S atoms.

Keywords: complexes, EPR spectroscopy, N-benzoyl-N'-substituted phenyl thiourea, thermal decomposition

Introduction

Extensive work has been reported on the complexing behaviour of disubstituted thiourea [1, 2]. In these complexes, it has been shown that one of the coordination sites is occupied by the thiocarbonyl S. N-benzoyl-N'-alkyl- and N-benzoyl-N'-aryl-thioureas have recently attracted interest in view of their potential use as highly selective reagents for liquid-liquid extraction [3].

Satpathy and co-workers synthesized polymeric octahedral complexes of the type ML·H_2O, where *L*=N-benzoyl-N'-phenyl- and N-benzoyl-N'-ortho-substituted-phenylthioureas (containing nitro, chloro or methoxy groups), with the ligands linked to the metal ions through the N, S and O atoms [4].

The potentially bidentate ligands: $R_1R_2NC(S)NHC(O)R$, where *R*=phenyl, and R_1, R_2=alkyl, form stable neutral complexes with a variety of transition metals.

The crystal structures of such complexes for *M*=Cu(II) [5], Ni(II) [6], Pd(II) [7], Pt(II) [8, 9] or Ru(III) [10] all exhibit very similar coordination to the metal ion, with the ligand coordinated to M(II) through the S and O atoms, with concomitant loss of a proton. In the case of d^{10} metal ions (Hg(II) [11], Ag(I) [12, 13] and Cu(I) [14]), this

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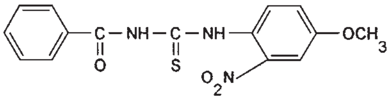
type of ligand can coordinate to the metal ion only through the S atom. The S-coordination of N-benzoyl-N'-propylthiourea to Pt(II) is known [15]. We report here the synthesis, characterization and thermal behaviour of Cu(II), Ni(II), Pt(II), Pd(II), Cd(II) and Hg(II) complexes of N-benzoyl-N'-2-nitro-4-methoxyphenylthiourea:



Experimental

The ligand N-benzoyl-N'-2-nitro-4-methoxyphenylthiourea was prepared according to the procedure described in the literature [16].

Synthesis of CuL

The Cu(II) complex may be prepared by addition a-acetate in excess of 4 mmol of copper(II) acetate in 20 ml of methanol to a methanolic solution of ligand (4 mmol in 20 ml). The mixture is stirred during 1/2 h, when the Cu(II) complex is formed as an olive-green solid. An excess of metal salt is required because the ligand can reduce Cu(II) to Cu(I) [14, 17]. (%C: calc. 45.80, exp. 44.95%; %N: calc. 10.69, exp. 10.24; %Cu: calc. 16.28, exp. 16.75.)

Synthesis of NiL·2H₂O

To a suspension of $[Ni(NH_3)_6]Br_2$ (2 mmol) in 15 ml of ethanol was added a solution of ligand (2 mmol) in ethanol (10 ml). The resulting brown mixture was stirred at 50°C for 2 h. The brown solid which precipitated out was filtered off, washed with ethanol, and then dried. (%C: calc. 42.29, exp. 41.75; %N: calc. 9.86, exp. 9.30; %Ni: calc. 13.77, exp. 14.15.)

Synthesis of PtL_2Cl_2 and $Pd(L–H)_2$

To a stirred suspension of anhydrous $PtCl_2$ or $Pd(CH_3COO)_2$ (2 mmol) in acetone (15 ml) was added dropwise a solution of ligand in acetone (4 mmol in 20 ml). The mixture was stirred at room temperature for 30 min. The resulting precipitate was filtered off and washed with acetone (for PtL_2Cl_2: %C: calc. 38.80, exp. 38.65; %N calc. 9.05, exp. 8.90; %Pt: calc. 21.01, exp. 21.15; for $Pd(L–H)_2$: %C: calc. 46.97, exp. 46.53; %N: calc. 10.96, exp. 10.42; %Pd: calc. 13.87, exp. 14.05.)

Syntheses of $Cd(L–H)_2$ and HgL_2Cl_2

These complexes were prepared as orange and yellow solids by a method similar to that for the corresponding Pd(II) and Pt(II) complexes, but with ethanol instead of acetone (for $Cd(L\text{–}H)_2$: %C: calc. 46.61, exp. 46.07; %N: calc. 10.87, exp. 10.62; %Cd: calc. 14.54, exp. 14.72; for HgL_2Cl_2: %C: calc. 38.57, exp. 38.23; %N: calc. 9.00, exp. 8.73; %Hg: calc. 21.47, exp. 21.15.)

Physical measurements

Elemental analyses were performed with a Carlo Erba L1108 automatic analyzer (C, N). Metal analyses were carried out by standard methods [18]. The molar conductivities of complexes were measured in DMF with a Radelkis OK/102 conductometer. The electronic spectra of the ligand and complexes were obtained by a diffuse-reflectance technique, MgO being used as dilution matrix, with a Carl Zeiss Jena Specord M40 spectrophotometer.

The IR spectra were run on an FT-IR BioRad (FTS-135) spectrophotometer in the range 4000–500 cm^{-1} in KBr pellets. The EPR spectra of the Cu(II) complex were recorded on polycrystalline powder and in pyridine solution, with a spectrometer ART F-5 model IFA, Bucharest. All the complexes (except that of Cd) were studied by thermogravimetry in a static air atmosphere, at sample heating rates of 20, 10 and 5°C min^{-1}, with a DuPont 2000 ATG.

Results and discussion

The range of values obtained in DMF for the molar conductivities of the complexes suggests that all are non-electrolytes.

The bands and assignments for the vibrational spectra of the ligand and the complexes prepared in this work are listed in Table 1. The assignments of the IR spectra of substituted thioureas and their complexes have been fairly well established. When the ligand is coordinated to the metal through S, the mainly C–S modes found at ~1345 and 720 cm^{-1} should be either lowered or split or both, sometimes with decreased intensity. For all the complexes examined, there is a clear lowering by about 15–20 cm^{-1} of the band at 720 cm^{-1}, indicating probable M–S bonding. This is an agreement with the findings on most of the thiourea complexes examined so far. For all the complexes, there were either slight increases or constancy of the various absorptions in the region 1600–1150 cm^{-1} (due to N–H bending and C–N stretch), which is also consistent with previous findings on S-coordinated substituted thiourea complexes [19–21]. The ν(CN) vibrations for the ligand are assigned to the bands at 1523(i), 1481(m), 1344(m) and 1163(m) cm^{-1}. The same vibrations are found at higher frequencies in the IR spectra of the complexes. This increase in frequency can be explained as resulting from a stronger double bond upon complex formation. One of the frequencies in the range 3110–3300 cm^{-1}, assigned to ν(NH) vibrations, is not present in the IR spectra of the Cu(II), Ni(II), Pd(II) and Cd(II) complexes. This indicates that deprotonation of one of the N–H groups occurs upon coordination.

The position of the band at ~1670 cm^{-1}, due to $\nu_{C=O}$ vibration, broadens and becomes of much lower intensity, shifts to a lower frequency region or disappears from the spectra of the Cu(II), Ni(II), Pd(II) and Cd(II) complexes. The position of this

Table 1 IR bands (cm^{-1}) of N-benzoyl-N’-2-nitro-4-methoxyphenylthiourea and its complexes

L	CuL	$NiL\cdot 2H_2O$	PtL_2Cl_2	$Pd(L–H)_2$	$Cd(L–H)_2$	HgL_2Cl_2	Assignments
–	–	3390	–	–	–	–	ν_{OH}
3282	–	–	3285	–	3339	3290	ν_{NH}
3110	–	3120	3154	3115	–	3115	–
1672	1617	–	1687	1626	–	1691	$\nu_{C=O}$
1597	1590	–	–	–	1593	–	δ_{NH}+phenyl
1573	1570	1570	1576	1573	–	1574	–
1523	1520	1522	1521	1515	1535	1534	$\nu_{asN–C–N}$
1481	1460	1490	1499	1483	1499	1490	$\nu_{C–N}+\nu_{C–S}$
1344	1395	1379	1352	1337	1357	1353	$\nu_{sN–C–N}+\nu_{C–S}$
1314	1308	1307	1315	1303	1307	1315	$\nu_{C–NO_2}$
1269	1272	1272	1274	1282	1285	1272	phenyl
1223	1218	1214	1232	1226	1210	1233	–
1163	–	1182	1178	1175	1182	1166	$\nu_{C–N}$
1087	1096	1093	–	–	1085	–	phenyl
1067	1068	1071	1067	1067	1063	1059	–
1029	1031	1032	1030	1025	1033	1025	$\nu_{C–OCH_3}$
851	856	858	849	850	862	850	phenyl
805	802	802	803	806	804	802	$\nu_{C–NO_2}$
720	693	696	711	696	708	709	$\nu_{C=S}$
664	670	668	670	657	678	679	phenyl

band is not changed in the IR spectra of the Pt(II) and Hg(II) complexes, suggesting that the C=O group is not involved in coordination to Pt(II) and Hg(II). The Cu(II) and Ni(II) complexes are considered to have polymeric structures in which the ligand coordinates via the N, O and S atoms.

Table 2 Electronic spectral data* on the N-benzoyl-N'-2-nitro-4-methoxyphenylthiourea complexes (nm)

Compound	Electronic spectra				
L	257	367	–	–	–
CuL	243	360	418	610	–
$NiL\cdot 2H_2O$	250	329	366	390	523
PtL_2Cl_2	241	360	426(sh)	–	–
$Pd(L–H)_2$	245	380	427(sh)	–	–

*sh=shoulder

Electronic spectral results are included in Table 2. The UV-visible absorption spectra of the Cu(II), Ni(II), Pt(II) and Pd(II) complexes are typical of square-planar complexes of these metal ions [22]. The solid reflectance spectrum of the Cu(II) complex reveals a strong band at around 610 nm, corresponding to a ligand-field transition, characteristic of elongated tetragonal octahedral or square-planar stereochemistry. The band which appears at 418 nm can be considered as reflecting a charge-transfer transition.

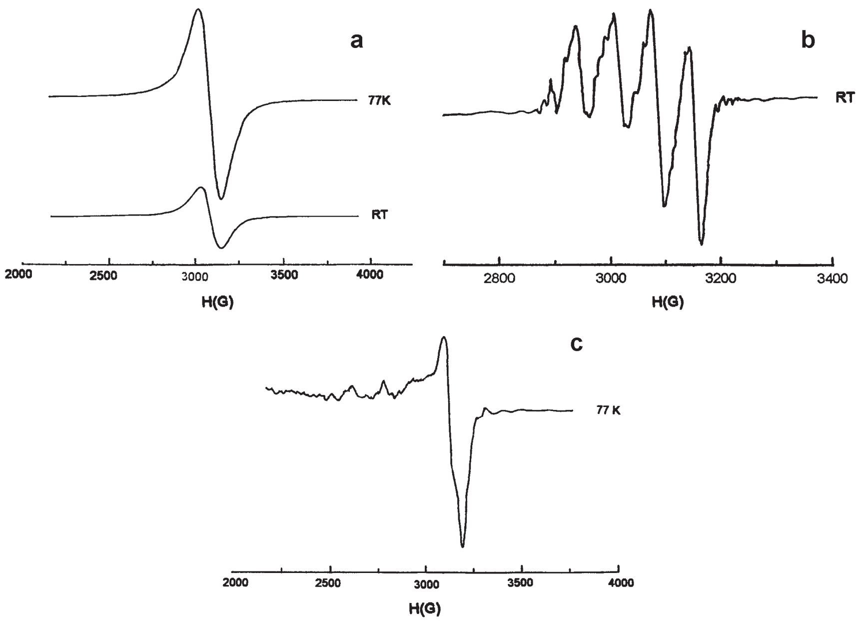


Fig. 1 EPR spectra of Cu(II) complex: a – polycrystalline powder, and pyridine solution at b – room temperature; or at c – 77 K

The EPR spectra obtained for the polycrystalline sample at room temperature and 77 K are presented in Fig. 1a, and those in pyridine solution in Fig. 1b and 1c. The spectrum recorded at 77 K is very similar to the room-temperature spectrum, indicating no significant change in stereochemistry. The broad isotropic feature found for solid CuL suggests a significant interaction between Cu(II) centers (g=2.079). The g values for the frozen pyridine solution are different from that found for the powder compound, suggesting axial interaction with the pyridine molecules ($g_{\parallel}$=2.255, $g_{\perp}$=2.014). The Cu(II) spectrum in solution has four well-defined copper hyperfine lines (A_0=69 G at room temperature, and $A_{\parallel}$=162 G and $A_{\perp}$=23 G in frozen solution at 77 K). The compound therefore possesses a square-planar configuration with the values of hyperfine splitting constants typical of the D_{4h} symmetry of the Cu(II) ion. From the above parameters, α^2 is evaluated by using the following approximate expression [23]:

$$\alpha^2=A_{\parallel}/0.036+(g_{\parallel}-2.0023)+3/7(g_{\perp}-2.0023)+0.04$$

where $A_{\parallel}$ is the parallel coupling constant expressed in cm^{-1}. The large value of α^2 (0.75) for the Cu(II) complex suggests O and N bonding [24].

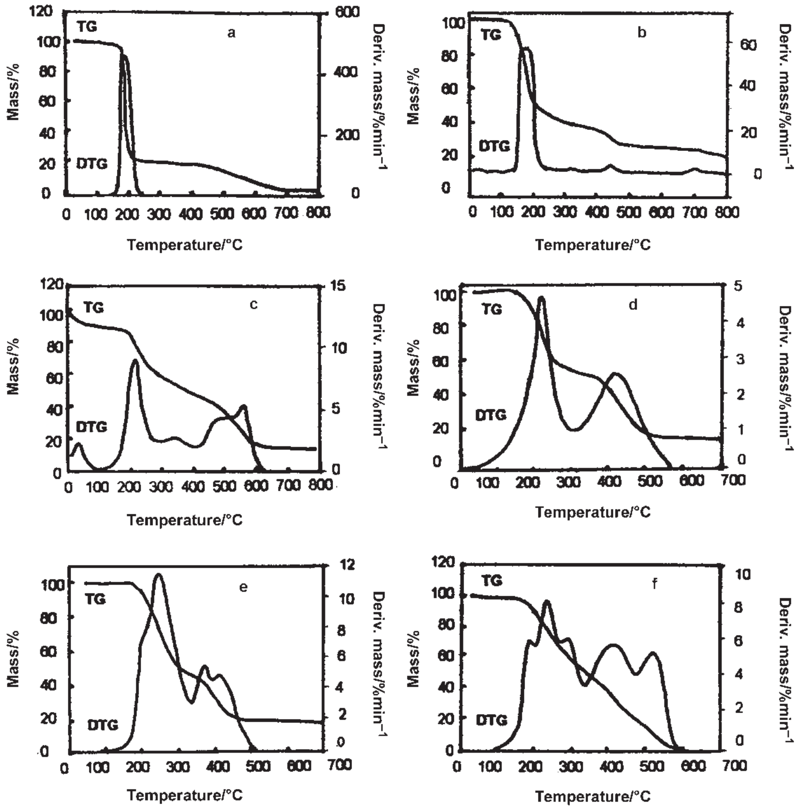


Fig. 2 TG and DTG curves for a – ligand L; b – CuL; c – NiL·2H_2O; d – PtL_2Cl_2; e – $Pd(L-H)_2$ and f – HgL_2Cl_2

Thermal behaviour

The thermal decompositions of these complexes were studied by TG. In air, the Cu, Pd and Ni complexes thermally degrade to CuO, PdO and NiO, while the Pt complex does so to the metal. There is very good agreement between the theoretical and observed mass losses (Table 3).

Table 3 Thermogravimetric analysis data in air

Compound	Overall mass loss/%			Stepped mass loss/%	
	Temp. range/°C	Calc.	Found	Temp. range/°C	Mass loss
CuL	100–800	79.65	78.03	100–230	56.72
		(CuO)		230–680	17.45
				680–800	3.86
$NiL\cdot2H_2O$	120–520	82.36	84.16	20–125	7.65
		(NiO)		125–280	30.29
				280–400	11.94
				400–625	34.14
PtL_2Cl_2	120–520	78.98	77.09	120–275	43.21
		(Pt)		275–520	36.50
$Pd(L–H)_2$	150–475	84.03	82.76	150–330	54.31
		(PdO)		330–475	27.41
HgL_2Cl_2	110–605	100	100	110–340	49.48
				340–475	30.75
				475–605	18.65

The Cu complex (Fig. 2b) decomposes in three steps. The first two steps correspond to the actual decomposition of the complex and the final step involves conversion of the sulphide to the oxide (theoretical loss: 4.07, experimental loss: 3.86%). The thermogravimetric curve of the complex $NiL\cdot2H_2O$ (Fig. 2c) reveals four steps. The first, in the range 20–125°C, corresponds to the loss of two water molecules (theoretical loss: 8.47; experimental loss: 7.65%). The other three steps correspond to the decomposition of the complex. The Pt complex decomposes in essentially two stages. The first stage of decomposition is a sequential combination of dehalogenation of the complex, followed by the loss of one molecule of ligand (theoretical loss: 43.32; experimental loss: 43.20%). The second stage of decomposition corresponds to the loss of the second molecule of ligand (theoretical loss: 35.67; experimental loss: 36.50%). Coordinated chloride is slowly evolved initially (Fig. 2d). Bourne and Koch have recently shown [15] by means of X-ray diffraction that the *cis* isomer is obtained through reaction of the Pt(II) salt with N-benzoyl-N’-propylthiourea. One of the reasons is that the carbonyl oxygen atom is locked into a ring by an N–H…O hydrogen-bond. It may be presumed that the *cis* isomer also predominates in the case of the

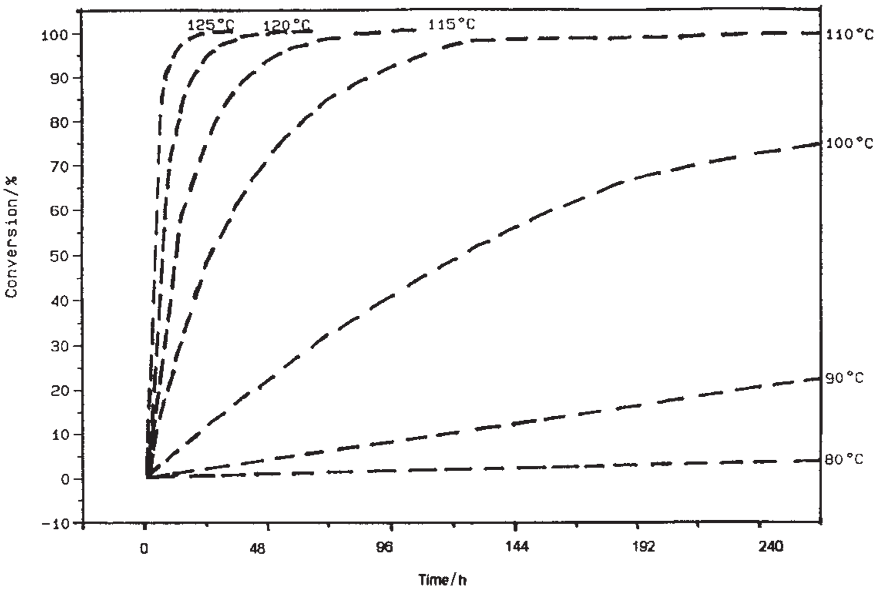


Fig. 3 Isotherms of mass loss of CuL

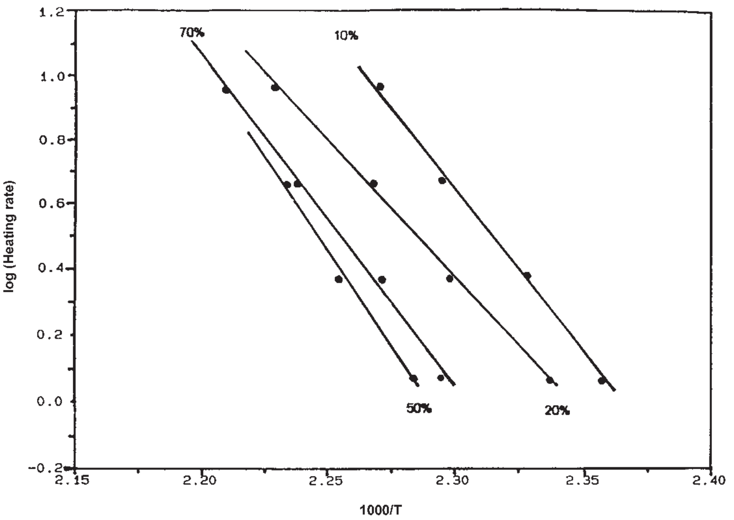


Fig. 4 Plots of log(heating rate) *vs.* $1/T$ for isothermal decomposition of CuL

Pt(II) complex with N-benzoyl-N'-2-nitro-4-methoxyphenylthiourea. In view of the high trans effect [25] of unidentate thioureas, the initial elimination of coordinated chloride is expected. In contrast, the presence of the *trans* isomer should lead to the initial evolution of the two thiourea molecules. Thus, the presence of the *cis* isomer is more probable than that of the *trans* isomer.

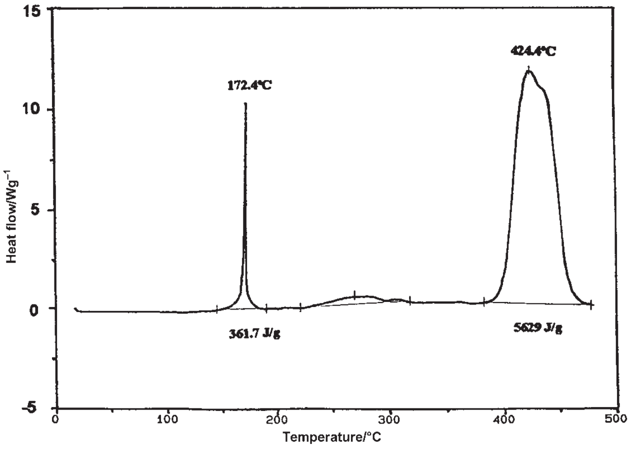


Fig. 5 DSC curve of CuL

The Pd complex decomposes in the temperature range 150–475 and a pronounced discontinuity occurs in the region of 350°C, at a mass loss of about 54%. The discontinuity represents a combination of desulphurization followed by conversion of the sulphide residue to the oxide (84.03% mass loss at 475°C) (Fig. 2e). In this case, we can conceive that M–S links are retained and extended, owing to metal sulphide formation, during the thermal decomposition [26].

Figure 3 illustrates the isothermal mass loss (as a percentage of the initial mass) *vs.* time at 80, 90, 100, 110, 115, 120 and 125°C for the Cu(II) complex. There is a relatively slow change in mass with time at 80, 90 and 100°C, but at temperatures greater than 100°C the initial period is characterized by a very fast mass loss. For Δm=const., a plot of log(heating rate) *vs.* $1/T$ (Fig. 4) should be a straight line with a slope which relates to the activation energy. Figure 4 shows such straight lines for $10\leq\%\Delta m\leq70$. In this range of $\%\Delta m$, the values of the activation energy are located in the range 129.9–167.9 kJ mol^{-1} (Table 4). For the Cu(II) complex, the DSC curve was also recorded (at a heating rate of 5°C min^{-1}); this is depicted in Fig. 5.

Table 4 Kinetic parameters at different conversion levels for isothermal decomposition of CuL

% Conversion	E_a/kJ mol^{-1}	log$A$/min^{-1}
10	165.8	18.6
20	138.9	15.4
50	129.9	14.5
70	167.9	19.4

E_a is the activation energy, and A is the pre-exponential factor

From the TG curves for the Ni, Pt, Pd and Hg complexes, the reaction order (n) and activation energy (E_a) of the thermal decomposition were obtained by the method

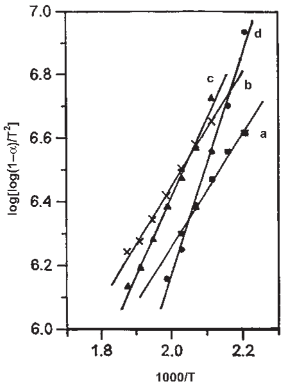


Fig. 6 Linearization plots for a – NiL·$2H_2O$; b – Pd(L–H)$_2$; c – PtL_2Cl_2 and d – HgL_2Cl_2

of Coats and Redfern [27]. The linearization plots for the complexes are shown in Fig. 6. The order of reaction in each case is unity (Table 5).

Table 5 Non-isothermal kinetic parameters

Compound	n	E_a/kJ mol^{-1}	r
NiL·$2H_2O$	1	34.2	0.9875
Pd(L–H)$_2$	1	46.6	0.9934
PtL_2Cl_2	1	67.4	0.9856
HgL_2Cl_2	1	34.4	0.9965

r is the correlation of the linear regression

It is obvious that the activation energy depends on the electronegativity of the metal atom and follows the sequence Ni(II)<Hg(II)<Pd(II)<Pt(II).

Conclusions

The initial elimination of coordinated chloride leads to the conclusion that the *cis* isomer probably predominates in the case of the Pt(II) complex.

There is a significant difference between the thermal decompositions of the complexes containing the monodentate-bound thiourea ligand (Pt(II) and Hg(II)) and the other complexes.

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