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# IR, TG, DTG AND DTA STUDIES OF BIS-(4-AMINOSALICYLATO)-DIAQUO COMPLEXES OF VO(II), Cu(II), Ni(II), Co(II), Fe(II) AND Mn(II) *

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## ABSTRACT

Reaction of the 4-aminosalicylate anion with VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) gave bis-(4-aminosalicylato)-diaquo complexes. The structure of these complexes was predicted from elemental analyses and IR spectra. The decomposition of the complexes was studied by TG, DTG a id DTA techniques. The decomposition process consisted of two steps: elimination of two water molecules followed by simultaneous decomposition of the dehydrated complex with metal oxide as the end product. The thermal stability of the complexes follows the order: VO(II), > Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II), which is also the order of covalency of the M–O bond.

## INTRODUCTION

The versatile chelating ability of 4-aminosalicylic acid (4-ASA) with various metals is well established. Structural studies have shown that it can form various types of complexes having different types of bonding, depending on the nature of the metal ion and reaction conditions. Much effort has been devoted to the preparation and study of metal chelates of 4-ASA, mainly because of the possibility of their use as antimicrobial agents.

We are greatly interested in the thermal study of transition metal complexes of 4-ASA, and have already investigated the antifungal and antibacterial activity of these complexes [1–4]. In view of the importance of the structural activity relationships, it was thought worthy to undertake a thermogravimetric study of metal complexes of 4-ASA. Such a study will provide valuable information about the dehydration, the pyrolysis of the anhydrous complex and the intermediate products formed during decom-

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position, which will facilitate the synthesis of analogous biologically active complexes.

In continuation of our earlier work [5–7], the present study deals with the thermal decompositions of the complexes VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) with 4-ASA. The stoichiometry and structure of all the complexes and their dehydrated products are discussed on the basis of analytical and IR studies.

## EXPERIMENTAL

### *Materials and methods*

The complexes were prepared by the method described previously [8]. Equimolar solutions of metal salts and the ligand were prepared and mixed in the stoichiometric ratio (M : L = 1 : 2). The solid complexes obtained were washed thoroughly with ethanol, dried and recrystallized from dimethyl formamide. All the reagents used were of BDH AnalaR grade. Metal contents were estimated by the conventional gravimetric method [9]. Elemental analyses (carbon, nitrogen and hydrogen) were carried out in the usual way. The bonding in the complexes was established by an IR spectral study.

## INSTRUMENTAL

### *Elemental analyses*

Metal content was determined by the conventional methods [9]. Carbon, hydrogen and nitrogen analyses were carried out using a Colemann CHN analyser (model 29).

### *IR spectra*

IR spectra of all the bis-(4-aminosalicylato)-diaquo complexes and their dehydrated products were recorded using a Perkin-Elmer grating IR-spectrophotometer (model 377) by the KBr disc technique. The IR spectrum of the ligand was also recorded for comparison. The 4000–400 $cm^{-1}$ region was scanned for thirteen min.

Far infrared spectra were recorded in the region 500–50 $cm^{-1}$ employing a Polytec FIR 30 Fourier far-infrared spectrometer.

### *Thermogravimetry (TG)*

Thermogravimetry was carried out on a Stanton recording thermobalance (HT model) of 1-mg sensitivity in static air with a heating rate of 4°C $min^{-1}$.

TABLE 1

Analytical data for bis-(4-aminosalicylato)-diaquo complexes and dehydrated products

| | Complex | Colour | m (%) | | C (%) | | H (%) | | N (%) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| I | $Cu(4\text{-}ASA)_2 \cdot 2H_2O$ | Dark green | 15.74 | 15.88 | 41.63 | 42.10 | 3.96 | 4.10 | 6.94 | 7.16 |
| II | $Cu(4\text{-}ASA)_2$ [a] | Dirty green | 17.28 | 17.20 | 45.71 | 46.00 | 3.27 | 3.30 | 7.62 | 7.55 |
| III | $Ni(4\text{-}ASA)_2 \cdot 2H_2O$ | Green | 14.72 | 15.29 | 42.14 | 41.97 | 4.01 | 3.92 | 7.02 | 7.20 |
| IV | $Ni(4\text{-}ASA)_2$ [a] | Dark green | 16.18 | 16.30 | 46.33 | 46.27 | 3.31 | 3.00 | 7.72 | 7.80 |
| V | $Co(4\text{-}ASA)_2 \cdot 2H_2O$ | Mauve | 14.77 | 15.26 | 42.11 | 42.88 | 4.01 | 4.14 | 7.01 | 7.30 |
| VI | $Co(4\text{-}ASA)_2$ [a] | Mauve | 16.17 | 16.30 | 46.29 | 46.32 | 3.31 | 3.12 | 7.72 | 7.75 |
| VII | $Mn(4\text{-}ASA)_2 \cdot 2H_2O$ | Brown | 13.91 | 13.58 | 42.54 | 42.48 | 4.05 | 4.09 | 7.09 | 7.18 |
| VIII | $Mn(4\text{-}ASA)_2$ [a] | Tan | 15.30 | 15.45 | 46.80 | 46.90 | 3.50 | 3.44 | 7.80 | 7.95 |
| IX | $Fe(4\text{-}ASA)_2 \cdot 2H_2O$ | Dark brown | 14.10 | 14.38 | 42.44 | 41.98 | 4.04 | 4.28 | 7.07 | 7.28 |
| X | $Fe(4\text{-}ASA)_2$ [a] | Dark brown | 15.51 | 15.20 | 46.69 | 46.72 | 3.33 | 3.29 | 7.76 | 7.70 |
| XI | $VO(4\text{-}ASA)_2 \cdot 2H_2O$ | Dark brown | 16.44 | 15.99 | 41.28 | 41.79 | 3.93 | 4.08 | 6.88 | 7.04 |
| XII | $VO(4\text{-}ASA)_2$ [a] | Dark brown | 18.04 | 17.92 | 45.30 | 45.48 | 3.24 | 3.10 | 7.55 | 7.28 |

[a] Dehydrated product.

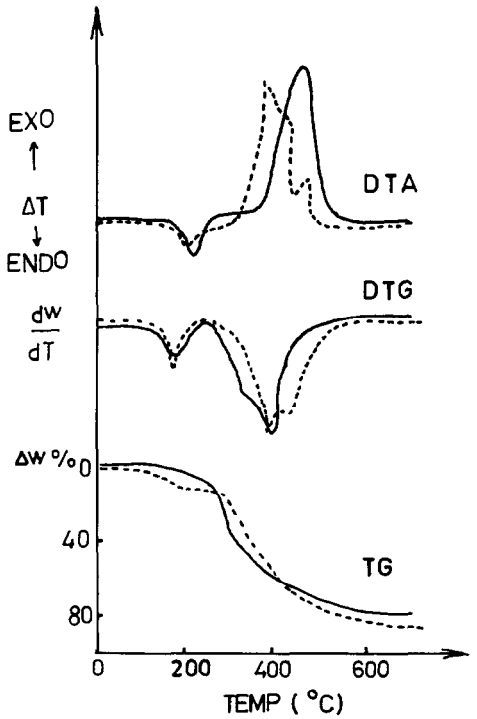


Fig. 1. TG, DTG and DTA curves of bis-(4-aminosalicylato)-diaquo complexes: (——) Cu(II); (------) Ni(II).

The chart speed was maintained at 3 in. $h^{-1}$. All the samples (~ 100 mg) were of the same particle size and were packed as uniformly as possible in a platinum crucible. The same crucible was used throughout all the experiments.

*Differential thermal analyses (DTA)*

A DTA assembly with a temperature programmer (F and M Scientific 240, Hewlett Packard) and a thermocouple (Platinel-II, Engelhard Ltd., U.S.A.) were used. DTA curves were recorded with a Rikadenki Kogyo recorder in static air at a heating rate of 4°C $min^{-1}$. Alumina was used as a reference standard.

## RESULTS

Analytical data of the complexes are presented in Table 1. TG, DTG and DTA curves are shown in Figs. 1–3 while the corresponding transition temperatures, TG weight loss data and DTA peak temperatures are listed in Tables 2 and 3. The positions of the characteristic IR bands are shown in Table 4.

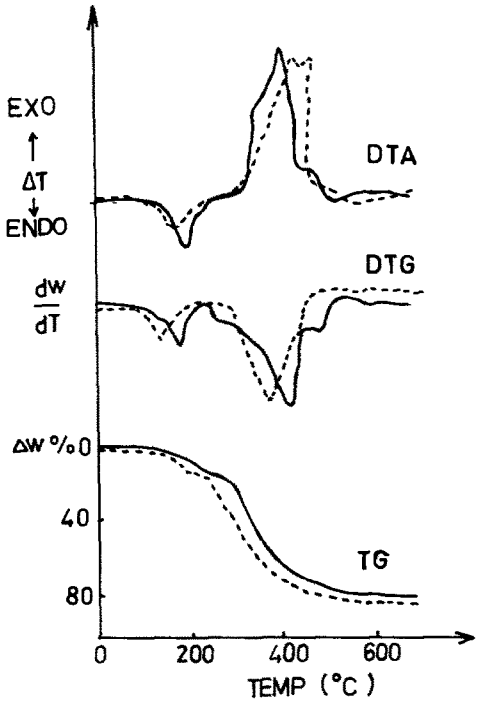


Fig. 2. TG, DTG and DTA curves for bis-(4-aminosalicylato)-diaquo complexes: (———) Co(II); (------) Mn(II).

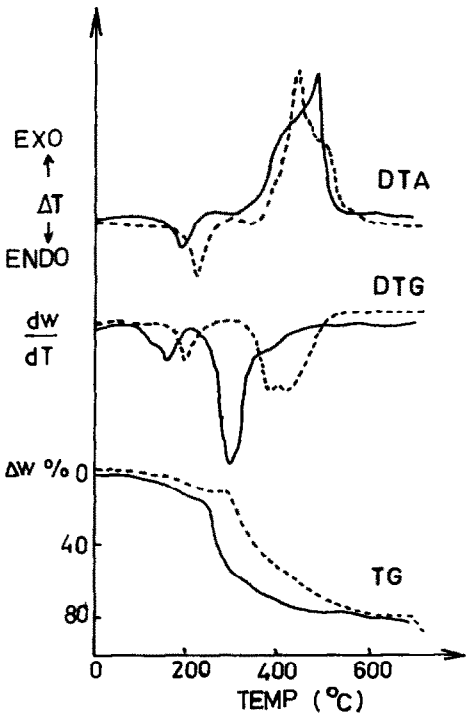


Fig. 3. TG, DTG and DTA curves for bis-(4-aminosalicylato)-diaquo complexes: (———) Fe(II); (------) VO(II).

TABLE 2

Analytical data for the bis-(4-aminosalicylato)-diaquo complexes [a]. Decomposition product(s) could not be isolated and identified owing to the lack of a clear-cut horizontal on the TG curve as the intermediate products are not stable to the required extent

| | Complex | Decomp. stage | Temp. Range (°C) | Colour | Composition of the residue | % Weight loss (%$\Delta W$) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Calc. | Obs. |
| I | $Cu(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 100–250 ± 2 | | $Cu(4\text{-}ASA)_2$ | 8.92 | 8.75 |
| | | II | 270–660 ± 4 | Black | CuO | 80.28 | 80.00 |
| II | $Ni(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 90–220 ± 4 | | $Ni(4\text{-}ASA)_2$ | 9.02 | 9.00 |
| | | II | 235–680 ± 3 | Greenish balck | NiO | 81.26 | 81.50 |
| III | $Co(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 100–240 ± 2 | | $Co(4\text{-}ASA)_1$ | 9.02 | 9.0 |
| | | II | 260–720 ± 4 | Dark brown | CoO | 81.21 | 81.00 |
| IV | $Mn(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 80–210 ± 3 | | $Mn(4\text{-}ASA)_2$ | 9.11 | 9.25 |
| | | II | 220–620 ± 2 | Grey green | MnO [b] | 82.03 | 81.00 |
| V | $Fe(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 80–220 ± 2 | | $Fe(4\text{-}ASA)_2$ | 9.09 | 9.00 |
| | | II | 240–680 ± 4 | Dark brown | FeO [c] | 81.84 | 80.00 |
| VI | $VO(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 120–270 ± 3 | | VO(4-ASA) | 8.84 | 8.75 |
| | | II | 290–680 ± 4 | Dark blue | O=O=O [d] | 79-62 | 78.00 |

[a] All the experiments were carried out in air at a heating rate of 4°C $min^{-1}$.

[b] In the final residue, the possibility of formation of $Mn_3O_4$ cannot be ruled out as the experiments were carried out in air.

[c] FeO was the major end product above 600°C, however, below this temperature it becomes contaminated by $Fe_3O_4$, as the metal is characterised by its ability to form such an oxide.

[d] The end product was expected to be a mixture of vanadium di- and penta-oxides. Formation of $V_2O_5$ may be de due to the oxidation of vanadium dioxide in air.

TABLE 3

Horizontal, maxima and range of DTG and DTA peaks for bis-(aminosalicylato)-diaquo complexes

| | Complex | Decomposition stage | Range of TG horizontal (°C) | Maxima of DTG effect (°C) | Range of DTG effect (°C) | Maxima of DTG trace (°C) | Range of DTG effect (°C) |
|---|---|---|---|---|---|---|---|
| I | $Cu(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 100–250 ± 2 | 186 | 133–213 | 220 Endo | 186–253 |
| | | II | 270–660 ± 4 | 400 | 333–466 | 460 Exo | 379–513 |
| II | $Ni(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 90–220 ± 4 | 166 | 133–186 | 210 Endo | 185–226 |
| | | II | 235–680 ± 3 | 372 | 339–400 | 400 Exo | 352–406 |
| | | | | 433 | 413–433 | 460 Exo | 446–466 |
| III | $Co(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 100–240 ± 2 | 192 | 172–200 | 220 Endo | 166–233 |
| | | II | 260–720 ± 4 | 433 | 392–453 | 420 Exo | 406–433 |
| | | | | 500 | 485–519 | 480 Exo | 579–519 |
| IV | $Mn(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 80–210 ± 3 | 146 | 133–166 | 200 Endo | 142–206 |
| | | II | 200–620 ± 2 | 386 | 333–420 | 440 Exo | 319–452 |
| V | $Fe(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 80–220 ± 2 | 172 | 166–179 | 205 Endo | 166–219 |
| | | II | 240–680 ± 4 | 313 | 286–366 | 480 Exo | 479–513 |
| VI | $VO(4\text{-}ASA)_2 \cdot 2H_2O$ | I | 120–270 ± 3 | 200 | 172–233 | 230 Endo | 226–252 |
| | | II | 290–680 ± 4 | 400 | 353–385 | 460 Exo | 366–472 |

TABLE 4

Characteristic IR frequencies for bis-(4-aminosalicylato)-diaquo complexes

| Assignment | 4-ASA | Cu(II) | Ni(II) | Co(II) | Mn(II) | Fe(II) | VO(II) |
|---|---|---|---|---|---|---|---|
| $\nu(COO^-)$asym | 1660 (s) | 1620 (s) | 1610 (s) | 1622 (s) | 1625 (s) | 1625 (s) | 1635 (s) |
| $\nu(COO^-)$sym | 1470 (s) | 1442 (s) | 1438 (s) | 1450 (s) | 1455 (s) | 1465 (s) | 1455 (s) |
| $\nu$(O–H)str [a] | 2400–3700 (330) (sb) | 2800–3650 (3290) (sb) | 2700–3660 (3200) (sb) | 2700–3690 (3280) (sb) | 2680–3675 (3310) (sb) | 2790–3680 (3215) (sb) | 2750–3700 (3320) (sb) |
| $\delta$(OH) | 1282 (s) | 1282 (s) | 1280 (s) | 1306 (s) | 1306 (s) | 1287 (s) | 1294 (s) |
| $\delta(H_2O)$rocking | – | 880 (s) | 850 (s) | 850 (s) | 835 (s) | 828 (s) | 885 (s) |
| $\nu$(M–O)+(C–C) | – | 505 (wb) | 515 (m) | 509 (sh) | 510 (mb) | 516 (w) | 520 (sh) |
| $\nu$(M–O)+ring def | – | 440 (sh) | 460 (w) | 425 (m) | 420 (wb) | 430 (m) | 440 (ms) |
| $\Delta$(C=O) | – | 178 | 172 | 172 | 170 | 160 | 180 |

s = strong, b = broad, w = weak, m = medium, sh = shoulder.

[a] In some cases broad bands of the O–H stretching frequency (2400–3700 $cm^{-1}$) overlapped the sharp bands of N–H (3400, 3500 $cm^{-1}$).

## DISCUSSION

### *Stoichiometry and structure of the complexes*

The analytical data reported in Table 1 indicate that the stoichiometry of all the complexes is $ML_2 \cdot 2H_2O$ (M = VO(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II); L = anion of 4-ASA).

The infrared spectrum of solid 4-ASA is almost identical to that of its complexes in the region 2000–625 $cm^{-1}$. The frequencies of most interest with regard to the structure of the complexes are the C–O and O–H vibrations. The $\nu$(C=O) band at 1660 $cm^{-1}$ is shifted to a lower frequency ($\sim$ 1610 $cm^{-1}$) in all the complexes showing that complexation has taken place through the carboxyl group [10,11]. The appearance of new band in the neighbourhood of 800 $cm^{-1}$ in all the complexes shows that the water molecules are coordinated to the metal ion [12–15]. The presence of a band at $\sim$ 315 $cm^{-1}$ confirms the presence of coordinated water [16]. The presence of water in the coordinated form is further borne out by the thermal decomposition data (Figs. 1–3). It may also be noted that the O–H (phenolic) bending peak at 1300 $cm^{-1}$ remained almost at the same position for 4-ASA and its complexes. This shows that there is no loss of protons by the phenolic OH group upon coordination.

### *Behaviour of the complexes*

All the complexes are insoluble in water and common organic solvents, suggesting a polymeric structure. Because of their insolubility in common organic solvents, the extent of polymerization could not be determined. Early reported data on magnetic susceptibility and electronic spectra indicated octahedral stereochemistry for all the complexes [17]. The thermal decomposition would appear to be consistent with this type of structure and would suggest that the water molecules are directly bonded to the metal ion along with two 4-ASA moieties to give a coordination number of six for each of the metal(II) ions.

The increase in the difference between $\nu$(COO)asym and $\nu$(COO)sym, $\Delta$(C=O), has been taken as a measure of increasing covalency of the M–O bond [18]. The 4-ASA complexes presented a band at $\sim$ 1610 $cm^{-1}$ (Table 4) for $\nu$(COO)asym and at $\sim$ 1440 $cm^{-1}$ for $\nu$(COO)sym. Thus, the covalent character of the M–O bond follows the order: Fe(II) < Mn(II) < Co(II) $\approx$ Ni(II) < Cu(II) < VO(II).

## THERMAL DECOMPOSITION

The thermal characteristics of the metal complexes of 4-ASA with Cu(II), Ni(II), Co(II), Mn(II), Fe(II) and VO(II) are indicated by their TG, DTG and DTA curves (Figs. 1–3).

Similar to the decomposition of salicylato (SA) complexes [5], the thermal decomposition of these complexes begins with the loss of two water molecules and, subsequently, the dehydrated complex decomposes into metal oxide as the final residue. However, the decomposition is more complicated in comparison to that of SA complexes, which is probably due to the substituted amino group.

Since all the six metal chelates of 4-ASA possess an identical structure [17], their thermal decomposition processes also have many common features. Almost all the chelates of 4-ASA exhibited a pronounced endothermal peak due to the loss of water molecules and or more exothermal peak(s) corresponding to the decomposition of the dehydrated complex.

In general, TG, DTG and DTA results of these complexes suggested their thermal decomposition in two stages.

(I) The first decomposition stage involves the loss of two water molecules which takes place in a single step. This step is found to be endothermic as shown by the DTA curve.

$$M(4\text{-ASA})_2\,2H_2O \rightarrow M(4\text{-ASA})_2 + 2H_2O \qquad (I)$$

(II) In this decomposition stage the dehydrated complex subsequently decomposes to yield a final residue of metal oxide. The main possible decomposition reaction of the dehydrated complex can be described by the following equations:

$$M(4\text{-ASA})_2 \rightarrow \begin{cases} MCO_3 + \text{gaseous combustion products} \\ \qquad (H_2, CO, CO_2, H_2O) \end{cases} \qquad (IIa)$$

$$NH_3 + \text{nitrogen oxides} \qquad (IIb)$$

$$MCO_3 \rightarrow MO + CO_2 \qquad (IIc)$$

The second decomposition period takes place over a wide range of temperature, demonstrating that this period is not unambiguous and uniform. A possible explanation of this could perhaps be that in this stage, not only reactions IIa and IIb took place but the decomposition step IIc also slowly started. Accordingly, the relevant section of the TG, DTG and DTA curves represents the results of more than one partial reaction. The liberation of various gaseous products, as a consequence of the combustion of the organic moiety of the complexes, i.e., the 4-ASA moiety, is found to be an exothermic reaction as indicated by the DTA curves.

The recorded DTA curves (Figs. 1–3) are observed to have unusual shapes. Such unusual shapes were also observed for transition metal salicylates reported by us and others [19–21]. Abnormal shapes are also found in malato-aquo [22] and EDTA [23] complexes of transition metals.

The abnormal shape of the exothermal peaks of the DTA curves is probably due to the various gaseous combustion products escaping as a consequence of the decomposition of the organic skeleton, i.e., the 4-ASA

moiety of the complex. A large and broad exothermal peak over a wide temperature range on the DTA curve for decomposition of dehydrated complexes also indicates, beside the decomposition, oxidation and combustion processes.

## THERMAL CHARACTERISATION OF THE COMPLEXES

The thermal characterisation of the complexes, viz. temperature range, composition of the residue, percentage weight loss, range of horizontal and range of DTA effect, are summarized in Tables 2 and 3 (Figs. 1–3). Some of the thermal behaviours are worth noting.

In the case of Ni(II)–4-ASA, prior to the second exothermal peak, and partially merged into it, a small exothermal peak appears at 460°C, indicating that the second decomposition period involves two exothermic reactions. Perhaps it is due to the simultaneous decomposition of the anhydrous complex and the metal carbonate formed during the thermal dehydration of the complex.

The dehydrated Mn(II)–4-ASA complex decomposes to give a final residue which was expected to be a mixture of MnO and $Mn_3O_4$. Similarly, in the second decomposition period (240–680°C), the dehydrated Fe(II)–4-ASA complex decomposed to give FeO as a major end product. However, the possibility of the formation of $Fe_3O_4$ cannot be ruled out [5].

Finally, in the case of VO(II)–4-ASA, the end product was found to be a mixture of vanadium di- and penta-oxides.

It is noticeable that the thermal dehydration temperature of these complexes increases in the same sequence as found in SA complexes [5]. Similarly, the dehydration temperature (Table 2), increases with increasing coordinated water frequency (Table 4). This may also be explained in terms of the percentage of metal in the complexes (Table 1).

Perusal of Tables 2 and 3 and Figs. 1–3 indicates that in all the six complexes of 4-ASA, the TG weight loss has established the amount of water present (decomposition stage I) and also the composition of the final residues of the second decomposition stage. These results supported the predicted composition and structure of these complexes.

### *Isolation of intermediate products*

In order to isolate intermediate dehydrated products of the thermal decomposition, samples were heated in air to an appropriate temperature in a crucible and the residues analysed. The decomposition products have been confirmed by analytical, IR and X-ray *K*-absorption edge studies [24]. However, all the intermediate products of the decomposition steps could not be isolated and identified owing to the lack of a clear-cut horizontal on the TG curve, as the intermediate products are not stable to the required extent.

It is worthy to note that, as a result of dehydration, colour intensity is increased followed by a change in stereochemistry.

The IR spectra confirm the dehydration (step I), since the peaks and bands characteristic of coordinated water disappeared in the IR spectrum of the first decomposition product.

We have studied the X-ray *K*-absorption spectra of Cu(II), Ni(II) and Co(II) complexes ($ML_2 \cdot 2H_2O$) as well as their dehydrated products [24] and have indicated that a change in stereochemistry from octahedral to tetrahedral takes place as a consequence of dehydration. Details of the study will be published elsewhere.

*Thermal stability of the complexes*

If the initial decomposition temperature is taken as a measure of the thermal stability of the complexes, we can conclude that the stability of the metal complexes increases roughly in the order: Mn(II) < Fe(II) < Ni(II) < Co(II) < Cu(II) < VO(II).

It is interesting to note that the dehydration temperature of the complexes increases with increasing coordinated water frequency. This is also in the order mentioned above.

## CONCLUSIONS

The results of this study on the thermal decomposition of 4-ASA complexes showed that thermal analyses can be useful for the determination of the number of molecules of bound water, for detecting contamination of starting reagents and to evaluate the agreement between the expected and actual composition of a compound. It may also provide a means for correlating microbial activity with the change in the stereochemistry of the active species.

A knowledge of heating curves is useful for gravimetric analysis of a compound. For quantitative analyses of the compounds studied, only a horizontal formed at the first and the last stages of the decomposition is suitable. Particularly, the latter is of much quantitative importance.

On increasing the heating rate, DTA and DTG peaks, and horizontals on the TG traces changed in the manner reported by Schultze [25].

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