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THERMOCHROMISM AND THERMAL DECOMPOSITION OF V(III) AND VO(IV) COMPLEXES WITH SCHIFF BASE DERIVATIVES

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ABSTRACT

The thermal behaviour of the dimeric V(III) complexes (**I**$_a$ and **III**) and monomeric VO(IV) complex (**II**) of Schiff bases derived from condensation of 2-hydroxy-1-naphthaldehyde with 1,3-propanediamine (**I**$_a$, **II**) and with ethylenediamine (**III**) respectively was studied. The observed thermochromism in crystalline **I**$_a$ was studied using differential thermal analysis (DTA), X-ray powder diffraction, electronic spectroscopy and IR spectroscopy. This thermochromism is attributed to valence and structural changes from dark green dimeric V(III) complex in pseudo-octahedral geometry to orange monomeric VO(IV) complex in square pyramidal geometry, indicating that VO(IV) complex could be prepared from V(III) using a solid state thermal reaction. The effect of the length of the methylene chain of the ligand on the success of this reaction is discussed. The thermal stability of the investigated complexes is discussed in terms of the stability of the chelate ring. The kinetics of the thermal decompositions and the other thermal reactions are discussed. The energies of activation were determined.

INTRODUCTION

The use of thermal methods of analysis as a technique for studying the bonding and structure of coordination compounds has increased greatly in the last few years [1]. Kinetic and thermodynamic data for reactions in solid state have been considered in recent studies [2–8]. Wendlandt [9] reported a decreasing trend in thermal stability as the ligand on Cu(II) sulphate was changed from ethylenediamine to 1,2-propanediamine and to 1,3-propanediamine. Lozano et al. [10] studied the thermal decomposition reactions and the thermal parameters associated with VO(IV) complexes with substituted pyridines. Recently, Donia and Ebeid [11] studied the thermochromism in Ni(II) complexes with Schiff base derivatives of 4-aminoantipyrine. Amer et al. [12] studied the complexes of V(III) and VO(IV) with Schiff bases derived from some aliphatic diamines and 2-hydroxy-1-naphthaldehyde. The

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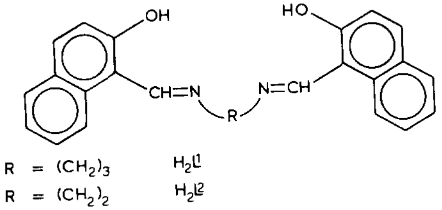
complexes were prepared and characterized by elemental analysis and IR, electronic and EPR spectroscopies. The V(III) complexes were found to be dimeric through oxygen and water bridges, while the VO(IV) are monomeric. Also, the solution reaction of V(III) complexes with dioxygen to give the monomeric VO(IV) complexes was studied.

The major goal of the present work is to prepare the monomeric VO(IV) complexes from the dimeric V(III) complexes, using a solid state thermal reaction in addition to the solution reaction. The associated thermal decomposition of the complexes and the other thermal reactions as well as their kinetics were studied. The observed thermochromism in the dimeric V(III) complex $\mathbf{I}_a$ is discussed in terms of structural and spectroscopic changes.

EXPERIMENTAL

The ligands H_2L1 and H_2L2 were prepared by the standard method for Schiff base condensation. The ligands have the following structure



The dimeric V(III) complexes ($\mathbf{I}_a$ and **III**) of H_2L1 and H_2L2 respectively were prepared as follows. The ligand (0.01 mol) suspended in dioxygen-free hot ethanol (150 cm^3) was mixed with triethylamine (0.02 mol), then V(III) chloride in dioxygen-free ethanol (50 cm^3) was added dropwise to the ligand solution. The mixture was refluxed with continuous stirring for 1 h under dry dinitrogen. The complex was filtered off, washed with acetone and dried in vacuo.

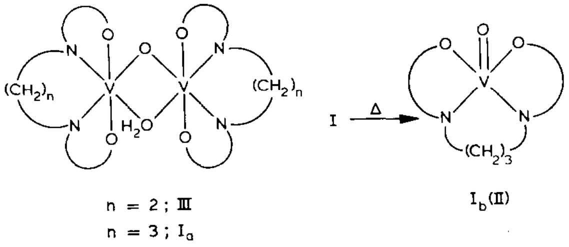
The monomeric VO(IV) complex **II** of H_2L1 was prepared as follows. The ligand (0.01 mol) suspended in hot ethanol (150 cm^3) was mixed with triethylamine (0.02 mol), then vanadyl chloride in ethanol (50 cm^3) was added dropwise. The mixture was refluxed for 1 h. The complex was filtered off, washed with acetone and dried in vacuo.

Thermal analysis of the complexes was carried out using a Shimadzu XD-30 thermal analyser. X-ray powder diffraction was recorded using a Shimadzu XD-3 diffractometer by applying the Cu $K\alpha$ line. Electronic spectra were measured in a Nujol mull using a Perkin–Elmer 550S spectrophotometer. IR spectra were measured in KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer.

RESULTS AND DISCUSSION

Thermal behaviour

The dimeric V(III) complex with the H_2L1 (**I**$_a$) is dark green and turns orange on heating to about 167 °C for 10 min. The corresponding orange form is hereafter designated (**I**$_b$). The temperature range of thermochromism coincides with the exothermic differential thermal analysis (DTA) thermogram peak, as shown in Fig. 1. The DTA thermogram of **I**$_a$ shown in Fig. 1 consists of an exothermic peak at about 167 °C followed by another relatively sharp exothermic peak at about 262 °C which is assigned to material decomposition. The thermal and other analytical measurements of the thermoproduct **I**$_b$ and the monomeric VO(IV) complex **II** confirm that the two compounds are the same. This indicates that the exothermic peak at about 167 °C can be assigned to the thermochemical change of the dimeric V(III) complex: **I**$_a$ to monomeric VO(IV); **II** as shown in Scheme 1. This exothermic peak is absent in the DTA thermogram of the orange form (**I**$_b$).



Scheme 1.

The DTA thermogram of the monomeric VO(IV) complex **II** shown in Fig. 1 consists of a relatively sharp exothermic peak at about 262 °C, consistent with the decomposition peak of **I**$_a$ (more precisely the decomposition of the thermoproduct **I**$_b$). The thermogram also shows an additional weak endothermic peak at about 214 °C, which is assigned to crystalline rearrangements [13]; this assignment was also confirmed by X-ray measurements. This peak is absent in the thermograms of preheated (up to 220 °C) samples of **II** and **I**$_b$, indicating that the thermoproduct **I**$_b$ is more crystalline than **II**. This may be attributed to the very slow rate of the solid state reaction compared with the rate of the solution reaction. Consequently, it is possible to prepare **II** using the solid state reaction.

Figure 1 shows the thermogram of the dimeric V(III) complex **III**, which consists of a relatively sharp exothermic decomposition peak at about 298 °C, indicating that the thermal stability of **II** against thermal decomposition is higher than that of **I**$_a$. This behaviour can be discussed on the basis of the thermal stability of the saturated five-membered chelate ring present in (**III**) being greater than that of the six-membered ring present in **I**$_a$ [9,14].

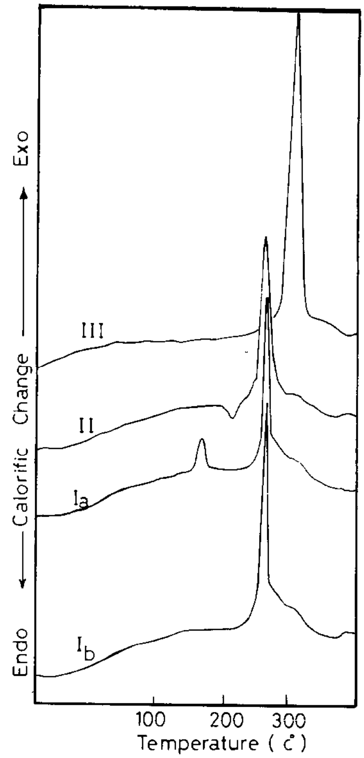


Fig. 1. DTA of the solid complexes **III**, **II**, I_a and I_b.

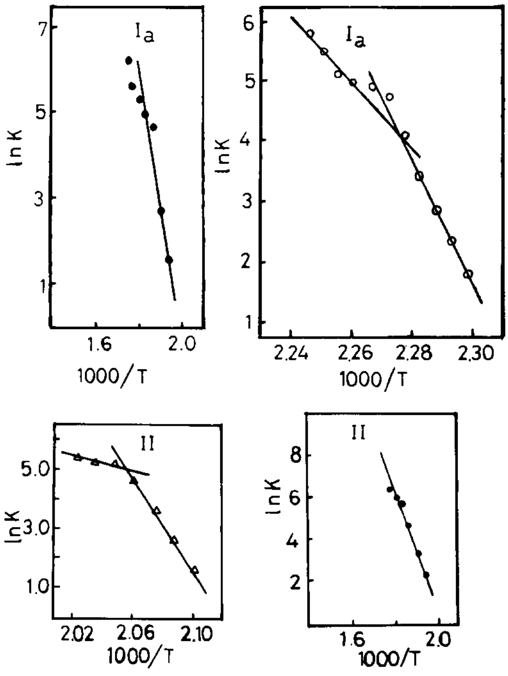


Fig. 2. Arrhenius plots constructed from DTA thermograms of I_a and **II**. ●, decomposition; ○, thermochemical reaction; △, crystallization.

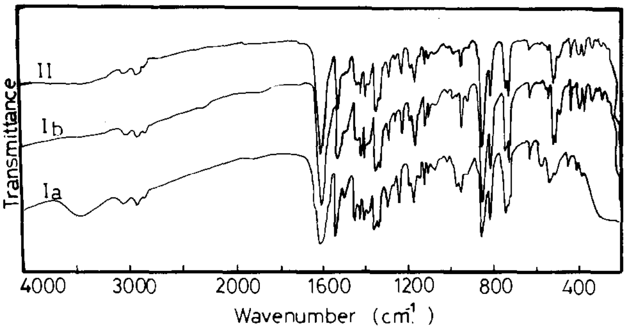


Fig. 3. IR spectra of the complexes $\mathbf{I}_a$, $\mathbf{I}_b$ and **II**.

The higher thermal stability of **III** may contribute to the failure of the solid state thermal reaction for preparation of the monomeric VO(IV) complex from the V(III) complex **III**. This result coincides with that obtained from the reaction of V(III) complexes with dioxygen in solution [12]. Studies both in the solution phase and in the solid phase lead to the conclusion that the success of preparation of the monomeric VO(IV) complexes from the dimeric V(III) complexes is mainly dependent on the length of the methylene chain of the ligand. The energies of activation (E_a) of the thermochemical reaction (V(III) complex → VO(IV) complex), the thermal decomposition and the crystalline rearrangements of $\mathbf{I}_a$ and **II** were evaluated from DTA thermogram as in previous work [9,15]. Generally, the reactions follow first-order kinetics in the acceleration period of the reaction, while the deceleration period shows a different activation energy.

Arrhenius plots were constructed and these are shown in Fig. 2; the energy of activation was obtained from the slope. For $\mathbf{I}_a$ the energies of

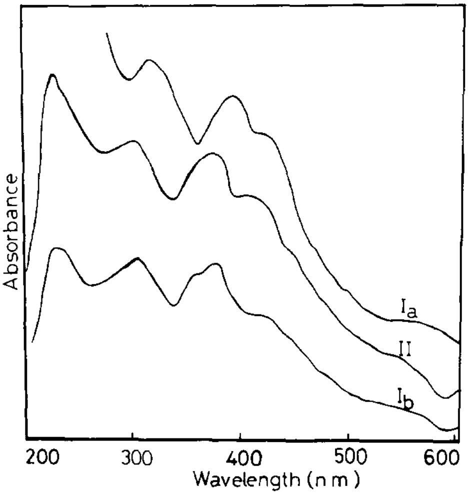


Fig. 4. Electronic spectra of the complexes $\mathbf{I}_a$, $\mathbf{I}_b$ and **II**.

activation of the thermochemical reaction and the thermal decomposition are $E_a = 778$ kJ mol^{-1} and $E_a = 233.4$ kJ mol^{-1} respectively. For **II** the energies of activation of the thermal decomposition and the crystalline rearrangements are $E_a = 227.5$ kJ mol^{-1} and $E_a = 654.7$ kJ mol^{-1} respectively.

Spectroscopic study

The IR spectra of $\mathbf{I}_a$ and **II** have been discussed previously [12]. The IR spectra of the thermoproduct $\mathbf{I}_b$ and the VO(IV) complex **II** (Fig. 3) are exactly the same, indicating at first glance that the thermoproduct $\mathbf{I}_b$ and the monomeric VO(IV) complex **II** are the same compound. This is also supported by the appearance and disappearance of a ν(V=O) band at 965 cm^{-1} [16,17] and ν(OH) band at 3450 cm^{-1} in the spectrum of $\mathbf{I}_b$ in comparison with that of $\mathbf{I}_a$. This is evidence for the view that the transformation of $\mathbf{I}_a$ to $\mathbf{I}_b$ is associated with a valence change from V(III) to VO(IV) and decomposition of the oxygen-aquo four-membered ring through loss of

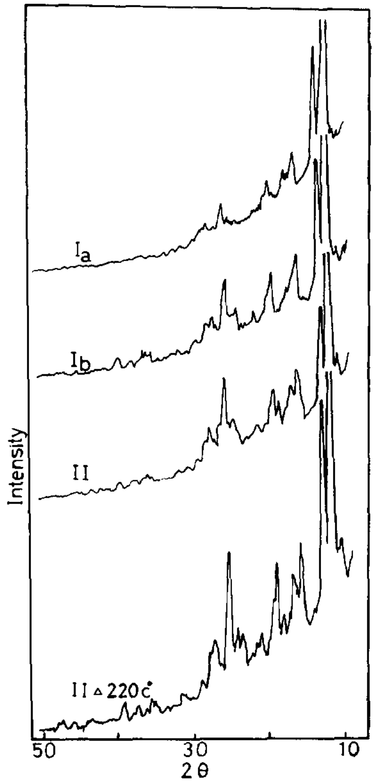


Fig. 5. X-ray powder diffraction patterns of the complexes $\mathbf{I}_a$, $\mathbf{I}_b$ and **II**, and that of **II** heated up to 220 °C.

coordinated water. The IR spectra of $\mathbf{I}_a$ and $\mathbf{I}_b$ show many bands with different shapes as well as different intensities. This might be attributed to the structural change.

The electronic and reflactance spectra of the complexes $\mathbf{I}_a$ and **II** have been discussed previously [12], and it was concluded that $\mathbf{I}_a$ has a six-coordinate pseudo-octahedral structure while **II** has a five-coordinate square pyramidal geometry.

The electronic spectra of the thermoproduct $\mathbf{I}_b$ and the monomeric VO(IV) complex **II** (Fig. 4) are exactly the same, confirming that the two compounds are initially the same. The spectrum of $\mathbf{I}_b$ displays bands at 370 nm (sh), 395 nm (m) and 430 nm (sh) which are assigned to charge transfer, and a broad band at 550 nm which is assigned to d–d transition. Thus the complex $\mathbf{I}_b$ has square pyramidal geometry [16–18].

The structural change accompanying the valence change process ($\mathbf{I}_a \rightarrow \mathbf{I}_b$) was examined by X-ray powder diffraction (Fig. 5). The pseudo-octahedral V(III) dimer $\mathbf{I}_a$ possesses broader and lower intensity peaks than those of the square pyramidal VO(IV) monomer $\mathbf{I}_b$, indicating the lower degree of crystallinity of $\mathbf{I}_a$ and the possible existence of microstrains [19,20].

The observed crystalline rearrangement (see below) for VO(IV) complex **II** with thermal dealing was examined by X-ray powder diffraction before and after heating, as depicted in Fig. 5. The sample heated up to 220 °C shows sharper and more intense peaks, indicating the occurrence of crystalline rearrangment on heating.

CONCLUSION

The present paper reports a successful, simple and quantitative method for preparation of a monomeric VO(IV) complex from the dimeric V(III) complex $\mathbf{I}_a$. For the investigated complexes the success of this method depends on the length of the methylene chain of the ligand, exactly as the observed trend for the oxygenation reactions in solution. However, attention must be paid to the solid state thermal reactions, which have great economic importance in comparison with the solution reactions. The observed thermochromism has been discussed in terms of structural and spectroscopic changes. The difference in the thermal stability of the investigated complexes was attributed to the size of the chelate ring.

REFERENCES

1 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition Metal Ammine Complexes, Elsevier, Amsterdam, 1967.
2 G.G.T. Guarini and R. Spinicci, J. Therm. Anal., 4 (1972) 435.

3 R.S. Botell, H. Chang and D.A. Lusardi, J. Inorg. Nucl. Chem., 41 (1979) 909.
4 J.E. House, Thermochim. Acta, 40 (1980) 225.
5 C.A. Jepsen and J.E. House, J. Inorg. Nucl. Chem., 43 (1981) 9531.
6 N. Ghiassee, P.G. Clay and G.N. Walton, J. Inorg. Nucl. Chem., 43 (1981) 2909.
7 C.E. Bamberger, K. Brookhart and P.R. Robinson, Inorg. Chim. Acta., 57 (1982) 161.
8 G.S. Harris and J.S. Mackechie, Polyhedron. 1, (1982), 215.
9 W.W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 833.
10 R. Lozano, J. Martinez, A. Martinez and A. Doadrio Lopes, Polyhedron, 2 (1983) 977.
11 A.M. Donia and E.M. Ebeid, Thermochim. Acta, 131 (1988) 1.
12 S.A. Amer, M. Gaber and R.M. Issa, Polyhedron, in press.
13 H.H. Willard, L.L. Merritt and J.A. Dean, Instrumental Methods of Analysis, 5th edn., Van Nostrand, New York, 1974, p. 502.
14 C.F. Bell and K.A.K. Lott, Modern Approach to Inorganic Chemistry, 3rd edn., 1972, p. 183.
15 J. Thomas and T.A. Clarke, J. Chem. Soc., A, (1968) 457.
16 J. Selbin, L.H. Holmes and S.P. McGlynn, J. Inorg. Nucl. Chem., 25 (1963) 1359.
17 G.A. Kolawole and K.S. Patel, J. Chem. Soc., Dalton Trans., (1981) 1241.
18 D.K. Rastogi and P.C. Pachauri, J. Inorg. Nucl. Chem., 39 (1977) 151.
19 W.W. Beeman, P. Kasberg and M.B. Webb, Handbuch der Physik, Band XXXII, Springer, Berlin, 1957, p. 321; W.E. Garner, Chemistry of the Solid State, London, 1955, p. 109.
20 A.R. Tourky, M.S. Farag, T.M. Salem, and Z.M. Hanafi, Z. Phys. Chem., 227 (1964) 145.