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# THERMAL DECOMPOSITION STUDIES ON COBALT(II) COMPLEXES OF 4-N-(4'-ANTIPYRYLMETHYLIDENE)AMINOANTIPYRINE WITH VARYING COUNTER IONS

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The phenomenological, kinetic and mechanistic aspects of the nitrate, chloride, bromide and iodide complexes of cobalt(II) with 4-N-(4'-antipyrylmethylidene)aminoantipyrine (AA) have been studied by TG and DTG techniques. The kinetic parameters such as activation energy, pre-exponential factor and entropy of activation were computed. The rate controlling process at all stages of decomposition is random nucleation with one nucleus on each particle (Mampel model)

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

## Introduction

Antipyrine and its derivatives possess interesting pharmacological properties [1, 2]. But, comparatively little is known about complexes of antipyrine derivatives with 3d-metal ions [3–6], especially their thermal studies [7–10]. In view of this, and as part of our continuing interest on thermal [7–10] aspects of antipyrine derivatives, we present a report regarding the thermal studies of a new series of cobalt(II) complexes of a Schiff base antipyrine ligand containing a variety of counter ions such as, nitrate, chloride, bromide and iodide.

## Experimental

The ligand, 4-N-(4'-antipyrylmethylidene) aminoantipyrine (AA) and its Co(II) complexes were prepared and characterised 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 $\text{min}^{-1}$). The kinetic evaluation of the thermal decomposition of the complexes was done using a computer program in Qbasic.

## Results and discussion

Results from elemental analysis, electrical conductance in non-aqueous media, magnetic moments and infrared as well as electronic spectra all show [4] that the complexes have the formulae $[Co(AA)_2)]X_2$($X$=$NO_3^-$ or $Br^-$ or $I^-$) and, $[Co(AA)Cl_2]$. AA acts as a neutral bidentate ligand coordinating through the carbonyl oxygen of ($C^1$=O) and the azomethine nitrogen in all the complexes. The molar conductance data and the infrared spectra reveal that both anions remain as counter ions in the nitrate, bromide and iodide complexes, but in the chloride complex both counter ions are in a coordinated fashion. Electronic spectra and magnetic moment data suggest a tetrahedral geometry around the Co(II) ion in all these complexes.

### *Phenomenological aspects*

The TG and DTG curves of the complexes are illustrated in Figs 1–4 while the corresponding thermal analysis data is presented in Table 1.

The nitrate complex is represented as $[Co(AA)_2](NO_3)_2$. Up to a temperature of 269°C there is no mass loss, indicating that either water or solvent molecules are absent in this complex. Thermal decomposition occurs in two stages. The first stage starts at 269°C and ends at 296°C with the DTG peak at 280°C. The observed mass loss (12.57%) is attributed to the decomposition of two nitrate ions. Infrared spectral analysis supported the absence of nitrate ion in the intermediate product obtained at 296°C. The second stage starts at 296°C and comes to an end at 666°C. The corresponding mass loss (80.43%) is at-

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

| Complex | Stage of decomposition | TG platenau/°C | DTG peak/°C | Mass loss found (calcd.)/% |
|---|---|---|---|---|
| $[Co(AA)_2](NO_3)_2$ | I | 269–296 | 280 | 12.57<br>(12.62) |
| | II | 296–666 | 553 | 80.43<br>(81.71) |
| $[Co(AA)Cl_2]$ | I | 278–433 | 332 | 36.59<br>(37.78) |
| | II | 433–720 | 677 | 36.95<br>(37.78) |
| $[Co(AA)_2]Br_2$ | I | 236–442 | 311 | 39.13<br>(39.29) |
| | II | 442– | – | continuous |
| $[Co(AA)_2]I_2$ | I | 167–238 | 222 | 23.18<br>(22.75) |
| | II | 238–433 | 326 | 35.50<br>(35.98) |
| | III | 433–543 | 519 | 36.23<br>(35.98) |

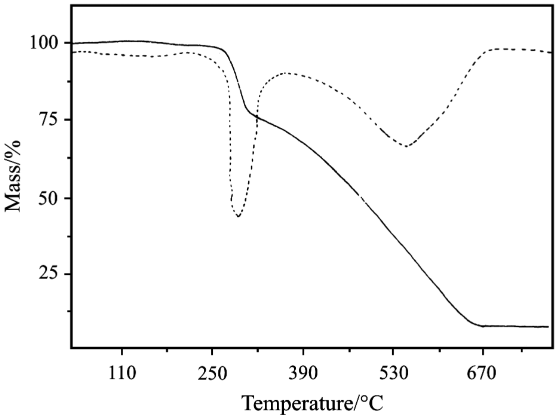

**Fig. 1** TG and DTG curves of $[Co(AA)_2](NO_3)_2$

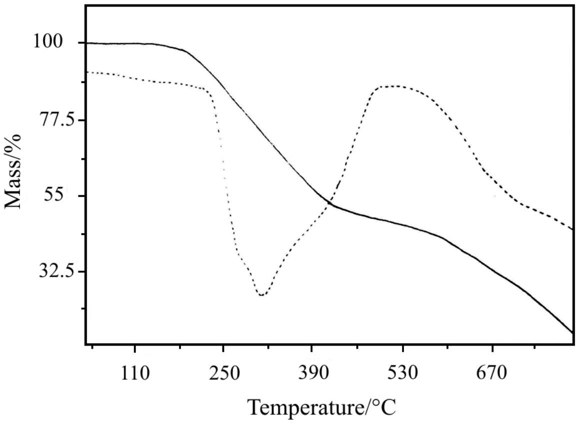

**Fig. 3** TG and DTG curves of $[Co(AA)_2]Br_2$

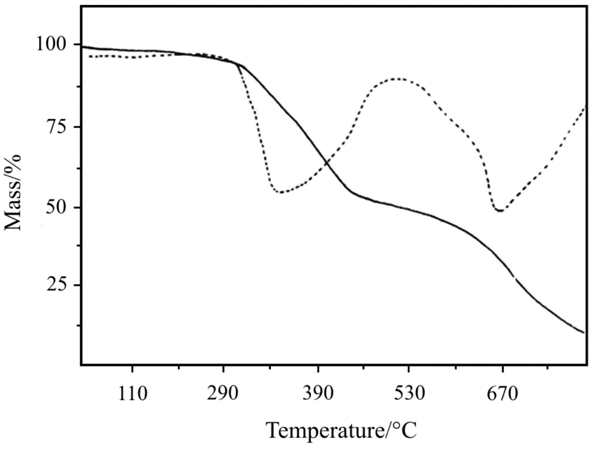

**Fig. 2** TG and DTG curves of $[Co(AA)Cl_2]$

tributed to the decomposition of two molecules of AA. The rate of mass loss is maximum at 553°C as indicated by the DTG peak. The decomposition reaches completion at 666°C and the final residue is qualitatively proved to be anhydrous metal oxide.

Similarly chloride complex, $[Co(AA)Cl_2]$, undergoes a two-stage decomposition. In this incidence there is no mass loss up to 278°C again indicating that small molecules such as water or solvent are absent in this complex. The primary decomposition begins at 278 and ends at 433°C. The corresponding mass loss (36.59%) is due to the decomposition of half of the molecule of AA. The infrared spectrum of the residue taken at this intermediate stage shows the presence of AA suggesting partial removal of the ligand at this temperature. The second stage of thermal decomposition starts at 433 and comes to an end at 720°C, and has a corresponding mass loss (36.95%) asso-

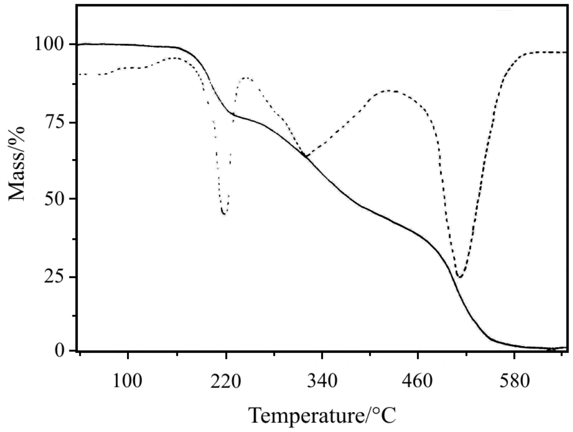

**Fig. 4** TG and DTG curves of $[Co(AA)_2]I_2$

ciated with the removal of the remaining half of the ligand molecule. Qualitative analysis confirms the final residue as an anhydrous metal chloride. The rate of mass loss is found to be maximum at 332 and 677°C for the first and second stages of decomposition respectively as indicated by the DTG peaks.

The bromide complex is formulated as $[Co(AA)_2]Br_2$. There is no mass loss up to 236°C again indicating that either water or solvent molecules are absent in this complex. Similar to the previous two complexes thermal decomposition occurs in two individual stages. The first stage starts at 236 and ends at 442°C with the DTG peak at 311°C. The corresponding mass loss (39.13%) is, like the chloride complex, attributed to the decomposition of one molecule of AA. The second stage of decomposition, which starts at 442°C is a continuous one. The steady mass loss observed in this stage may be due to the expulsion of the remaining ligand molecule together with volatilisation of the anhydrous metal bromide residue [7, 11] above 678°C.

The iodide complex, $[Co(AA)_2]I_2$, undergoes a three-stage decomposition pattern in the range 167–543°C. There is no mass loss up to 167°C indicating the absence of either water or solvent molecules in this complex. The first decomposition stage starts at 167 and ends at 238°C with the DTG peak at 222°C. The corresponding mass loss (23.18%) is attributed to the decomposition of two iodide ions. The second stage of decomposition starts at 238 and comes to an end at 433°C with the DTG peak at 326°C. The corresponding mass loss (35.50%) is associated with the decomposition of a molecule of AA. The final decomposition stage occurs in the temperature range 433–543°C with the DTG peak at 519°C. A corresponding mass loss (36.23%) is due to the decomposition of the remaining molecule of AA. The decomposition reaches completion at 543°C with the final residue qualitatively proved to be the anhydrous metal oxide.

### *Kinetic aspects*

To study the kinetics of thermal decomposition all the well characterized decomposition stages were taken into account. The kinetic parameters such as the activation energy ($E$) and the pre-exponential factor ($A$) were calculated using Coats–Redfern equation [12].

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

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

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

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

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

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

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

| Complex | Stage | $E$/kJ mol$^{-1}$ | A/s$^{-1}$ | $\Delta S$/J K mol$^{-1}$ |
|---|---|---|---|---|
| $[Co(AA)_2](NO_3)_2$ | I | 58.70 | $1.25\cdot10^{10}$ | –56.89 |
| | II | 292.24 | $9.38\cdot10^{-2}$ | –272.17 |
| $[Co(AA)Cl_2]$ | I | 61.39 | 0.58 | –255.20 |
| | II | 125.21 | 5.00 | –241.14 |
| $[Co(AA)_2]Br_2$ | I | 51.09 | 0.25 | –261.70 |
| $[Co(AA)_2]I_2$ | I | 59.11 | $2.43\cdot10^{4}$ | –165.16 |
| | II | 133.99 | 0.60 | –254.84 |
| | III | 208.69 | $1.24\cdot10^{4}$ | –174.60 |

**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 I | Stage II | Stage III |
| 1 | $\alpha^2$ | –0.9845 | –0.9974 | –0.9875 | –0.9826 | –0.9838 | –0.9835 | –0.9821 | –0.9854 |
| 2 | $\alpha+(1-\alpha)\ln(1-\alpha)$ | –0.9913 | –0.9755 | –0.9939 | –0.9909 | –0.9916 | –0.9915 | –0.9900 | –0.9925 |
| 3 | $[1-(1-\alpha)^{1/3}]^2$ | –0.9829 | –0.9831 | –0.9771 | –0.9729 | –0.9676 | –0.9798 | –0.9681 | –0.9813 |
| 4 | $[1-(2/3)\alpha]-(1-\alpha)^{2/3}$ | –0.9937 | –0.9992 | –0.9959 | –0.9938 | –0.9941 | –0.9943 | –0.9926 | –0.9950 |
| 5 | $-\ln(1-\alpha)$ | –0.9990 | –0.9999 | –0.9990 | –0.9993 | –0.9991 | –0.9995 | –0.9991 | –0.9996 |
| 6 | $[-\ln(1-\alpha)]^{1/2}$ | –0.9989 | –0.9542 | –0.9987 | –0.9992 | –0.9984 | –0.9994 | –0.9986 | –0.9995 |
| 7 | $[-\ln(1-\alpha)]^{1/3}$ | –0.9986 | –0.8572 | –0.9980 | –0.9990 | –0.9968 | –0.9992 | –0.9970 | –0.9992 |
| 8 | $1-(1-\alpha)^{1/2}$ | –0.9946 | –0.9982 | –0.9958 | –0.9942 | –0.9937 | –0.9951 | –0.9922 | –0.9959 |
| 9 | $1-(1-\alpha)^{1/3}$ | –0.9970 | –0.9935 | –0.9978 | –0.9971 | –0.9966 | –0.9976 | –0.9955 | –0.9981 |

The values of various kinetic parameters calculated are given in Table 2. The activation energies ($E$) for the individual stages of decomposition are range between 51.09–292.24 kJ mol$^{-1}$. While, the corresponding values for the pre-exponential factor ($A$) range from $9.38\cdot10^{-2}$–$1.25\cdot10^{10}$ s$^{-1}$. The respective values for the entropy of activation ($\Delta S$) are from –272.17 to –56.89 J K mol$^{-1}$. No definite trend was observed for either the values of A or $\Delta S$ among the different stages of decomposition in the present series. The fact that 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 point [7, 8]. However, negative values of entropy of activation indicate that the activated complex has a more ordered structure than the reactants [7–9, 13].

### *Mechanistic aspects*

The assignment of the specific 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 [14], are used to enunciate the mechanism of thermal decomposition at 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' [7–10, 13].

## Conclusion

The TG data reveal that though the stoichiometry of the nitrate, bromide and iodide complexes are the same, the nitrate complex is most stable. All complexes undergo a two-stage decomposition pattern, except the iodide complex which has a pattern of three decomposition stages. The chloride complex, the molecular composition of which is different from the other complexes, follows a two-stage decomposition process. Among the series, the iodide complex is the least stable and the nitrate complex is the most stable.

There is no definite trend observed either in the value of $A$ or in the value of $\Delta S$ in the different stages of decomposition among the series. However, the activation energy can be correlated to the steric strain, which occurred for the intermediate compound.

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

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## 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 A. M. Donia and F. A. El-Saied, Polyhedron, 21 (1988) 2149.
4 N. T. Madhu and P. K. Radhakrishnan, Trans. Met. Chem., 25 (2000) 287.
5 N. T. Madhu and P. K. Radhakrishnan, Synth. React. Inorg. Met.-Org. Chem., 31 (2001) 315.
6 N. T. Madhu, P. K. Radhakrishnan, M. Grunert, P. Weinberger and W. Linert, Rev. Inorg. Chem., 23 (2003) 1.
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, 407 (2003) 73.
9 N. T. Madhu, P. K. Radhakrishnan, M. Grunert, P. Weinberger and W. Linert, J. Therm. Anal. Cal., 76 (2004) 813.
10 C. R. Vinodkumar, M. K. M. Nair and P. K. Radhakrishnan, J. Therm. Anal. Cal., 61 (2000) 143.
11 J. A. Dean, Inorganic Chemistry (Section 4) in: Langes Hand Book of Chemistry, McGraw-Hill International Edition, New York 1987.
12 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
13 S. Mathew, C. G. R. Nair and K. N. Ninan, Thermochim. Acta, 155 (1989) 247.
14 V. Satava, Thermochim. Acta, 2 (1971) 423.

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