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THERMAL DECOMPOSITIONS OF SOME DIVALENT TRANSITION METAL COMPLEXES OF TRIETHANOLAMINE

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Abstract

The thermal behaviours of the Ti(II), Mn(II), Fe(II), Ni(II), Cu(II) and Zn(II) complexes of triethanolamine were studied by means of thermogravimetry, differential thermogravimetry, differential thermal analysis infrared spectrophotometry and elemental analysis. The sequence of thermal stability of the metal complexes, determined by using the initial decomposition temperature, was found to be Ti(II)≅ Mn(II)>Fe(II)>Ni(II)>Zn(II)>Cu(II). Some of the kinetic parameters, such as the activation energy and order of reaction for the initial decomposition reaction, were calculated and the relationship between the thermal stability and the chemical structure of the complexes is discussed.

Keywords: complexes, transition metals, triethanolamine

Introduction

Thermal analysis plays an important role in studies of the structures and properties of metal complexes. Thermal analysis techniques such as DTA, TG and DSC are routinely applied to determine the thermal stability ranges, the thermal character of the decomposition processes, the decomposition enthalpies and the melting points of the complexes and the stoichiometry of the derived volatile decomposition products. A number of solid-state reactions, such as the thermal isomerization, thermal phase transitions, thermal racemization and thermal decomposition of some metal complexes, have been studied by means

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of thermal analysis [1–11]. The present work describes the thermal decomposition characteristics of some divalent transition metal complexes of triethanolamine ($NTEH_3$) in terms of the stability in the solid state.

Experimental

The metal(II) complexes of $NTEH_3$ were prepared from the respective analytical grade metal chlorides and $NTEH_3$ according to the procedure described previously [12].

TG, DTG and DTA data were obtained simultaneously by using a Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser. The measurements were carried out in a dynamic atmosphere of dry nitrogen at a flow rate of 80 $ml \cdot min^{-1}$ up to 900°C. The heating rate was 10 $deg \cdot min^{-1}$ and the sample masses were in the range 4 to 6 mg. Highly sintered α-Al_2O_3 was used as the reference material.

To identify the decomposition reactions involved, large amounts of the metal(II) complexes of $NTEH_3$ were heated in a tube furnace at predetermined temperatures in a flowing nitrogen atmosphere. The decomposition temperatures used were obtained from the TG and DTG curves of the related complexes. The solid residues remaining after the decompositions were analysed by using elemental analysis and IR spectrophotometry.

The energy of activation (E_a) and order of reaction (n) for the first step in the thermal decomposition of the complexes were determined by using the Jeres modification [13] of the Freeman and Carroll method [14], applying the relation

$$[\Delta \ln(d\alpha/dT)/\Delta \ln(1-\alpha)] = n - E_a[\Delta(1/T)/\Delta \ln(1-\alpha)]/R$$

where E_a=energy of activation, T=temperature in K, R=gas constant, $\alpha = (m_{initial}-m)/(m_{initial}-m_{final})$ and n=order of reaction.

Results and discussion

All of the complexes were subjected to TG/DTA analysis from ambient temperature up to 900°C in a dynamic nitrogen atmosphere. DTA, TG and DTG curves of the Ti(II), Mn(II), Fe(II), Ni(II), Cu(II) and Zn(II) complexes of $NTEH_3$ are shown in Figs 1–6, respectively. Thermoanalytical data derived from the thermal curves are presented in Table 1. The DTA curves indicated that the decompositions of the complexes take place after melting. However, melting and decomposition occur at the same time for the Ni(II) complex. TG curves of the Ti(II), Mn(II) and Fe(II) complexes of $NTEH_3$ exhibited a one-

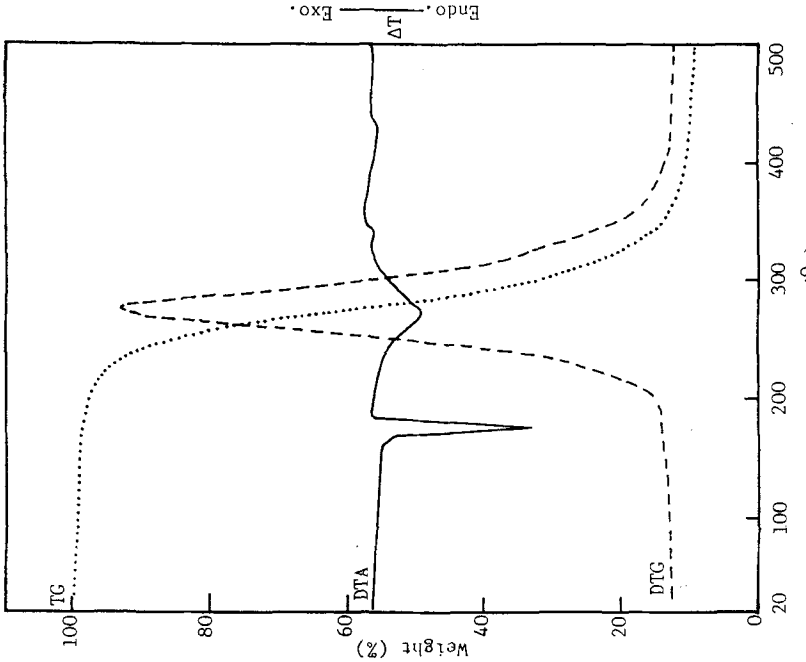

Fig. 2 DTA, TG and DTG curves of $[Mn(NTEH_3)_2]Cl_2$

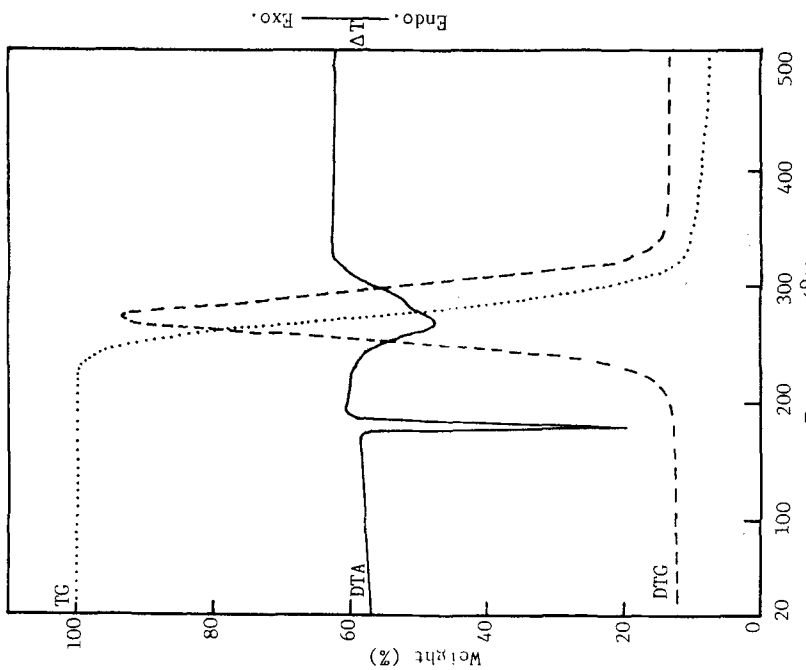

Fig. 1 DTA, TG and DTG curves of $[Ti(NTEH_3)_2]Cl_2$

Table 1 Thermoanalytical results for the metal complexes of triethanolamine

Complex	Melting point/ °C	Stage	Temp. range/ °C	DTG $_{max}$/ °C	Weight loss/ %		Solid decomposition product
					exp.	calcd.	
$[Ti(NTEH_3)_2]Cl_2$	179	1	224–338	272	89.95	88.52	Ti
$[Mn(NTEH_3)_2]Cl_2$	177	1	225–412	274	87.40	87.05	Mn
$[Fe(NTEH_3)_2]Cl_2$	174	1	210–405	277	85.15	86.86	Fe
$[Ni(NTEH_3)_2]Cl_2$	227	1	203–260	238			
		2	260–316	291	68.92	69.72	$NiCl_2$
		3	316–398	326			
$[Cu(NTEH_3)_2]Cl_2$	147	1	172–246	240			
		2	246–300	286	69.96	68.94	$CuCl_2$
		3	300–370	314			
$[Zn(NTEH_2)]Cl]Cl$	146	1	195–298	223			
		2	298–373	340	44.22	43.54	$ZnCl_2$+ZnO
		3	373–400	390			

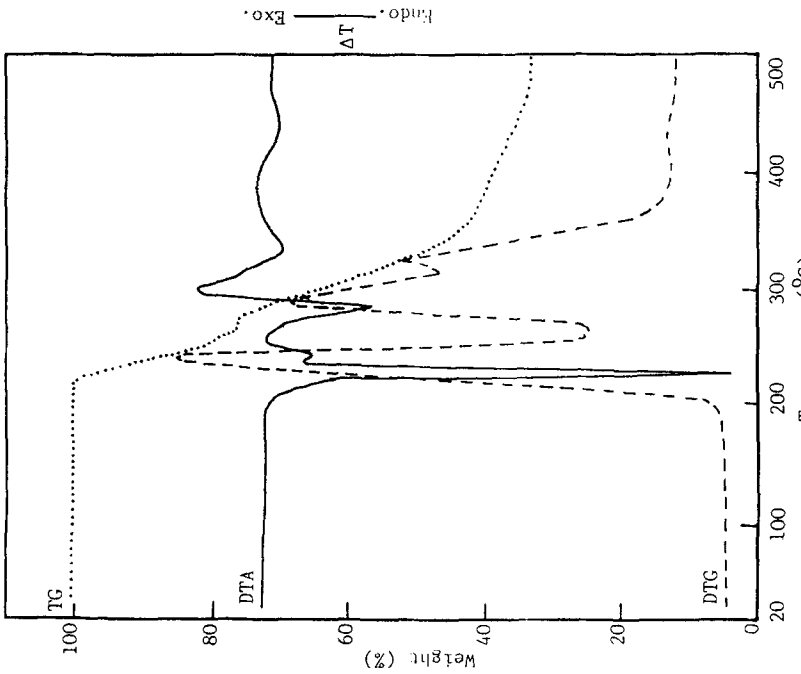

Fig. 4 DTA, TG and DTG curves of $[Ni(NTEH_3)_2]Cl_2$

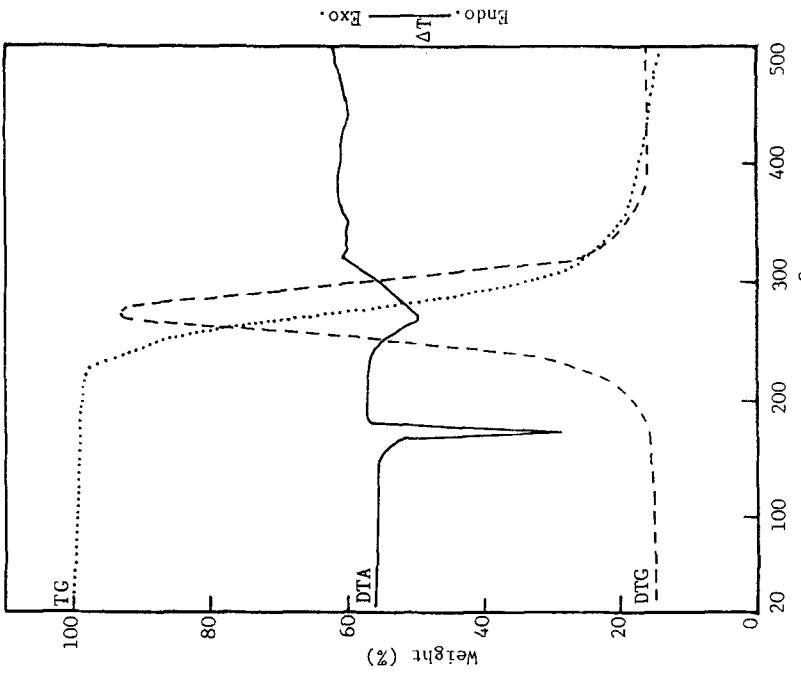

Fig. 3 DTA, TG and DTG curves of $[Fe(NTEH_3)_2]Cl_2$

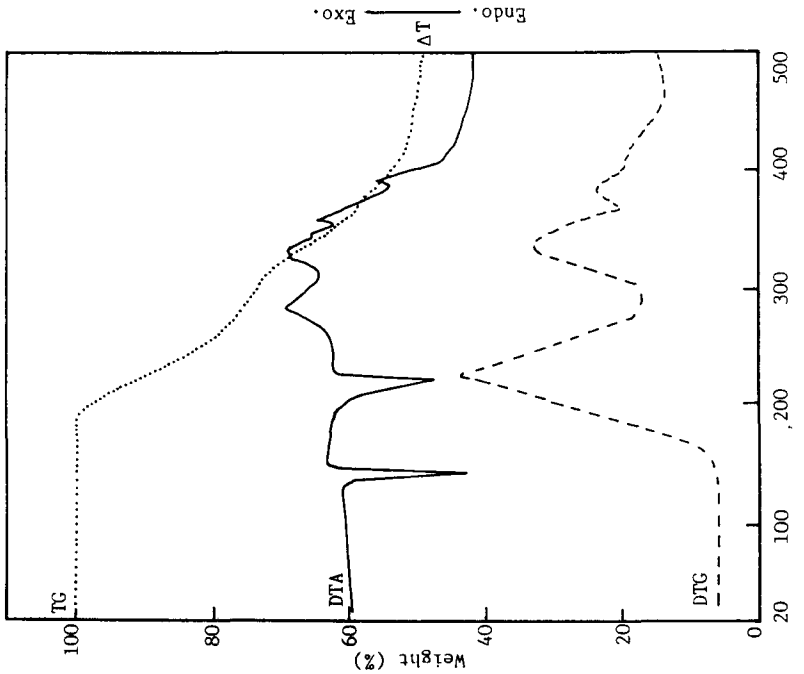

Fig. 6 DTA, TG and DTG curves of $[Zn(NTEH_2)]Cl]Cl$

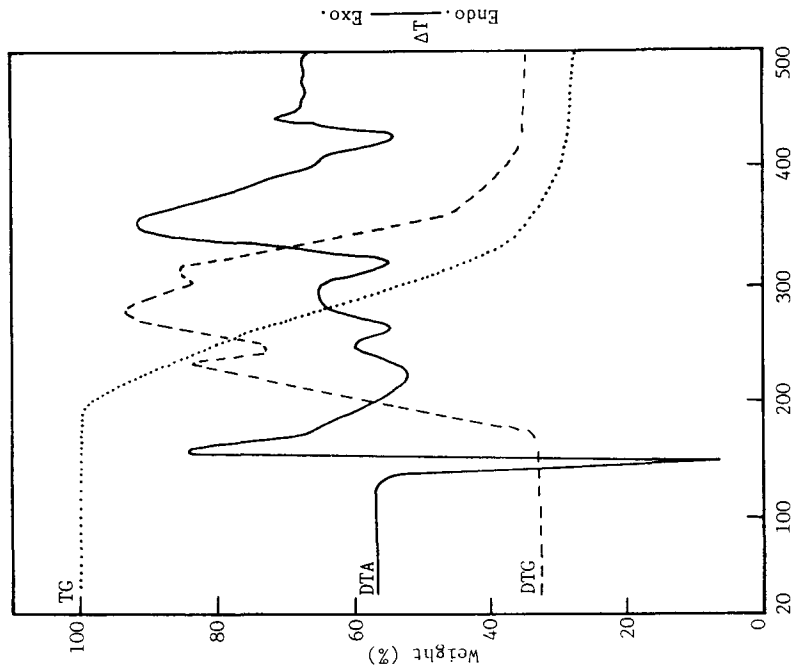

Fig. 5 DTA, TG and DTG curves of $[Cu(NTEH_3)_2]Cl_2$

stage mass loss on heating, while the Ni(II), Cu(II) and Zn(II) complexes showed a three-stage weight loss. All the complexes displayed considerable thermal stability, decomposition beginning within the temperature range 170–230°C. The complexes underwent continuous loss in mass up to nearly 700°C, but the loss above about 500°C was so slow that the thermal analyser did not record a specific DTG peak. The sequence of thermal stability was found to be Ti ≅ Mn > Fe > Ni > Zn > Cu when the initiation temperature (T_i) was taken as a parameter. The thermal decomposition behaviour of the Co(II) complexes of $NTEH_3$ was also investigated. It was observed that this complex sublimed at the melting point (170°C) and it was therefore excluded from this work.

The chemical and IR analyses of the solid residues formed at the temperatures given in Table 1 showed that the resultant final products consisted mainly of the respective metals for the Ti(II), Mn(II) and Fe(II) complexes. The Ni(II), Cu(II) and Zn(II) complexes exhibited rather complex decomposition behaviour and produced unstable intermediates, which were almost impossible to isolate because of the very small temperature differences between the steps, as seen in the TG and DTA curves (Figs 4–6). However, mass loss calculations suggested that the first decomposition stage for the Ni(II), Cu(II) and Zn(II) complexes corresponded to the removal of $NTEH_3$ from these complexes. The solid intermediates formed were very unstable and rapidly underwent further decomposition until a stable metal chloride ($NiCl_2$ or $CuCl_2$) was formed at about 400°C. Where possible, the intermediates were deducted from the elemental analyses and IR spectra. In the case of zinc, a mixture of metal chloride and metal oxide (1:1 ratio) was obtained as the final decomposition product. The experimental mass losses in Table 2 are consistent with the observed values in each transition stage, confirming the formation of the decomposition products of the complexes.

The thermogravimetric data were treated according to the Freeman–Carroll equations [14] for the first decomposition process of the complexes. The Jeres modification [13] of the Freeman–Carroll method was used to calculate the kinetic data. A plot of $[\Delta\ln(d\alpha/dT)/\Delta\ln(1-\alpha)]$ *vs.* $[\Delta(1/T)/\Delta\ln(1-\alpha)]$ is shown in Fig. 7. The slope of the plot gave the value of $-E_a/R$, and the order of the decomposition reaction (n) was determined from the ordinate intercept. The kinetic results are given in Table 2. The energies of activation for the first decomposition reaction were 16.45, 15.81, 16.32, 21.67, 21.94 and 25.95 $kJ \cdot mol^{-1}$, respectively, for the Ti(II), Mn(II), Fe(II), Ni(II), Cu(II) and Zn(II) complexes. The order of reaction for the first thermal decomposition reaction was found to be zero.

Since the heats of formation (ΔH_f°) of the metal complexes of $NTEH_3$ are not known, in order to assess the thermal stabilities of the complexes in the solid state, the initial decomposition temperature (T_i) was plotted against the negative

Table 2 Kinetic data for the first decomposition stage of the metal complexes of triethanolamine

Decomposition reaction			Evolved group	E_a / kJ·mol^{-1}	n	r*
$[Ti(NTEH_3)_2]Cl_{2(s)}$	$\xrightarrow{224-338°C}$	$Ti_{(s)}$ + Gas product	$2NTEH_3+Cl_2$	16.45	zero	0.998
$[Mn(NTEH_3)_2]Cl_{2(s)}$	$\xrightarrow{225-412°C}$	$Mn_{(s)}$ + Gas product	$2NTEH_3+Cl_2$	15.81	zero	0.996
$[Fe(NTEH_3)_2]Cl_{2(s)}$	$\xrightarrow{210-405°C}$	$Fe_{(s)}$ + Gas product	$2NTEH_3+Cl_2$	16.32	zero	0.994
$[Ni(NTEH_3)_2]Cl_{2(s)}$	$\xrightarrow{203-260°C}$	$X^*_{(s)}$ + Gas product	$NTEH_3$	21.67	zero	0.999
$[Cu(NTEH_3)_2]Cl_{2(s)}$	$\xrightarrow{172-246°C}$	$X^*_{(s)}$ + Gas product	$NTEH_3$	21.94	zero	0.998
$[Zn(NTEH_2)]Cl]Cl_{(s)}$	$\xrightarrow{195-298°C}$	$X^*_{(s)}$ + Gas product	$NTEH_3$	25.95	zero	0.999

*donates the unstable solid intermediate

** correlation coefficient of linear plot

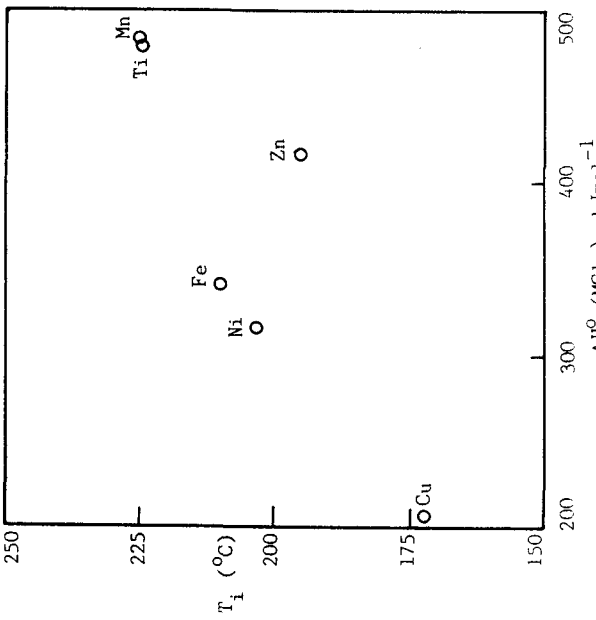

Fig. 8 Initial decomposition temperature of the complexes of triethanolamine *vs.* heat of formation of the respective metal chlorides

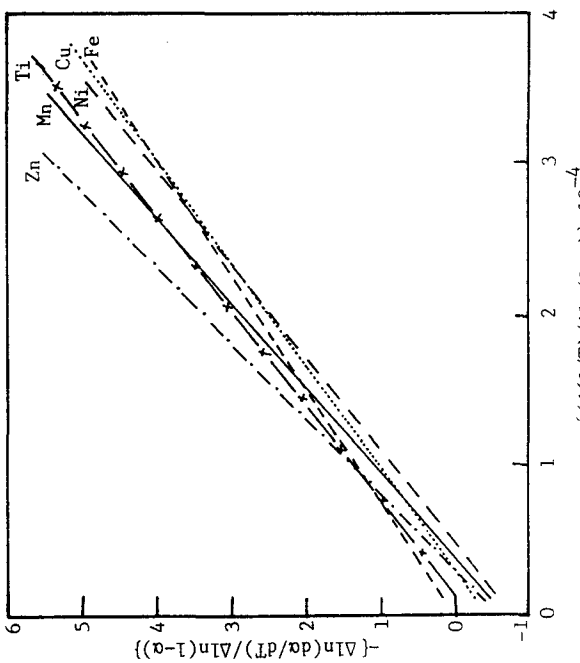

Fig. 7 Freeman and Carroll's type of plot for the first decomposition process of the complexes of triethanolamine

heat of formation ($-\Delta H_f^\circ$) [15] of the respective metal chlorides, as shown in Fig. 8. From Fig. 8, it may be said that T_i is a function of ΔH_f°. In other words, the T_i values increase with increasing $-\Delta H_f^\circ$, and the thermal stabilities of these complexes follow the same sequence as in the first transition series. Only zinc deviates from this trend. Since $-\Delta H_f^\circ$ is a measure of the stability of the compounds, the relationship confirms that T_i alone can be used as a parameter to determine the thermal stabilities of the complexes. Therefore, the thermal stability sequence of the complexes in the solid state is Ti(II) $\cong$ Mn(II) > Fe(II) > Ni(II) > Zn(II) > Cu(II). Similar findings on the thermal stabilities of different divalent metal complexes were reported by Wendlandt *et al.* [16], Wendlandt and Horton [17] and Nagar and Sharma [10], while the results published by Choudhari *et al.* [8] were controversial.

The deviation of the Zn(II) complex from the expected behaviour may be attributed to its chemical structure: the metal complexes of $NTEH_3$ are all of the high-spin type and have octahedral geometry, except the Zn(II) complex, which has a trigonal bipyramidal structure, in which the chlorine atom is directly bonded to the Zn(II) cation [12]. $NTEH_3$ acts as a neutral ligand in the octahedral complexes of Ti(II), Mn(II), Fe(II), Ni(II) and Cu(II), and each $NTEH_3$ molecule uses the nitrogen atom and two of the oxygen atoms for bonding, acting as a tridentate ligand. All the bonds in these complexes are covalent. However, the Zn(II) complex contains a $NTEH_3$ molecule in the ionic state ($NTEH_2^-$) such that one of the hydrogens in the molecule is absent and, in addition to the three covalent bonds, the ligand forms an ionic bond with the Zn(II) cation. This may increase the thermal stability of the Zn(II) complex. The Irving–Williams [18] series of stability of the complexes in solution predicts almost the reverse sequence of the series for the thermal stability in the solid state. The same sequence as found in this study was reported for the thermal stabilities of the same metal ions with different ligands by earlier workers [10, 16, 17].

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Zusammenfassung — Mittels TG, DTG, IR-Spektrofotometrie und Elementaranalyse wurde das thermische Verhalten der Ti(II)-, Mn(II)-, Fe(II)-, Ni(II)-, Cu(II)-, und Zn(II)- Komplexe von Triethanolamin untersucht. Die anhand der Temperatur für die einsetzende Zersetzung ermittelte Reihenfolge für die thermische Stabilität der Metallkomplexe lautet: Ti(II)≅Mn(II) > Fe(II) > Ni(II) > Zn(II) > Cu(II). Einige der kinetischen Parameter, wie Aktivierungsenergie und Reaktionsordnung für die einsetzende Zersetzungsreaktion wurden berechnet und die Beziehung zwischen Stabilität und chemischer Struktur der Komplexe besprochen.