

Thermal, magnetic and X-ray diffraction studies on mixed-ligand dimetavanadato complexes of manganese(II)

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Abstract. Novel mixed-ligand dimetavanadato complexes of Mn(II) of composition $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$ and $[\text{Mn}(\text{pz})(\text{H}_2\text{O})_2(\text{VO}_3)_2]\text{H}_2\text{O}$ (where en = 1,2-diaminoethane, pz = hexahydropyrazine) have been synthesized. The probable structures of the complexes have been worked out on the basis of elemental analysis, IR spectra, magnetic measurements and thermogravimetric analysis. X-ray powder diffraction study has been carried out to determine the unit lattice parameters. Magnetic moment values indicate high-spin complexes of manganese. Dynamic thermogravimetric data of the relevant steps of thermal degradation have been analysed for the study of solid-state kinetics. Non-isothermal methods by Piloyan–Novikova, Coats–Redfern and Horowitz–Metzger have been employed for evaluating the kinetic parameters viz. energy of activation, frequency factor and entropy of activation. The mechanism of non-isothermal decomposition of complexes is ‘phase boundary contracting cylinder nucleation’.

Keywords. Dimetavanadate complexes; thermal/kinetic parameters; manganese (II) complexes.

1. Introduction

Vanadates of different metals are reported to catalyse various redox reactions. The applications of manganese and vanadium compounds in biology and industry is also well-known (Alexander 1929; Lawrance and Sawyer 1978; Wilkinson 1987). Literature reveals that heteropoly vanadates of Mn(II) have been studied in the past (Fynn and Pope 1970), but no systematic studies have been made so far on manganese dimetavanadato complexes involving amines. This paper deals with the coordination behaviour of d^5 manganese in the presence of the ligands 1,2-diaminoethane (en) and hexahydropyrazine (pz) with oxoanion of vanadium(V) (Sinha and Sahu 1979). The metal complexes under the present investigation may be useful in catalysing redox processes at rather high temperatures. These studies are also important for understanding the chemistry of the solid state during thermal degradation and various catalytically useful steps viz. the Mn–O–V bond, coordinatively unsaturated labile complexes, stereospecificity, ligand field activation energy and mechanism of atom and electron transfer processes (Shriver *et al* 1991).

2. Experimental

AnalaR grade chemicals were used in the synthesis of complexes.

Binary Mn(II) complexes. Manganese metavanadate $[\text{Mn}(\text{VO}_3)_2]$ was prepared by heating (for 1 h) an aqueous solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and NH_4VO_3 in the molar ratio 1:2. On cooling, a dark reddish-brown solid separated out, which was washed with double distilled water and dried over anhydrous CaCl_2 .

Mixed-ligand Mn(II) complexes. The calculated quantity of powdered $\text{Mn}(\text{VO}_3)_2$ was refluxed on a water bath with an ethanolic solution of ethylenediamine/aquo-ethanolic solution of hexahydropyrazine in molar ratio of (M:L) 1:1 in order to get the complexes $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$ and $[\text{Mn}(\text{pz})(\text{H}_2\text{O})_2(\text{VO}_3)_2] \cdot \text{H}_2\text{O}$ respectively. The products thus obtained were separated by filtration, washed successively with aqueous alcohol and acetone, and finally dried over P_4O_{10} .

3. Physical measurements

Metal contents were estimated gravimetrically in both $\text{Mn}(\text{VO}_3)_2$ and its complexes. Manganese was determined by complexometric titration using Eriochrome black-T and vanadium as silver vanadate as per recommended procedures (Vogel 1968; Fynn and Pope 1970). The IR spectra have been recorded on a Perkin-Elmer IR-397 spectrophotometer (KBr , cm^{-1}). Magnetic susceptibility measurements of the complexes were done on Gouy's balance at room temperature using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a calibrating agent and diamagnetic corrections were made using Pascal's constants (Lewis and Wilkins 1960). For TG analysis (figure 1) the samples were heated at the rate of 15 K min^{-1} in air using a platinum (DTA-TGA) sample holder. X-ray powder diffraction pattern was recorded on an X-ray machine attached to a PW-1700 diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation intensity 35/20 kV/mA.

4. Results and discussion

Elemental analysis data (table 1) reveal that the empirical compositions are $[\text{MnV}_2\text{C}_2\text{H}_{12}\text{N}_2\text{O}_8]$ and $[\text{MnV}_2\text{C}_4\text{H}_{14}\text{N}_2\text{O}_8] \cdot \text{H}_2\text{O}$ for en and pz complexes respectively.

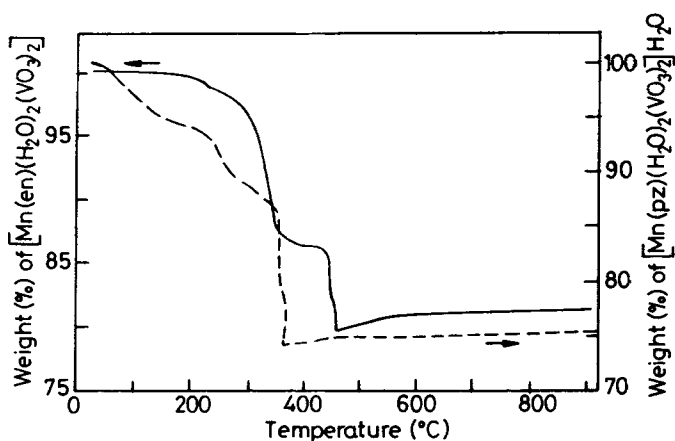


Figure 1. Thermograms of $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$ (—) and $[\text{Mn}(\text{pz})(\text{H}_2\text{O})_2(\text{VO}_3)_2] \cdot \text{H}_2\text{O}$ (---).

Table 1. Analytical and magnetic data of complexes.

| Compound | Colour | Analysis % (Exp.) (Calcd.) | | | | | Mn | $X_M (\times 10^{-6})^*$ | $X'_M (\times 10^{-6})^*$ | μ_{eff} (BM) |
|--|-----------|----------------------------|----------------|----------------|------------------|------------------|----------|--------------------------|---------------------------|-------------------------|
| | | C | H | N | V | Mn | | | | |
| $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$ | Orange | 6.54 (6.88) | 3.56 (3.44) | 7.89 (8.02) | 14.67 (14.58) | 15.01 (15.73) | 14366.90 | 14505.14 | 5.99 | |
| $[\text{Mn}(\text{pz})(\text{H}_2\text{O})_2[\text{VO}_3)_2] \cdot \text{H}_2\text{O}$ | Dirty red | 12.72 (12.21) | 3.98 (4.07) | 7.50 (7.12) | 12.81 (12.95) | 13.40 (13.97) | 11144.54 | 11308.32 | 5.29 | |

en = 1,2-diaminoethane; pz = hexahydropyrazine; *in cgs units

4.1 Infrared spectral studies

The assignments of IR spectra have been made on the bases of the reported data on the metavanadate ion (Miller and Wilkinson 1952; Bailer *et al* 1973) and amine complexes. Miller and Wilkins (Wells 1979) reported three bands ν_5 , ν_3 and ν_1 due to the metavanadate ion.

The bands at 3500, 1600 and 760 cm^{-1} in the IR spectrum of the en complex have been assigned to O–H stretching, bending and rocking modes of coordinated water (Das *et al* 1983; Nakamoto 1986). The band at 430 cm^{-1} indicates Mn–O. The N–H stretching and bending bands appear at 3300 and 1590 cm^{-1} in en ligand; these have been found to shift to lower frequencies on coordination (Powell and Shepped 1961). The new band $\nu_{\text{M-N}}$ at 535 cm^{-1} showed the coordination of en through amido nitrogen (Kathal and Gautam 1990). Two absorption bands observed in this complex at 925 (ν_5) and 750 (ν_1) cm^{-1} may be due to the unidentate coordination of metavanadate group.

The IR spectrum of pz complex gives bands at 3540, 3220, 1625 and 530 cm^{-1} which have been assigned to characteristic coordinated water modes (Nakamoto 1986). The IR bands at 3320–3360 cm^{-1} in cyclic secondary amine ligand have been found red-shifted by 30–40 cm^{-1} in its complex and a new band at 475 cm^{-1} . $\nu_{\text{M-N}}$ has also been recorded. This indicates the involvement of pz imido group in coordination (Nakamoto 1986). Three absorption bands due to the unidentate metavanadate anion have been observed at 950 (ν_5), 800 (ν_3) and 760 (ν_1) cm^{-1} in the complex spectra (Addison *et al* 1971).

4.2 Magnetic measurements

Both the complexes are paramagnetic (at 307 K). The literature value of the observed magnetic moment of Mn(II) system with d^5 unpaired electron in the 6s ground state is ≈ 5.9 BM (Figgis 1987). The observed magnetic moment value, 5.99 BM for en complex is magnetically normal for a high-spin six-coordinated octahedral Mn(II) complex. The observed μ_{eff} value for five coordinated (D_{3h} or C_{4v} symmetry) pz complex is 5.29 BM, which is slightly less than normal for a d^5 , octahedral Mn(II) complex. This may be interpreted by correlating spin state, stereochemistry, anisotropy and nature of the ligand atoms besides considering some other factors responsible for anomalous magnetic moments (Shaw and Sattoni 1969; Borehan and Chiswell 1977; Cotton and Wilkinson 1979; Figgis 1987; Dutta and Syamal 1993).

4.3 Thermal decomposition

The thermogram of en complex clearly indicates its thermal stability up to 473 K. On increase of temperature, two coordinated water molecules are lost in the range 473–608 K (Fabretti *et al* 1977) (% remaining weight, observed/calculated = 90.0/89.6). On further raising the temperature, weight loss occurs between 673 and 731 K (% remaining weight, obs./cal. = 79.7/79.3). This may be due to the decomposition of the unchelated part (Aswar and Bhave 1991) of the en ligand. The residue after complete pyrolysis of complex may be considered a mixture of manganese and vanadium oxides (Tashiro 1940; Mcchael and Stewart 1971).

The mass loss curve of pz complex shows the degradation of one molecule of crystal water before 423 K (Nikolaev *et al* 1969) (% remaining weight, obs./cal. = 95.0/95.4).

Above 423 K, the loss in weight occurs up to 593 K. This corresponds to elimination of two coordinated water molecules from the complex (% remaining weight, obs./cal. = 86.8/87.0). The gradual mass loss between 598 to 648 K has been considered as due to the degradation of the non-coordinated part of pz ligand (% remaining weight, obs./cal. = 74.2/72.0). The residue after complete decomposition is a mixture of oxides of manganese and vanadium (Tashiro 1940; Mcchael and Stewart 1971).

4.4 Kinetics of composition

The fractional weight loss ($\alpha = W_o - W_t / W_o - W_f$) and the corresponding $(1 - \alpha)^n$ have been calculated from the TG curves at different temperatures (n depends upon reaction model) (Ravindran and Sundaram 1977). The decomposition reactions of the compounds were subjected to non-isothermal kinetic studies and the weighted least-squares method (LSM) was used for obtaining the best linear plots by applying the data to various equations (Horowitz and Metzger 1963; Coats and Redfern 1964; Piloyan and Novikova 1966). The values of slope and energy of activation (E^*) were obtained from the plots (figures 2, 3 and 4) (Kaul and Sharma 1991). The values of frequency factor (Z) and entropy of activation (ΔS^*) were calculated as below (Rema *et al* 1992).

$$Z = (E/RX)B \exp(E/RX^2), \quad (1)$$

$$Z = (RX/h) \exp(S/R), \quad (2)$$

For Horowitz method $X = T_m$ (peak temperature); for Piloyan and Redfern methods, $X = T$ (decomposition temperature), where $h =$ Planck constant; $k =$ Boltzmann constant, $\beta =$ rate of heating and $R =$ molar gas constant. It is found that the best linear fit for both the compounds has been obtained for $n = 1/2$ or $g(\alpha) = 2[1 - (1 - \alpha)^{1/2}]$ in C-R and H-M methods.

A perusal of table 2 reveals that the values of the kinetic parameters obtained by C-R, P-N and H-M methods are more or less consistent. Generally, the value of Z increases with decrease in E^* . However, there are some more inherent physical and

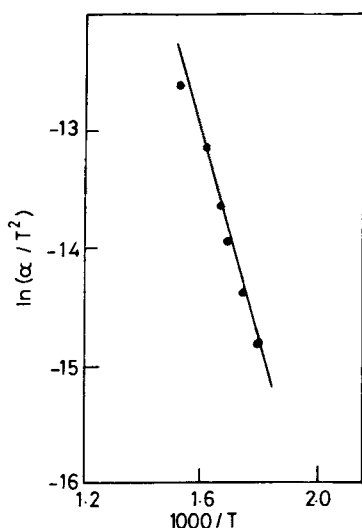


Figure 2. Piloyan-Novikova plot of $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$.

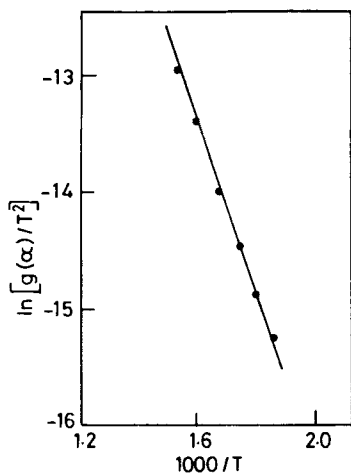


Figure 3. Coats-Redfern plot of $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$.

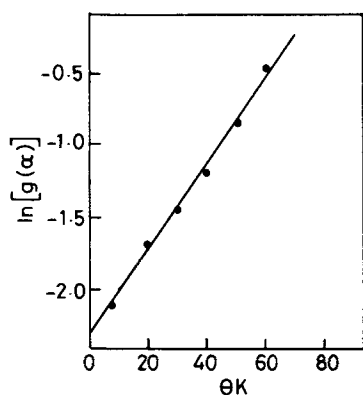


Figure 4. Horowitz-Metzger plot of $[\text{Mn}(\text{en})(\text{H}_2\text{O})_2(\text{VO}_3)_2]$.

chemical factors viz. thermodynamic, kinetic, stereospecific etc., which may cause a change or deviation in this trend (Benson 1976). The negative values obtained for entropy of activation indicate that activated complexes have more ordered structures than the reactants and that the reactions are slower than normal (Chourasia *et al* 1993).

4.5 X-ray studies

The XRD pattern records sixty-five and twenty-one reflections between 5 and 80° (2θ) for en and pz complexes respectively. The maximum intensity peaks were found at 2θ = 18.9575 and 6.700 corresponding to $d = 4.6775 \text{ \AA}$ and 13.0653 Å for en and pz complexes respectively. The diffraction patterns have been indexed by the inspection and trial method (Lipson and Steeple 1970; Woolfson 1980) for the orthorhombic crystal system. The unit cells for complexes have been found to be of the orthorhombic type. The XRD lattice parameters for the above complexes are as follows:

Table 2. Kinetic parameters of Mn(II) dimetavanadato complexes.

| Compound | Equation due to* | Decomp. stage | E^* (kJ mol ⁻¹) | Z (s ⁻¹)($\times 10^2$) | ΔS^* (JK ⁻¹ mol ⁻¹) |
|---|------------------|---------------|-------------------------------|---|--|
| [Mn(en)(H ₂ O) ₂ (VO ₃) ₂] | P-N | First | 34.02 | 2.663 | -63.529 |
| | C-R | | 36.12 | 2.834 | -63.267 |
| | H-M | | 31.81 | 2.279 | -64.524 |
| [Mn(pz)(H ₂ O) ₂ (VO ₃) ₂] \cdot H ₂ O | P-N | First | 63.85 | 6.819 | -58.583 |
| | C-R | | 73.75 | 8.628 | -57.594 |
| | H-M | | 71.72 | 4.296 | -62.676 |

*P-N – Piloyan–Novikova; C-R – Coats–Redfern; H-M – Horowitz–Metzger

X-ray data of [Mn(en)(H₂O)₂(VO₃)₂]

Crystal system: Orthorhombic;

$A = 0.00241$; $B = 0.003515$; $C = 0.00199$;

$a = 15.72968$ Å; $b = 13.02459$ Å; $c = 17.31013$ Å;

Cell volume, $V = 3546.3633$ Å³; $n = 14$;

$D(\text{obs.}) = 2.3439$ g. cm⁻³ ($D = \text{density}$);

$D(\text{cal.}) = 2.2866$ g. cm⁻³.

X-ray data of [Mn(pz)(H₂O)₂(VO₃)₂] \cdot H₂O

Crystal system: Orthorhombic;

$A = 0.00231$; $B = 0.00165$; $C = 0.00143$;

$a = 16.03965$ Å; $b = 18.97836$ Å; $c = 20.39246$ Å;

Cell volume, $V = 6207.5914$ Å³; $n = 5$;

$D(\text{obs.}) = 0.5254$ g. cm⁻³ ($D = \text{density}$);

$D(\text{cal.}) = 0.5253$ g. cm⁻³.

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