

THERMAL DECOMPOSITION STUDY ON NICKEL(II) COMPLEXES OF 1,2-(DIIMINO-4'-ANTIPYRINYL)ETHANE WITH VARYING COUNTER IONS

N. T. Madhu¹, P. K. Radhakrishnan², and W. Linert^{1*}

¹Institute for Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163/AC, 1060 Vienna, Austria

²School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, Kerala, India

The phenomenological, kinetic and mechanistic aspects of the nitrate, chloride, bromide and iodide complexes of nickel(II) with 1,2-(diimino-4'-antipyrinyl)ethane (GA) have been studied by TG and DTG techniques. The kinetic parameters like activation energy, pre-exponential factor and entropy of activation were computed. The rate controlling process in all stages of decomposition is random nucleation with one nucleus on each particle (Mampel model).

Keywords: Coats–Redfern, decomposition, kinetics, nickel(II) complexes

Introduction

Because of the different possibilities to coordinate the antipyrine derivatives with transition metal ions and consequently their flexible complexing behaviour, the synthesis and structural studies of pyrazolone based ligands and their metal complexes have drawn the attention of many investigators [1–6]. But, comparatively little is known on the thermal studies [7, 8] of such complexes. In view of this, and as part of our continuing interest on thermal [7–9] aspects of antipyrine derivatives, we now report thermal studies of a new series of nickel(II) complexes of a Schiff base antipyrine ligand (Fig. 1) with a variety of counter ions such as, nitrate, chloride, bromide and iodide.

Experimental

The ligand, 1,2-(diimino-4'-antipyrinyl)ethane (GA) and its Ni(II) complexes were prepared and character-

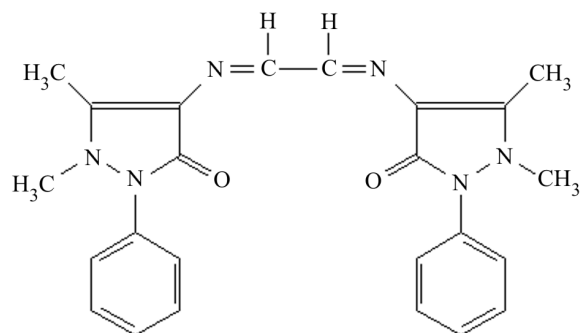


Fig. 1 1,2-(diimino-4'-antipyrinyl)ethane

ized as previously described [4]. Thermogravimetric analyses were undertaken on a Delta Series TGA 7 thermal analyzer in a nitrogen atmosphere (sample mass 10 mg, heating rate at 10°C min⁻¹). The kinetic evaluation of the thermal decomposition of the complexes was done using a computer program in Qbasic.

Results and discussion

The elemental analysis, electrical conductance in non-aqueous media, magnetic moments and infrared as well as electronic spectra show [4] that the complexes have the formulae [Ni(GA)₂]₂X₂ (X=NO₃⁻, Cl⁻, Br⁻ or I⁻). GA acts as a neutral tetradentate ligand coordinating through both the carbonyl oxygens and the azomethine nitrogens in all the complexes. The molar conductance data and the infrared spectra reveal that both the anions remain as counter ions in all the complexes. Electronic spectra and magnetic moment data suggest a square planar geometry around the Ni(II) ion in all these complexes.

Phenomenological aspects

The TG and DTG curves of the complexes are given in Figs 2–5 and the corresponding thermal analysis data is presented in Table 1.

The perchlorate complex is stable up to 234°C. Above which the thermal studies could not be conducted due its explosive nature.

The nitrate complex is formulated as [Ni(GA)](NO₃)₂. It undergoes a two stage decomposi-

* Author for correspondence: wlinert@mail.zserv.tuwien.ac.at

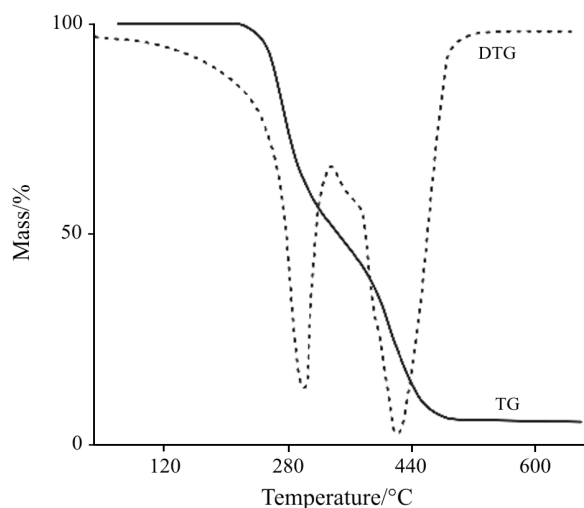


Fig. 2 TG and DTG curves of $[\text{Ni}(\text{GA})](\text{NO}_3)_2$

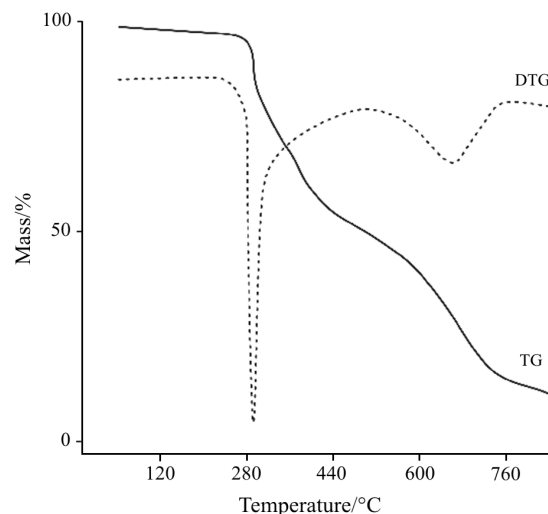


Fig. 3 TG and DTG curves of $[\text{Ni}(\text{GA})]\text{Cl}_2$

tion process and there is no mass loss up to 235°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 235°C and comes to an end at 350°C. The observed mass loss (44.34%) is due to the decomposition of one nitrate ion and half of the ligand molecule. The infrared spectrum of the residue after this stage shows the presence of GA and the nitrate ion indicating only partial decomposition of the ligand and the nitrate ion at this stage. The maximum rate of mass loss occurs at 313°C as indicated by the DTG peak. The second stage begins at 350 and ends at 501°C with the DTG peak at 438°C. The corresponding mass loss (44.67%) is attributed to the decomposi-

tion of the remaining nitrate ion and half of the molecule of GA. The decomposition gets completed at 501°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The chloride complex, $[\text{Ni}(\text{GA})]\text{Cl}_2$, undergoes decomposition in two stages in the range 193–768°C. There is no mass loss up to 193°C revealing that small molecules like water or solvents are absent in this complex. The first stage begins at 193 and ends at 456°C. The observed mass loss (39.51%) is due to the decomposition of half of the molecule of GA. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The second stage starts at

Table 1 Phenomenological data for the thermal decomposition of the obtained complexes

| Complex | Stage of decomposition | TG plateaux/°C | DTG peak/°C | Mass loss found (calcd.%) |
|---|------------------------|----------------|-------------|---------------------------|
| $[\text{Ni}(\text{GA})](\text{NO}_3)_2$ | I | 235–350 | 313 | 44.34 (49.19) |
| | II | 350–501 | 438 | 44.67 (45.19) |
| $[\text{Ni}(\text{GA})]\text{Cl}_2$ | I | 193–456 | 289 | 39.51 (38.38) |
| | II | 456–768 | 675 | 38.38 (38.38) |
| $[\text{Ni}(\text{GA})]\text{Br}_2$ | I | 221–471 | 313 | 44.63 (45.46) |
| | II | 471–629 | 564 | 44.28 (45.46) |
| $[\text{Ni}(\text{GA})]\text{I}_2$ | I | 168–434 | 276 | 45.01 (46.03) |
| | II | 434–599 | 537 | 45.70 (46.03) |

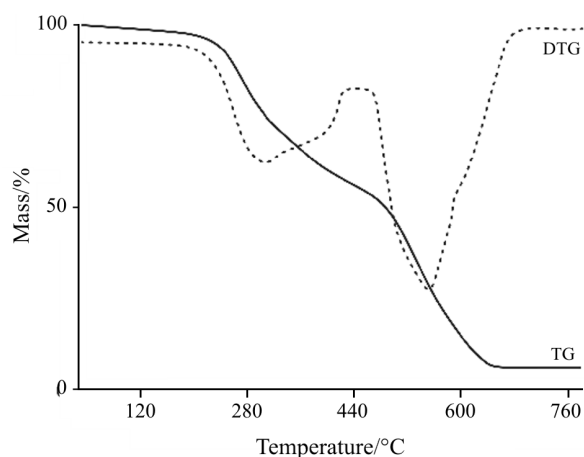


Fig. 4 TG and DTG curves of $[\text{Ni}(\text{GA})]\text{Br}_2$

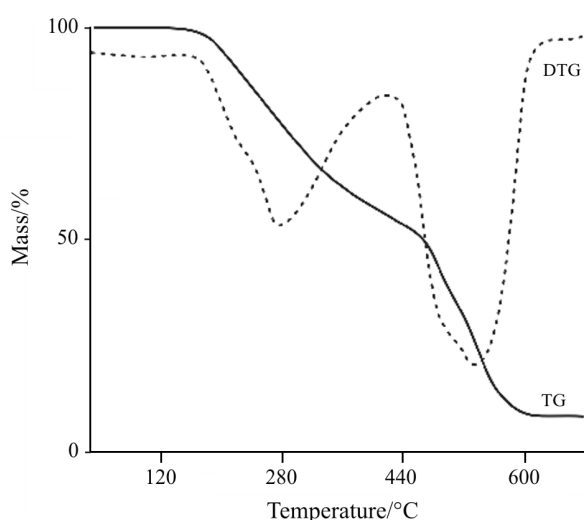


Fig. 5 TG and DTG curves of $[\text{Ni}(\text{GA})]\text{I}_2$

456 and comes to an end at 768°C, and the corresponding mass loss (38.38%) is due to the decomposition of the remaining half of the ligand molecule. The rate of mass loss is found to be maximum at 289 and 675°C respectively for the first and second stages of decomposition as indicated by the DTG peaks. The final residue is anhydrous metal chloride as confirmed by qualitative analysis.

The bromide complex, $[\text{Ni}(\text{GA})]\text{Br}_2$, undergoes a two stage decomposition pattern and there is no mass loss up to 221°C revealing the absence of either water or solvent molecules in this complex. The first stage of decomposition starts at 221 and ends at 471°C with the DTG peak at 313°C. The observed mass loss (44.63%) is due to the decomposition of half of the ligand molecule and one bromide ion. The infrared spectrum of the residue after this stage shows the presence of GA indicating only a partial removal of the ligand at this stage. The second stage begins at 471 and ends at 629°C with the DTG peak at 564°C. The corresponding mass loss (44.28%) is attributed to

the removal of the remaining half of GA and one bromide ion. The decomposition gets completed at 629°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The iodide complex, $[\text{Ni}(\text{GA})]\text{I}_2$, undergoes a two stage decomposition process in the range 168–599°C. The first stage begins at 168 and ends at 434°C. The observed mass loss (45.01%) is due to the decomposition of half of the molecule of GA and one iodide ion. The infrared spectrum of the residue after this stage shows the presence of GA indicating only partial removal of the ligand at this stage. The second stage starts at 434 and comes to an end at 599°C and the corresponding mass loss (45.70%) is due to the decomposition of the remaining half of GA and one iodide ion. The rate of mass loss is found to be maximum at 276 and 537°C respectively for the first and second stages of decompositions as indicated by the DTG peaks. The decomposition gets completed at 599°C and the final residue is qualitatively proved to be anhydrous metal oxide.

The TG results show that all the nickel(II) complexes of GA follow a two stage decomposition pattern. Even though the anions are not involved in coordination in these complexes, they exhibit a wide range in stability. Among the series the iodide complex is the least stable and the nitrate complex is the most stable. The difference in thermal stability of the complexes indicates that even though the anions are not involved in coordination they may have some marked influence on the thermal stability of the complexes and it is found in the order:



Kinetic aspects

All the well characterized decomposition stages were selected for the study of the kinetics of decomposition. The kinetic parameters like the activation energy (E) and the pre-exponential factor (A) were calculated (Table 2) using Coats–Redfern equation [10].

$$\log \left[\frac{g(\alpha)}{T^2} \right] = \log \frac{AR}{\phi E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.303RT}$$

where, T – temperature, A – pre-exponential factor, R – gas constant, ϕ – heating rate and E – activation energy.

In the present investigation $\log[g(\alpha)/T^2]$ plotted vs. $10^3/T$ gives straight lines whose slope and intercept are used to evaluate the kinetic parameters by the least squares method. The goodness of fit is checked by calculating the correlation coefficient.

The entropy of activation (ΔS) is also calculated for each stage of thermal decomposition in these complexes using the relationship,

Table 2 Kinetic parameters for the thermal decomposition of the obtained complexes

| Complex | Stage | $E/\text{kJ mol}^{-1}$ | A/s^{-1} | $\Delta S/\text{J mol}^{-1} \text{K}^{-1}$ |
|---|-------|------------------------|----------------------|--|
| [Ni(GA)](NO ₃) ₂ | I | 117.35 | $2.20 \cdot 10^4$ | -167.35 |
| | II | 155.04 | 43.63 | -220.73 |
| [Ni(GA)]Cl ₂ | I | 61.76 | 0.83 | -251.88 |
| | II | 131.25 | 39.82 | -222.34 |
| [Ni(GA)]Br ₂ | I | 43.32 | 0.13 | -267.02 |
| | II | 130.19 | 23.51 | -227.23 |
| [Ni(GA)]I ₂ | I | 31.95 | $4.61 \cdot 10^{-2}$ | -275.56 |
| | II | 127.19 | 28.85 | -225.26 |

$$A = \frac{kT_s}{h} e^{\Delta S/R}$$

where A – pre-exponential factor, k – Boltzman constant, T_s – peak temperature, ΔS – entropy of activation and R – gas constant.

The activation energies (E) in the different stages of thermal decomposition of nickel(II) complexes are in the range 31.95–155.04 kJ mol⁻¹. The corresponding values of pre-exponential factor (A) vary from $4.61 \cdot 10^{-2}$ to $2.20 \cdot 10^4$ s⁻¹. The respective values of the entropy of activation (ΔS) fall in the range -275.56 to -167.35 J mol⁻¹ K⁻¹. There is no definite trend either in the values of A or ΔS among the different stages of decomposition in the present series. But the activation energy for the second stage is greater than that of the first stage, may be due to the less steric strain occurring at that stage [7–9]. However, the negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants [7–9, 11].

Mechanistic aspects

The assignment of the mechanism of thermal decomposition is based on the assumption that the form of $g(\alpha)$ depends on the reaction mechanism. In the present investigation, nine forms of $g(\alpha)$, suggested by

Satava [12], are used to enunciate the mechanism of thermal decomposition in each stage. The correlation coefficient for all these nine forms were calculated and the form of $g(\alpha)$ for which the correlation has a maximum value is chosen as the mechanism of reaction (Table 3). In the present investigation, the highest value of correlation coefficient is obtained for

$$g(\alpha) = -\ln(1 - \alpha)$$

in all stages of decomposition. Hence the mechanism of decomposition is the random nucleation with one nucleus on each particle. This represents the ‘Mampel model’ [7, 8, 11, 12].

Conclusions

The TG data reveal that though the stoichiometry of all the complexes are the same, the nitrate complex is more stable and the iodide complex is the least stable among the series. All of them undergo a two stage decomposition pattern.

There is no definite trend observed either in the value of A or in the value of ΔS in the different stages of decomposition among the series. But the activation energy can be correlated to the steric strain that occurred for the intermediate compound.

Table 3 Correlation coefficients calculated using the nine forms of $g(\alpha)$ for the obtained complexes

| No. | Form of $g(\alpha)$ | Correlation coefficient (r) | | | | | | | |
|-----|--------------------------------------|---------------------------------|----------|------------------|----------|-----------------|----------|----------------|----------|
| | | nitrate complex | | chloride complex | | bromide complex | | iodide complex | |
| | | stage I | stage II | stage I | stage II | stage I | stage II | stage I | stage II |
| 1 | α^2 | -0.9567 | -0.9854 | -0.9724 | -0.9804 | -0.9695 | -0.9762 | -0.9778 | -0.9871 |
| 2 | $\alpha + (1-\alpha)\ln(1-\alpha)$ | -0.9745 | -0.9922 | -0.9855 | -0.9887 | -0.9842 | -0.9865 | -0.9891 | -0.9930 |
| 3 | $[1-(1-\alpha)^{1/3}]^2$ | -0.9462 | -0.9801 | -0.9993 | -0.9728 | -0.9200 | -0.9660 | -0.9292 | -0.9820 |
| 4 | $[1-(2/3)\alpha] - (1-\alpha)^{2/3}$ | -0.9821 | -0.9945 | -0.9909 | -0.9916 | -0.9895 | -0.9902 | -0.9928 | -0.9949 |
| 5 | $-\ln(1-\alpha)$ | -0.9992 | -0.9994 | -0.9994 | -0.9991 | -0.9991 | -0.9992 | -0.9995 | -0.9995 |
| 6 | $[-\ln(1-\alpha)]^{1/2}$ | -0.9989 | -0.9990 | -0.9993 | -0.9988 | -0.9986 | -0.9990 | -0.9984 | -0.9992 |
| 7 | $[-\ln(1-\alpha)]^{1/3}$ | -0.9987 | -0.9987 | -0.9991 | -0.9985 | -0.9974 | -0.9987 | -0.9938 | -0.9990 |
| 8 | $1-(1-\alpha)^{1/2}$ | -0.9847 | -0.9949 | -0.9915 | -0.9921 | -0.9885 | -0.9907 | -0.9912 | -0.9952 |
| 9 | $1-(1-\alpha)^{1/3}$ | -0.9921 | -0.9972 | -0.9969 | -0.9953 | -0.9947 | -0.9947 | -0.9959 | -0.9974 |

The mechanism for the solid state thermal decomposition for the different decomposition stages in all the complexes is found to be random nucleation with one nucleus on each particle. This represents the – Mampel model.

Acknowledgements

Thanks for financial support are due to the ‘Fonds zur Förderung der Wissenschaftlichen Forschung in Österreich’ (Project 15874-N03) and to the ‘Jubiläumsfondes’ of the Austrian National Bank (Project 10668).

References

- 1 M. Alaudeen, A. Abraham and P. K. Radhakrishnan, Proc. Ind. Acad. Sci. (Chem. Sci.), 107 (1995) 57.
- 2 C. J. Alice and C. P. Prabhakaran, Trans. Met. Chem., 15 (1990) 449.
- 3 N. T. Madhu, P. K. Radhakrishnan, M. Grunert, P. Weinberger and W. Linert, Rev. Inor. Chem., 23 (2003) 1.
- 4 N. T. Madhu and P. K. Radhakrishnan, Synth. React. Inorg. Met.-Org. Chem., 30 (2000) 1561.
- 5 N. T. Madhu and P. K. Radhakrishnan, Transition Met. Chem., 25 (2000) 287.
- 6 V. T. Thomas, N. T. Madhu and P. K. Radhakrishnan, Synth. React. Inorg. Met.-Org. Chem., 32 (2002) 1799.
- 7 N. T. Madhu, P. K. Radhakrishnan, M. Grunert, P. Weinberger and W. Linert, Thermochim. Acta, 400 (2003) 29.
- 8 N. T. Madhu, P. K. Radhakrishnan, M. Grunert, P. Weinberger and W. Linert, Thermochim. Acta, 400 (2003) 29.
- 9 N. T. Madhu, P. K. Radhakrishnan, E. Williams and W. Linert, J. Therm. Anal. Cal., 79 (2005) 157.
- 10 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
- 11 S. Mathew, C. G. R. Nair and K. N. Ninan, Thermochim. Acta, 155 (1989) 247.
- 12 V. Satava, Thermochim. Acta, 2 (1971) 423.

Received: July 25, 2005

Accepted: October 17, 2005

DOI: 10.1007/s10973-005-7268-5