STUDIES ON VANADIUM (V), MOLYBDENUM (VI) AND TUNGSTEN (VI) DIOXO AND PEROXO COMPLEXES OF POLYDE[redacted]ANDS

A

REPORT ON

Laboratory Project submitted for the partial fulfilment of the degree

of

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in

CHEMISTRY

(Industrial Methods of Chemical Analysis)

By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**Studies on vanadium(V), molybdenum(VI) and tungsten(VI) dioxo- and peroxo complexes of polydentate ligands**" in partial fulfilment of the requirement for the award of the Degree of **Master of Philosophy** submitted in the **Department of Chemistry** of the University is an authentic record of my own work carried out during a period from January 98 to **July 98** under the supervision of **Dr. M. R. Maurya**, Asstt. Professor, Department of Chemistry, University of Roorkee, Roorkee.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

N Bharti

Date : 30.7.98 **(NEELAM BHARTI)**

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

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Stirring of V_2O_5 in an aqueous solution of KOH and 30% H_2O_2 results in the formation of oxoperoxovanadium(V) species, $[VO(O_2)_2.X\ H_2O]$. Reaction of this species with 2-(α-hydroxymethyl)benzimidazole or 2-(α-hydroxyethyl)benzimidazole in 1:2 molar ratio gives the complex $K[VO(O_2)L_2]$ (where LH = ligand). Similar peroxo species of molybdenum and tungsten generated *in situ* by stirring, MoO_3 or $WO_3.H_2O$ with an excess of 30% H_2O_2 readily react with 2-(α-hydroxyethyl)benzimidazole in aqueous alcoholic solution to give the corresponding peroxo complexes of formula $[MO(O_2)L_2]$ (where M = Mo or W). All these complexes are crystalline in nature and light yellow to orange in colour. These complexes exhibit three IR active vibrational modes ~ 860 cm^{-1}, 760 cm^{-1} and 600 cm^{-1} which are characteristic of η^2-coordinated peroxo group. Reaction of $[MO_2(acac)_2]$ (where M = Mo or W, acacH = acetyl acetone) with the above ligands along with 2-(α-hydroxybenzyl)benzimidazole gives the corresponding dioxo complexes of general formula $[MO_2L_2]$. These complexes are dominated by the presence of two sharp bands ~ 900 cm^{-1} region due to ν_{sym} (O=M=O) and ν_{asym} (O=M=O) modes. The IR spectra also confirms the monobasic ON bidentate behaviour of the ligands. A broad band at ~ 420 nm in peroxovanadium(V) complexes, while at ~ 350 nm in peroxomolybdenum(VI) and tungsten(VI) complexes has been assigned due to the peroxo-metal charge transfer (LMCT) band.

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INTRODUCTION

1. INTRODUCTION

1.1 Scope of Thermogravimetry and Spectroscopy

1.1.1 Thermogravimetry :

Thermogravimetry enjoys a prestigious position among various industrial methods of chemical analysis due to its simplicity and wide scope in the field of inorganics, semiconductors, magnetic materials, ceramics, environment etc. Thermogravimetric method of analysis may be defined as a technique in which change in physical and/or chemical properties of a substance are measured as a function of temperature. Other simple thermal analytical techniques include:

(i) Differential thermal analysis (DTA) where the difference in temperature between a substance and inert reference material as a function of temperature or time is recorded and

(ii) Differential scanning colorimetry (DSC) whereby the energy necessary to establish a zero temperature difference between a substance and a reference material is recorded as a function of temperature or time.

The determination of the purity and thus suitability, thermal stability and thus correct drying temperature of the materials are potential applications of thermo gravimetric technique. Complex materials such as clays and soils have also been the subject of thermogravimetric study. The data suggests that lattice water and volatile organic materials may be quantitatively determined in pure clays and soils [1].

Thermogravimetric technique is very useful in the determination of the nature of water/ solvent molecule present in coordination compounds. Lattice water, hydrogen bonded lattice water and coordinated water all can be distinguished in coordination compounds by observing the thermolytic pattern of the hydrated complexes. Other intermediates and final residue lead to draw the conclusion about structure and bonding in complexes.

1.1.2. Spectroscopy [2, 3]

Spectroscopy is the branch of science which deals with the study of electromagnetic radiation and its interaction with molecule. In spectroscopy, molecule undergoes an energy transition from a lower to higher energy level by absorption of energy.

Every molecule has its characteristic feature, so wavelength (λ) of absorbed radiation depends upon the structure of molecule,

$$E = h\nu = \frac{hc}{\lambda}$$

where, λ = Wavelength, c = Velocity of light,

h = Planck's constant, E = Energy per photon and

ν = Frequency.

The molecular processes associated with each region are quite different. The various regions in electromagnetic radiation in decreasing wavelengths are :

	Region	Molecular processes
1	Radio wave region ($10^{2} - 10^{-2}$ cm)	Change of spin
2	Micro wave region ($10^{-2} - 10^{-4}$ cm)	Change of orientation
3	Infrared region ($10^{-4} - 10^{-6}$ cm)	Change of configuration
4	Visible and UV region ($10^{-6} - 10^{-8}$ cm)	Change of electron distribution
5	X-ray region ($10^{-8} - 10^{-10}$ cm)	Change of electron configuration
6	γ –ray region ($10^{-10} - 10^{-12}$ cm)	Change of nuclear configuration

(A) Infra red Spectrum [4-7]

The absorption of radiation in IR region gives different bands. The intensity and position of these bands gives rise to information about the presence or absence of the particular functional group and indicate the mode of bonding involved. The IR spectrum has basically two regions :

(i) High frequency region (4000-600 cm^{-1}) : This region is ligand sensitive region and gives information about the functional group ; 1400-900 cm^{-1} region is most important and is often called "finger print region".

(ii) Low frequency region (600-200 cm^{-1}) : This region is metal sensitive region.

IR Spectra of Coordination Complexes

IR spectrum of a molecule is function of its constituent atom, bond length and bond angles. When a ligand coordinates with metal atom, all factors changes and alter the above parameter slightly within the ligand. The IR spectra of the free ligand and the complex may be different in various ways :

(i) **Change in band position** : Bands associated with the stretching of bonds involving the coordinated atom usually move to longer wave length on coordination.

(ii) **Alteration in relative band intensities** : Coordination usually reduces the effective symmetry of the ligand vibrations which are IR inactive in the ligand but may become IR active in the complex.

(iii) **Band splitting** : As new bands appear, it may also cause splitting of bands in complex. Band position is expressed by the wave number ($\bar{\nu}$):

$$\nu = c / \lambda$$

$$\bar{\nu} = \nu / c = 1 / \lambda$$

ν = Frequency , c = Velocity of light and

λ = Wavelength

(B) Electronic Spectroscopy [8-14]

When a molecule absorbs radiation in UV/visible region, an electron is promoted to higher energy level. The time required for an electronic transition to occur is so short compared to the time required for one cycle of vibration (10^{-9} s), that the inter-nuclear distance of the vibrating molecules does not undergo appreciable change during the electronic transition (10^{-16} s). It has different regions :

(i) The visible region (400-750 nm)

(ii) Near ultraviolet region (200-400 nm)

(iii) Far ultraviolet region (below 200 nm)

Different electronic transition takes place in the molecule are as :

(i) $\sigma - \sigma^*$

(ii) $n - \sigma^*$

(iii) $\pi - \pi^*$

(iv) $n - \pi^*$

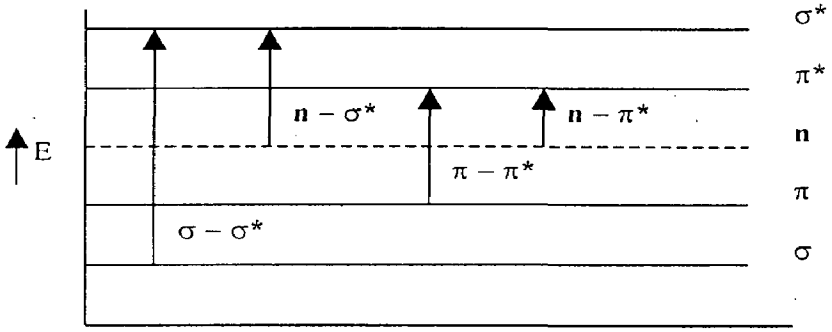


Fig. 1 : Different types of electronic transition

An expression of absorption intensity is derived from the Lambert-Beer law

$A = \varepsilon cl$

A = Absorbance, c = Concentration of solute,

l = Path length through absorbance and

ϵ = Molar absorptivity or molar extinction coefficient.

In transition metals, d-orbitals split up in presence of an external field. Different possible origins for the electronic absorption spectra of complexes are as :

(a) Spectra principally associated with the ligand ($\pi - \pi^*$)

(b) Spectra involving metal and ligand

(i) Metal to ligand ($M \rightarrow L$), (ii) Ligand to metal ($L \rightarrow M$)

(c) Spectra associated with metal influenced by the presence of ligand.

Identical functional groups in different molecules will not necessarily absorb exactly the same wavelength and the energy requirement may not be the same due to different structural environment.

Spectroscopic and thermogravimetric techniques taken together provide interesting results which are some times very difficult to obtain by other process. For example the isolation of oxomolybdenum (IV) and oxotungsten (IV) complexes requires very vigorous reaction conditions while these were easily obtained using help of

thermogravimetric technique via thermal reductive elimination process [15] and spectroscopy supported to the fact.

1.2 Biochemical Importance of Vanadium, Molybdenum and Tungsten

Dioxygen complexes of transition elements have been known since the mid 19th century, when the extraction of the blue peroxochromate into ether was described by Barreswil [16]. The accumulation of vanadium by plants as well as sea animals have been known since the turns of the century but interest in biochemical properties of peroxovanadates was stimulated when vanadium(V) dependent haloperoxidases were discovered in various marine algae [17] and in lichen [18].

Some peroxovanadium(V) complexes have shown anti tumour activity against L 1210 Murine leukemia [19]. Studies support the idea that intra molecular transfer play a role in some mechanism of vanadium biological activities. Biological activity of these compounds depends upon the attached ligand. Recently vanadium is recorganised as an essential element for mammals [20] although its biochemistry is not known [21-23].

Vanadium (V) has been found to be present as a mononuclear unit in the resting state of haloperoxidase enzymes [24]. The reduced form of the haloenzyme containing $[VO]^{2+}$ is inactive but regains its activity by reoxidation when exposed to air [25]. Vanadium is present in nitrogenase which is active in the conversion of acetylene to ethane. Vanadium is a cofactor in the enzymes like bromoperoxidase [24] and nitrogenase [26] and its various inhibitory interactions with other enzymes [27]. There has been some evidences that tunichromes, present in the ascidian blood cells have the ability, to bind vanadium [28]. Vanadobin , a component capable of storing vanadium in the vanadyl form has been isolated from these cells [29].

Peroxo heteroligand vanadates (V) has strong insulin mimetic activity observed for some vanadium peroxide, both *in-vivo* and *in-vitro* [30]. Vanadium (V) compounds continue to expand the horizons of their biochemical significance [31-34] in addition to their long time known catalytic properties [35].

Molybdenum is the only element among the second and third transition series known to be essential for life [36]. It was discovered in 1930 that molybdenum is essential for the growth of the nitrogen fixing organism Azotobactor [37]. Since then

various molybdenum dependent enzymes have been identified in several species of living system. The enzymes are found in simple bacteria as well as in complex mammalian systems.

Molybdenum has an important role in the cycle of nitrogen in biological system [38]. Molybdoenzymes participate in the initial reduction reaction of inorganic nitrogen and in oxidation of purines and pyrimidines [39], N_2 to NH_3 and NO_3^- to NO_2^-. Sulphite oxidase oxidises toxic SO_3^{2-} ion into harmless SO_4^{2-} ions.

Selected molybdoenzymes are [40] :

Enzyme	Substrate	Product
Aldehyde oxidase	RCHO	RCOOH
Carbon monoxide oxidase	CO	HCO_3^-
Sulphite oxidase	SO_3^{2-}	SO_4^{2-}
Formate dehydrogenase	HCO_2^-	HCO_3^-
Nitrate reductase	NO_3^-	NO_2^-

Pterin component found associated with Mo-Co in the degraded organic matter [41]. The metabolism of Mo-Co in human may proceed through urothione since it was observed that Mo-Co deficient children have no urothione present in their urine.

The principal area of current bioinorganic chemistry research is the isolation and characterisation of synthetic analogous of molybdoenzymes which is to produce ligation mode and to achieve the stereochemistry of metalloenzyme active site. It is very useful for interpreting the properties and reactions of many metals containing macromolecules.

Although tungsten and molybdenum possessquite similar chemistry, recently a variety of tungsten containing enzymes have been found [42-46] such as carboxylic acid reductase, formate dehydrogenase and aldehyde oxidoreductase. The disparity between tungsten and molybdenum may be due to low environmental abundance of tungsten. Like iron and manganese it may be rather more available in the environment of shallow and deep sea hydrothermal vents.

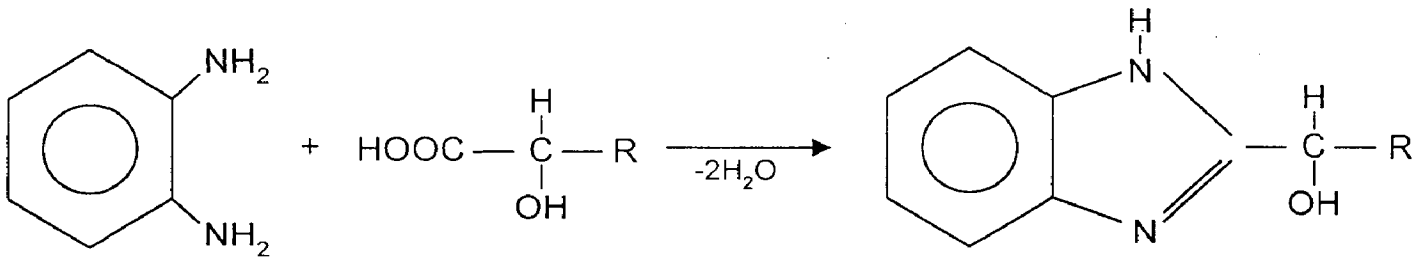
Aldehyde oxidoreductase obtained from bacteria is a monomeric protein of approximate molecular weight 85000, that contains one tungsten, seven iron and five sulphides. Another tungsten containing enzyme which has been characterised is formate

dehydrogenase from Clostridium thermoaciticum [42]. This enzyme contains two tungsten, two selenium, thirty six iron and fifty sulphure. It has a molecular weight of about 340000. An apparent tungsten co-factor was found after denaturation of formate dehydrogenase at pH 2.5.

Tungsten containing enzyme aldehyde dehydrogenase seems to be the first which reduces non-activated carboxylic group to aldehyde [43]. There is no further reduction of obtained aldehyde.

1.3 Historical Background of Hydroxy Alkyl/Aryl Benzimidazole and Literature Survey

2-α-hydroxymethyl-, 2-α-hydroxyethyl- and 2-α-hydroxybenzyl benzimidazole was first prepared by Phillips [47] in 1928 by the reaction of *o*-phenylenediamine and respective carboxylic acids in boiling dilute hydrochloric acid (Scheme 1).



R = H, CH_3, C_6H_5

Scheme 1

However, interest in such compounds started in early sixties during smallpox epidemic in Madras. 2-(α-hydroxybenzyl)benzimidazole and some of its derivatives showed the most promising activity against enteroviruses [48]. The parent compound showed good activity against the poliomyelitis virus type 2. While only small activity against the type 1 and 3 virus was noticed. However, such activity increases with the introduction of N-alkyl substituents; maximum being with 1-propyl derivatives (Fig. 2) which is active against all three poliovirus types [49]. Similar high protection action was also shown by the D-isomers of these compounds [50], 1-benzyl [51] and 1-methoxy ethyl [52] derivatives.

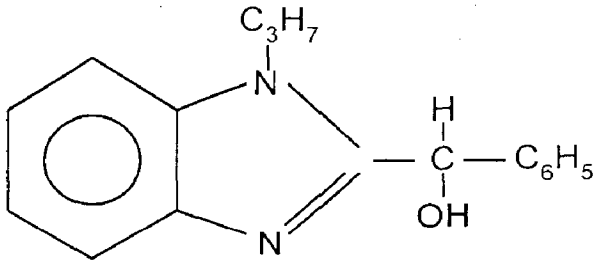


Fig. 2 : Structure of 1-n-propyl-2-(α-hydroxybenzyl)benzimidazole (PHOBB)

First metal complex of 1-n-propyl-2-(α-hydroxybenzyl)benzimidazole (PHOBB) with nickel (II) was reported by Piggott et al. in 1983 to model the active site of the enzyme urease [53]. Since then several papers dealing with metal complexes with such ligands have appeared in literature.

Reaction of MoO_2Cl_2 with the above ligand in dry ethanol gave a bridged molybdenum(VI) complex, $[Mo_2O_5(POBB)_2]$ having six and five coordinate molybdenum [54] (Fig. 3). The tertiary nitrogen is coordinated to the individual molybdenum while oxygen of the deprotonated hydroxyl group bridged between two molybdenum.

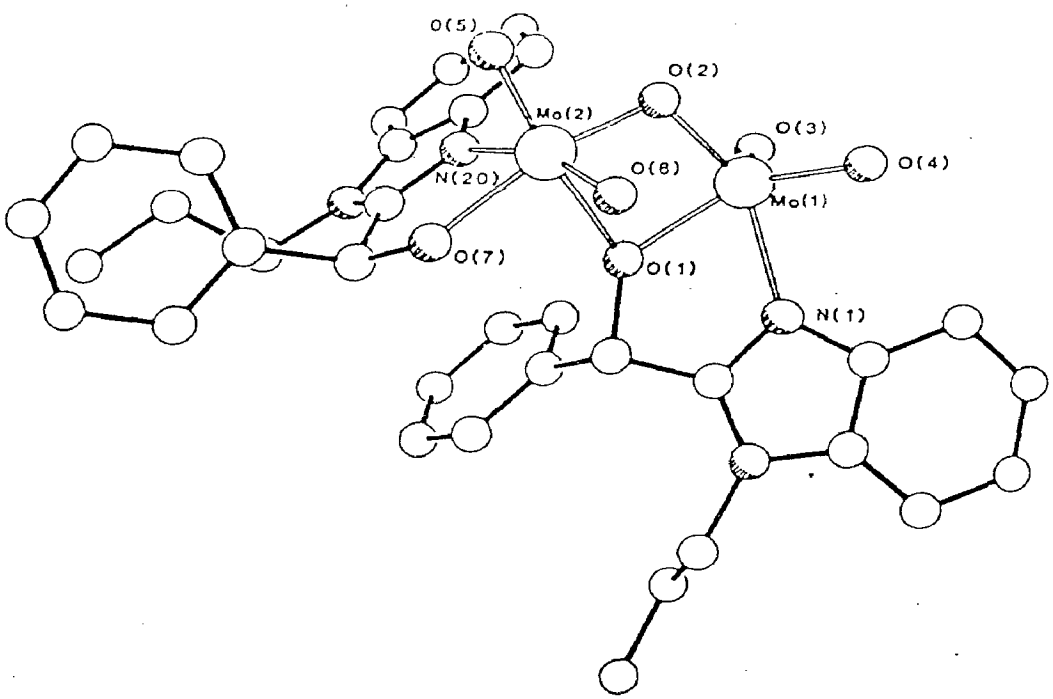


Fig. 3 : Crystal structure of $[Mo_2O_5(POBB)_2]$ taken from ref. 54.

Cobalt (II) and nickel (II) complexes of 2-(α-methoxybenzyl)benzimidazole have been reported to understand the binding of such virus inhibitors to proteins during the

anti-viral activity action [55]. The complexes formed have general formula $[ML_2X_2]$ (where M = Co(II), Ni(II), LH = ligand and X = Cl^-, Br^-, I^-, NO_3^-, ClO_4^-). Bonding in these complexes are through tertiary nitrogen and oxygen of the methoxy group.

The X-ray crystal structure and magnetic properties of a binuclear copper (II) complex of 2-(α-hydroxybenzyl)benzimidazole, $[Cu_2(C_{14}H_{12}N_2O)_2(C_{14}H_{11}N_2O)_2](ClO_4)_2.5C_2H_5OH$ has been reported by Piggott et. al. [56]. The molecule has two protonated ligands which are coordinated to a single copper atom through their imino nitrogen and the oxygen of their hydroxyl group. Other two deprotonated ligands each coordinate to a copper ion through their imino nitrogen atom and form a bridge between the two copper ions with their alkoxy oxygen atoms. The solvated complex is diamagnetic throughout the temperature range down to liquid nitrogen showing strongly antiferromagnetic interaction. However, the magnetic moment of a desolvated complexes is 0.99 BM per copper atom at 286.4 K and 0.78 BM at 76.1 K. It is presumed that heating the complex to remove solvent introduced some paramagnetic impurity by a side reaction. A similar bonding mode of the above ligand in complex $[Cu_2(C_{14}H_{12}N_2O)_2(C_{14}H_{11}N_2O)_2.(NO_3)_2].4Me_2SO$ has also been deduced. However, in complex $[Cu(C_{14}H_{11}N_2O)_2(SCN)_2]$, the two thiocyanate groups are *trans* to each other and ligand's behaviour is mono-basic bidentate ON donor.

2-(α-hydroxymethyl)benzimidazole $(HMBMZ)^-$ on interaction with K_3 $[Cr(NO)(CN)_5]$ in aqueous acetic acid solution gives mixed ligand cyano nitrosyl complex $[Cr(NO)(CN)_2(HMBMZ)_2.H_2O]$ [57]. Another nitrosyl complex $[Cr(NO)(acac)_2(HMBMZ)]$ has also been isolated according to the following scheme (2) [58].

$$[Cr(NO)(acac)_2 H_2O] + [HMBMZ]^- \xrightarrow[\text{reflux}]{CH_3OH} [Cr(NO)(acac)_2(HMBMZ)]$$

Scheme-2

Coordination through only imino nitrogen has been inferred on the basis of various physico chemical studies.

1.4 Peroxo and Dioxo Complexes of Vanadium, Molybdenum and Tungsten

Peroxovanadium(V) complexes and their potential applications as catalyst have been reviewed recently [59, 60]. The most studied complexes are with the biologically important polycarboxylic acids, such as iminodiacetic acid [61], citric acid [62, 63], nitrilotriacetic acid [64], nicotinic acid [65], amino acids and peptides [66].

Peroxovanadate complexes always contain vanadium in oxidation state V and are diamagnetic. The monoperoxo complexes of vanadium(V) with hydroxypolycarboxylato and amino poly carboxylato ligands are orange to red. They show a band at ~ 420 nm in their electronic spectrum due to its shorter bond length (O-O) where as diperoxo complexes exhibit such band at ~ 320 nm. Usually monoperoxo complexes display strong band at ~ 930 cm^{-1} due to (O-O) stretching in their IR spectra as compared to diperoxo complexes which exhibits such band at 890 cm^{-1}.

Imino diacetic acid ($IDAH_2$) reacts with vanadium(V) in presence of hydrogen peroxide to form crystalline compounds of the formula M [$VO(O_2)IDA$] (where M = K^+ or NH_4^+) [61]. These complexes crystallise as anhydrous from the aqueous solutions and are remarkably stable towards decomposition. The significant feature of IR spectra of these complexes are bands of coordinated IDA, peroxo frequencies and V = O stretching. The NH stretching shifts to higher energy and appears as a sharp band at 3215 cm^{-1} instead of 3100 cm^{-1} in free acid. The strong absorption band observed at 980 and 920 cm^{-1} are assigned to the ν (V = O) and ν (O-O) stretching, respectively [67, 68].

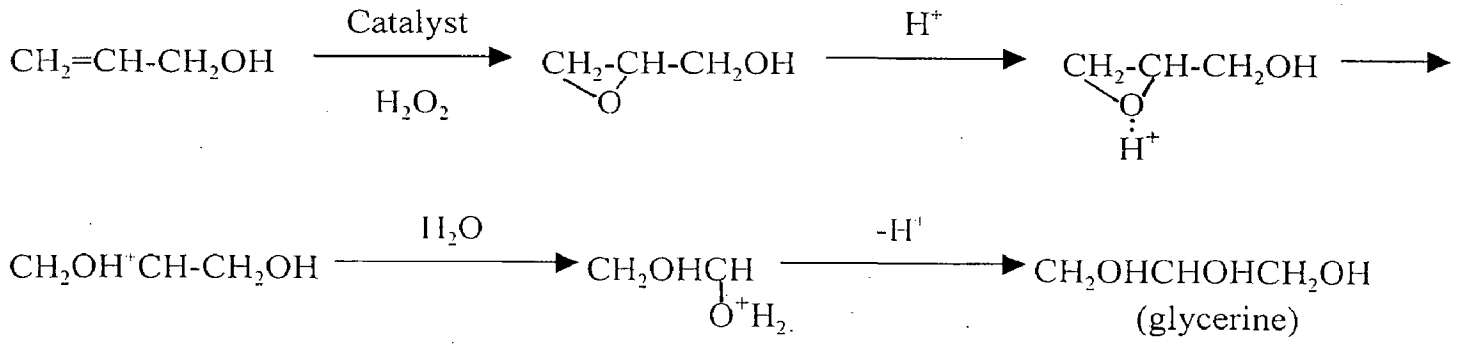
Peroxo citrato complexes of the formula $M[VO(O_2)\ (C_6H_6O_7)].H_2O$, (where M = K^+, NH_4^+, Cs^+ and $C_6H_6O_7^{2-}$ = citrate ion) have been prepared from aqueous solutions [63]. In acid solution (pH < 2) they decompose and these solutions show the typical absorption at ~ 450 nm, characteristic of the $[VO(O_2)]^+$ ion. UV/ visible spectra of peroxo citrato complexes in aqueous solution show a weak broad peroxo LMCT band around 415 nm. A dioxovanadium (V) complex, $K[VO_2\ (C_6\ H_6\ O_7)].\ H_2O$ has also been isolated when reaction was carried out in absence of H_2O_2 [68]. This pale green compound is diamagnetic but ionic in nature. It exhibits two sharp bands in its IR

spectrum centered at 955 cm^{-1} and 890 cm^{-1} due to ν_{sym} (O = V = O) and ν_{asym} (O=V=O) modes. This indicates the presence of *cis* $[VO_2]^{2+}$ moiety.

A crystalline red compound $[O\{VO(O_2)\ (C_8\ H_9\ NO_3)\}_2].\ C_2H_5OH$ was obtained from aqueous vanadium(V) peroxide solutions containing nicotinic acid. It contains one ethanol along with one mole of nicotinic acid per vanadium. The IR spectrum of this complex shows a band at 1707 cm^{-1} due to ν (CO) of protonated carboxylic group [69]. ν(V = O) stretch appears at 995 cm^{-1}. The lower energy region band at 395 and 340 cm^{-1} are due to (V-O) and (V-N) stretchings, respectively [70].

Dioxygen ligand is of interest not only because of its intrinsic nature but also because of its role in metal catalysed oxidation reactions such as epoxidation of olefine [71], preparation of hydroxyketones [72] and secondary alcohals [73]. According to Vaska [74] dioxygen either exists as covalently bonded peroxide or superoxide but mostly insensitive to the molecular surrounding.

The peroxo complexes of molybdenum and tungsten with different ligands such as 8-hydroxyquinoline, 2-amino benzoic acid, quinoline 2-carboxylic acid, 2-aminophenoxide, *o*-phenylenediamine, 2-amino ethanol, malonic acid etc. have been reported by Tarafder and Khan [75a, b]. The complex $[MoO(O_2)\ L_2]$ (where LH = 8-hydroxyquinoline) has been used as catalyst to generate glycerine from allyl alcohol and cyclohexanol to cyclohexanone. The possible reaction mechanism for the oxidation of allyl alcohol to glycerine has been suggested as shown in scheme 3.



Scheme-3

The schiff bases I, II and III (Fig. 4) also stabilized molybdenum(VI) and tungsten(VI) peroxo complexes, when MoO_3 or H_2WO_4 was treated with the respective

ligands in presence of H_2O_2 in aqueous alcoholic medium [75,76]. The isolated complexes have general formula [$MO(O_2)$ L] (where M = Mo or W and LH_2 = ligand I, II or III). The complexes [$MO(O_2)$ (sal-OAP)] (H_2sal-OAP = ligand I) transfer one of the oxygen from the peroxo group to triphenylphosphine and triphenylarsine (Scheme 4) while the other two complexes do not show such transfer.

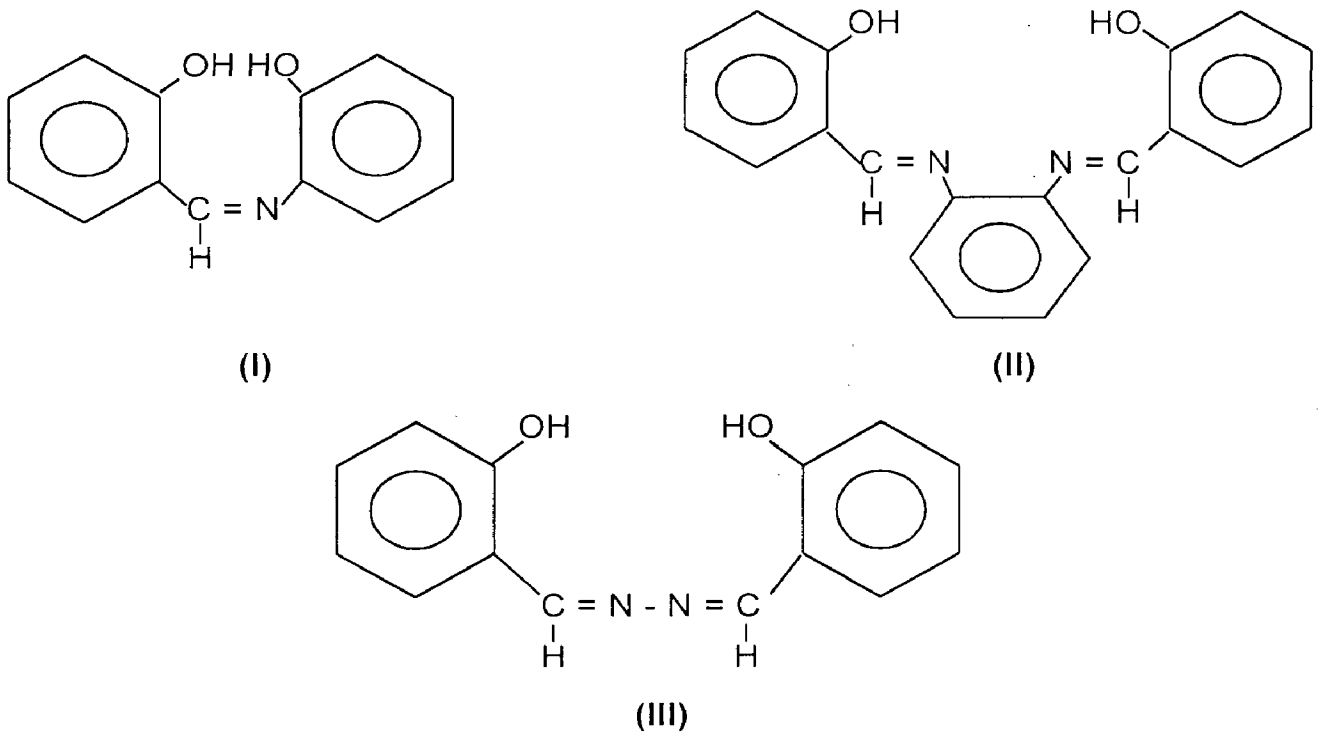


Fig. 4 : Structure of Schiff Bases I, II and III

$$[MO(O_2)(\text{sal-OAP})] + PPh_3 \longrightarrow [MO_2(\text{sal-OAP})] + OPPh_3$$

Scheme 4

A series of peroxomolybdenum(VI) and tungsten(VI) complexes with pyridine-2-carboxylic acid and pyridine-2, 6-dicarboxylic acid have been prepared and characterized. Depending upon the reaction conditions, the isolated complexes are anionic or neutral type. The X-ray crystal structure of oxo-peroxo (pyridine-2, 6-dicarboxylato) aquomolybdenum(VI), [$MoO(O_2)$ (pydc).H_2O] has been solved. The peroxo group and the two oxygen atoms as well as the N of the pyridine-2, 6-dicarboxylato ligand occupy the pentagonal plane while the oxo group and the water molecule are located in the apical position [77] (Fig. 5).

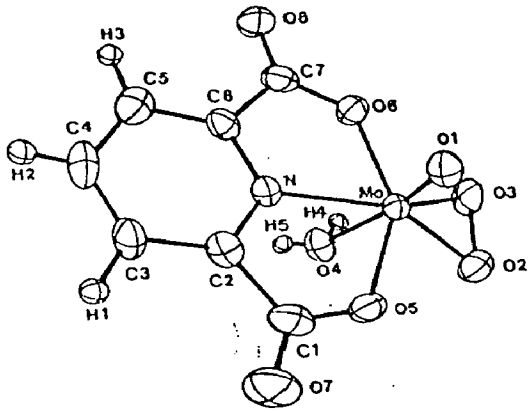
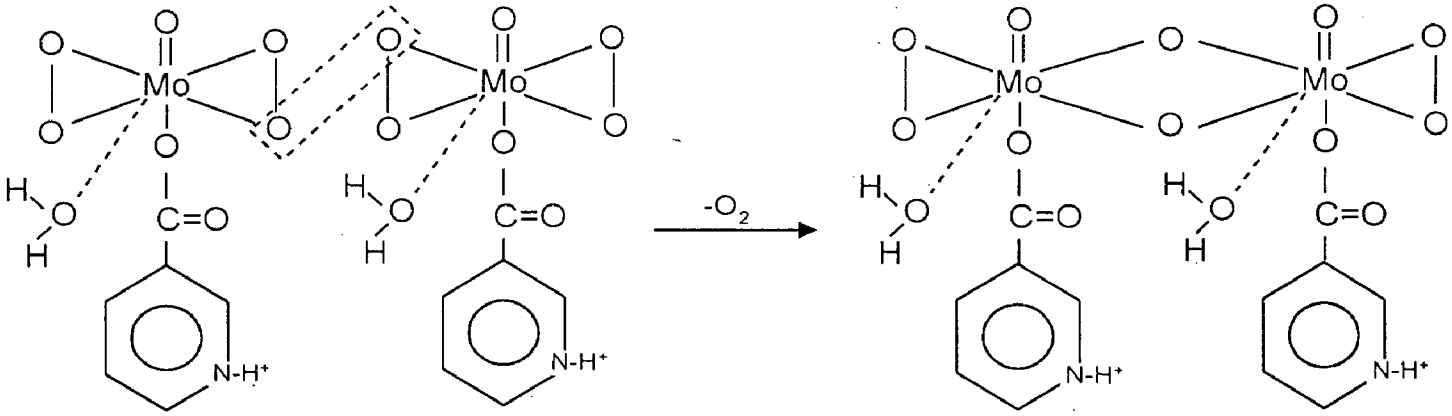


Fig. 5 : X-ray Crystal Structure of [$MoO(O_2)$(pydc).H_2O] taken from ref. 77.

Nicotinic acid (nic) forms two types of peroxomolybdenum complexes, [$MoO(O_2)$ (nicH).H_2O] and [$MoO_2(O_2)$ (N-nicoH)$_2$].H_2O by slightly modifying the reaction conditions and pH of the reaction mixture. In the previous complex, N of the pyridine moiety protonates while in the later one it exists as nicotinic acid-N-oxide molecule. The complex [$MoO(O_2)_2$ (nicH).(H_2O)] slowly loses one oxygen of the one peroxo group with time interval in the solid state to give [$MoO_2(O_2)_2$(nicH).(H_2O)] having bis(μ-oxo) bridge. A plausible formation of a bis ((μ-oxo) dimer from two [$MoO(O_2)_2$ (nicH) (H_2O)] monomers may be explained [64] as shown in scheme 5.



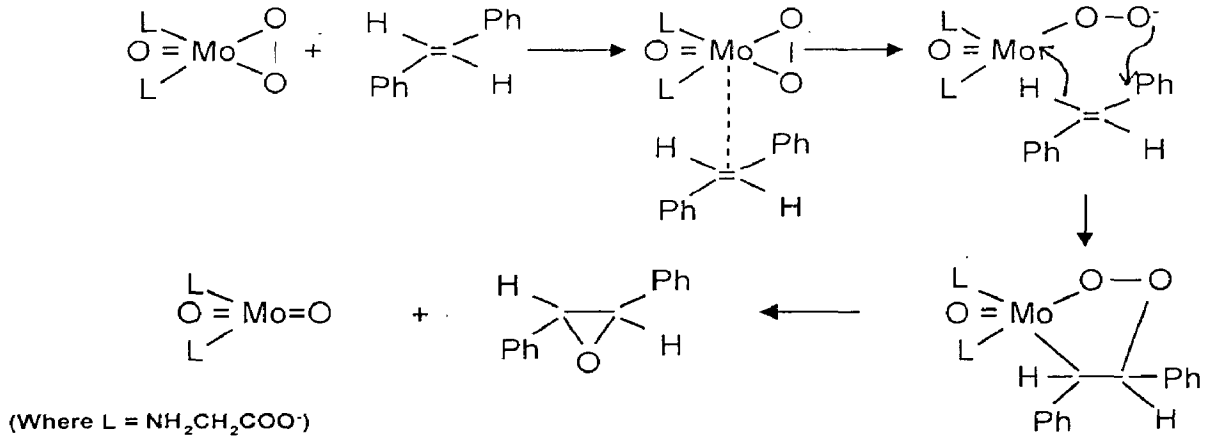
Scheme 5

Ethylenediaminetetraaceticacid (H_4EDTA) stabilized as [$WO(O_2)$ (H_2EDTA)] in the peroxotungsten(VI) complex [78] when it was treated with WO_3 in excess of 30% H_2O_2. A sharp band at 955 cm^{-1} in the IR spectrum due to ν (W=O) mode indicates the association of oxo group with tungsten. The metal peroxo grouping gives rise to three IR active vibrational modes at 860 cm^{-1}, 632 cm^{-1} and 600 cm^{-1}. These are predominantly (O-O) stretching (ν_1), the antisymmetric (W-O_2) stretch (ν_3) and the symmetric (W-O_2) stretch (ν_2).

An equimolar amount of malonic acid and MoO_3 dissolved in KOH along with excess of H_2O_2 at pH~3 produces pale yellow crystals of the potassiumoxodiperoxo oxalato molybdate(VI), K_2 $[MoO(O_2)_2$ $(C_2O_4)]$ on standing at room temperature. In solution malonic acid slowly converted into oxalic acid and then coordinated with molybdenum. The α-hydroxy succinic acid behaves very much like the malonic acid however succinic acid, the next higher homologue of the malonic acid does not convert into oxalic acid. The mechanism of the malonate → oxalate catalytic conversion is so far unknown [79].

The peroxo species $MoO(O_2)_2$. x H_2O generated *in situ* by the reaction of MoO_3 and excess of H_2O_2, reacts with α-amino acids (α-aa) to form complexes of the type $[MoO(O_2)_2$ (α-aa) $(H_2O)]$ (where α-aa = glycine, alanine, proline, valine, leucine, serine, asparagine, glutamine and glutamic acid). Except the glycine complex all the complexes are not very stable and lose peroxides and water on heating in vacuo. The visible spectra of the complexes in 0.1M KCl aqueous solutions shows a broad absorption band at around 315 nm (∈~1000) due to peroxo ligand to metal charge transfer band. Some of the structures of these complexes have been solved by single crystal X-ray method. The complexes have co-ordinated carboxylate oxygen and two peroxo groups in equatorial position while water molecule and oxo group in the apical position [80].

Peroxomolybdenum(VI) glycine complex reacts with *trans*-stilbene where it transfers one of the peroxo oxygen to *trans*-stilbene to give *trans*-stilbene oxide [81]. The mechanism may be shown as follows (scheme 6) .



Scheme 6

Peroxocomplexes of molybdenum and tungsten have also been used as potential precursors for molybdenum and tungsten complexes in various oxidation states[15,82-84]. The $[MO]^{2+}$ (where M = Mo or W) complexes of 2-(2-hydroxyphenyl) benzimidazole (Fig. 6) were obtained by thermal reductive elimination of peroxo group, while $[MO_2]^{2+}$ species were obtained through transfer of an oxygen from the peroxo group.

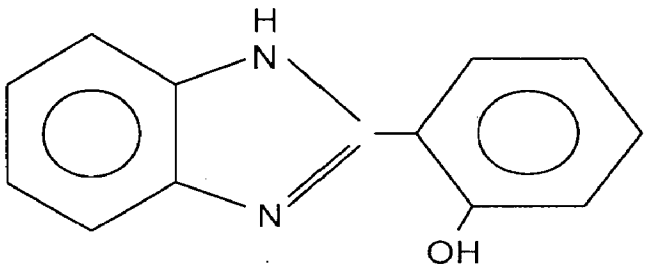


Fig. 6 : Structure of ligand IV

Synthesis, reactivity and catalytic properties of binuclear oxo-peroxo complexes of molybdenum(VI) and tungsten(VI) with methylene - or dithio - bridged ligand (Fig. 7) have been reported by Maurya et al. [85]. Reaction of these peroxo complexes, $[\{MO(O_2)\}_2\ L]$ (where LH_4 = ligand) with triphenyl phosphine shows the formation of triphenyl phosphine oxide and conversion of the peroxo complexes to the corresponding $[MO_2]^{2+}$ (where M = Mo or W) species. These complexes are effective catalyst in the oxidation of cyclohexanol to cyclohexanone using tert-butylhydroperoxide as an oxidant. While under similar conditions they fail to catalyse the oxidation of *trans*-stilbene, cyclohexane or styrene.

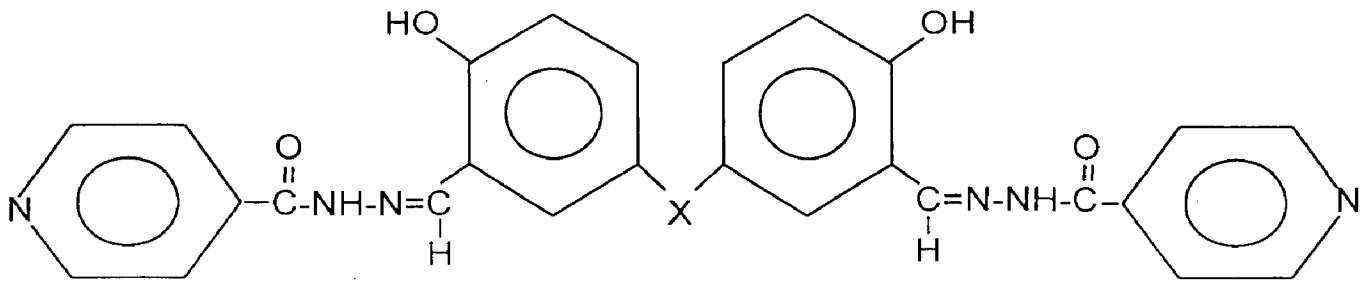


Fig. 7 : Structure of bridged ligand

1.5 Formulation of the Problem

The literature survey reveals that though peroxo complexes of vanadium(V), molybdenum(VI) and tungsten(VI) have very potential applications in various fields, very little work have been done on the synthesis and characterisation of such complexes. Therefore it was worthwhile to focus on synthetic approaches of peroxo complexes along with dioxo complexes and their characterisation using various physico-chemical methods.

EXPERIMENTAL

2. EXPERIMENTAL

2.1 Materials

Metal salts and all other reagents employed in the present study are as given :

	Chemicals	Grade	Company
1	*o*-phenylenediamine	LR	Merck
2	Glycolic acid	LR	Lancaster
3	Lactic acid	LR	Merck
4	Mandelic acid	LR	Merck
5	MoO_3	AR	S. D. Fine
6	H_2WO_4	GR	Loba chemie
7	V_2O_5	LR	Riedel-De-Haen A.G.
8	Ammonia	AR	Qualigens
9	Ethanol	LR	Merck
10	Methanol	LR	Merck
11	KOH/NaOH	LR	Merck
12	HNO_3	AR	Qualigens
13	HCl	AR	Qualigens
14	H_2O_2	LR	Merck
15	DMF	LR	Merck
16	8-hydroxyquinoline	AR	Glaxo

2.2 Preparation of Ligands

All ligands used here were prepared following the literature procedures [47].

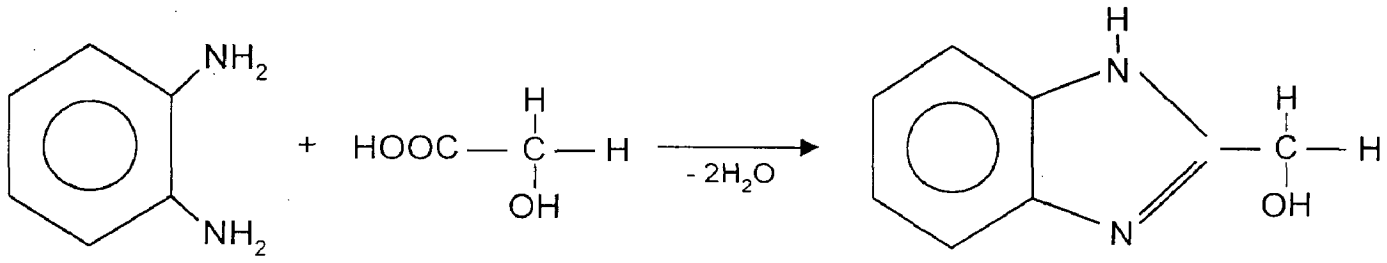
(I) **Preparation of 2-(α-hydroxymethyl) benzimidazole** :

o-phenylenediamine (2.16 g, 20 m mol) and glycolic acid (2.28 g, 30 m mol) were mixed together in 20 ml of 4 N HCl. The reaction mixture was heated at reflux in heating mantle for about 20 h and cooled to room temperature. After neutralization of this

solution with 1:1 ammonium hydroxide, the reaction flask was kept in refrigerator for 2 h. The precipitated brownish solid was filtered, washed with cold water and dried on a water bath. The powdery mass was transferred into flask, treated with charcoal in ethanol and refluxed for 1h. The filtered solution was evaporated to ~ 10 ml, introduced 10 ml of water and kept in refrigerator for over night. The white solid precipitated was filtered and dried on a water bath.

Yield : 1.26 g (28%). M. pt : 171°C

Reaction :

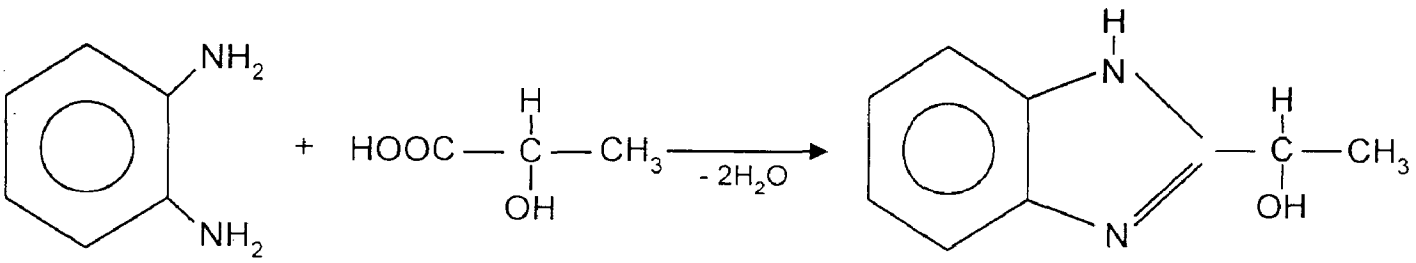


(II) Preparation of 2-(α-hydroxyethyl) benzimidazole :

This ligand was prepared using *o*-phenylenediamine (2.16 g, 20 m mol) and lactic acid (2.70 g, 30 m mol) in 20 ml of 4 N HCl and following the above procedure.

Yield : 1.37 g (28%). M. pt. : 178°C

Reaction :

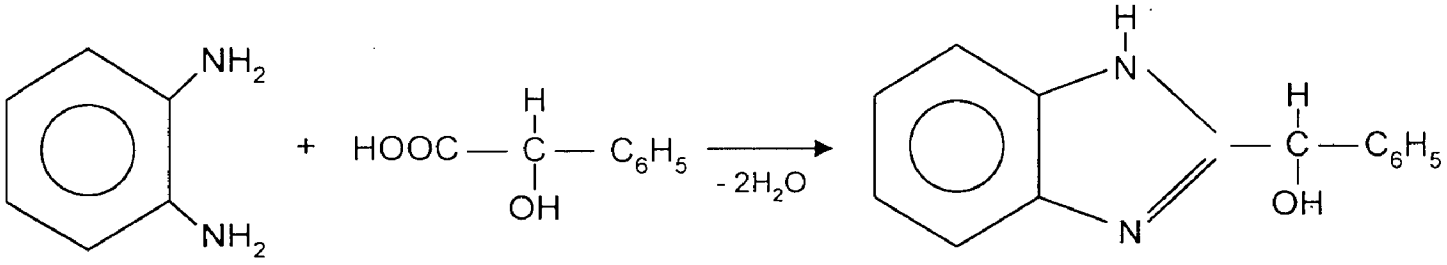


(III) Preparation of 2-(α-hydroxybenzyl) benzimidazole:

Mandelic acid (4.56 g, 30 m mol) and *o*-phenylenediamine (2.16g, 20 m mol) were dissolved in 20 ml of 4 N HCl and heated to ~ 100°C for 25 h. After cooling to ambient temperature, the reaction mixture was neutralized with 1:1 ammonium hydroxide while cooling the flask in an ice bath. The obtained semi solid mass was filtered, washed with water and dried on a water bath in watch glass where it slowly solidified. This was recrystalized from ethanol after charcoal treatment.

Yield : 2.37 g (35%). M. pt. : 205°C

Reaction :



Preparation of Complexes

(I) Preparation of $K[VO(O_2)(HMBMZ)_2].2H_2O$:

V_2O_5 (0.20 g, 1 m mol) was dissolved in 5 ml of aqueous solution of KOH (0.14g, 2.5 m mol) with stirring and filtered. The colourless clear solution was cooled in ice and hydrogen peroxide (30%, 1 ml) was added with stirring. 2-(α-hydroxymethyl) benzimidazole (0.59 g, 4 m mol) dissolved in water (15 ml) was then added dropwise with constant stirring. pH of the reaction mixture was adjusted to 4.5 with dil HCl. After 2h stirring was discontinued and flask was kept in refrigerator for overnight. The separated brown solid was filtered, washed with water : ethanol (1:2 v/v) and dried in vacuo. Finally compound was purified by suspending in ethanol and stirring.

(II) Preparation of $K[VO(O_2)(HEBMZ)_2].4H_2O$:

A colourless solution of potassium vanadate(V) was prepared by dissolving V_2O_5 (0.20 g, 1 m mol) in an aqueous solution (5 ml) of KOH (0.14 g, 2.5 m mol) and stirring at ambient temperature for 1 h. This was cooled after filtering and H_2O_2 (30%, 1 ml) was added dropwise with stirring. To this an aqueous solution (20 ml) of 2-(α-hydroxyethyl) benzimidazole (0.65 g, 4 m mol) was added with stirring. After 4 h of stirring (pH ~ 5) the separated orange brown solid was filtered, washed with water and dried in vacuo.

(III) Preparation of $[MoO(O_2)(HEBMZ)_2]$:

MoO_3 (0.30 g, 2 m mol) was stirred in H_2O_2 (30%, 25 ml) and filtered. To the filtrate an ethanolic solution (15 ml) of 2-(α-hydroxyethyl)benzimidazole (0.65 g, 4 m mol) was added with stirring. The reaction mixture was then cooled in an ice bath for

3 h while stirring and thereafter left in refrigerator for overnight. After reducing solvent under reduced pressure to ~ 5 ml and cooling yielded cream coloured solid, which was filtered, washed with cold ethanol. The crude mass was dissolved in minimum amount of ethanol, filtered and kept in refrigerator for few days where light orange crystals, separated out. It was filtered, and dried in vacuo at ambient temperature.

(IV) Preparation of $[WO(O_2)(HEBMZ)_2]$:

The cream coloured complex was prepared in the same way as employed for $[MoO(O_2)(HEBMZ)_2]$ using WO_3, H_2O_2 and 2-(α-hydroxyethyl)benzimidazole. Recrystallisation from ethanol was also carried out using above procedure.

(V) Preparation of $[MoO_2L_2]$ and $[WO_2L_2]$ [L^- = HMBMZ, HEBMZ and HBBMZ). A General Method :

$[MoO_2(acac)_2]$ (0.33g, 1 mmol) or $[WO_2(acac)_2]$ (0.44g, 1 mmol) was added as a solid in one portion to a well stirred hot solution of appropriate ligand (2 mmol) in methanol (20 ml). The resulting solution was refluxed on a water bath for 6h. The separated white solid was filtered, washed with methanol and dried in vacuo at room temperature.

2.3 Measurements and Analyses

Measurements

IR Spectra were recorded as Nujol mull on a Shimadzu Model 8201-PC FT-IR Spectrophotometer. Electronic spectra were run in DMF on a Beckman DU-6 spectrophotometer and UV-1601PC, UV-Visible spectrophotometer in the 250 to 750 nm range. The thermogravimetric analyses were conducted by the University Sophisticated Instrumentation Centre (USIC) of this University. All measurements were carried out in static air atmosphere using Al_2O_3 as reference. The temperature increment was adjusted to 10°C/min.

Analyses

Elemental analyses of the complexes were carried out by either microanalytical section of the National Chemical Laboratory, Pune or Department of Chemistry, University of Pune, Pune.

Molybdenum and tungsten were determined gravimetrically as dioxobis (8-quinolinolato)molybdenum(VI) and dioxobis(8-quinolinolato)tungsten(VI), respectively, after decomposing the complexes with conc. HNO_3 and H_2SO_4. % of molybdenum and tungsten was computed using the following formula :

(1) $$\% \text{ of Mo} = \frac{\text{C.F.} \times \text{Wt. of oxime ppt} \times 100}{\text{Wt. of complex taken}}$$

where C. F. is a chemical factor $= \dfrac{\text{Atomic weight of Mo}}{\text{Mol. Wt. of } [MoO_2(8.HQ)_2]}$

(2) $$\% \text{ of W} = \frac{\text{C.F.} \times \text{Wt. of oxime ppt} \times 100}{\text{Wt. of complex taken}}$$

where C. F. $= \dfrac{\text{Atomic weight of W}}{\text{Mol. Wt. of } [MoO_2(8.HQ)_2]}$

Vanadium was estimated from the residue (in the form of KVO_3) obtained in thermogravimetric analysis of respective compound.

RESULTS & DISCUSSION

3. RESULTS AND DISCUSSION

3.1 Analytical and Physico-chemical Studies

3.1.1 Peroxo Complexes

A colourless solution of potassium vanadate(V) prepared by dissolving V_2O_5 in an aqueous solution of KOH reacts with an excess of 30% H_2O_2 to generate *in situ* a non-isolable species $K[VO(O_2)_2.x\ H_2O]$. In presence of monobasic bidentate ligands, HMBMZ and HEBMZ, this species can be stabilised in the pH range ~ 4.5 to 5.5 to give isolable coloured solid complexes having compositions $K[VO(O_2)(HMBMZ)_2].2\ H_2O$ and $K[VO(O_2)(HEBMZ)_2].4\ H_2O$ respectively. These crystalline compounds are insoluble in most organic solvents, slightly soluble in DMF and remarkably stable. Both the complexes have water molecules associated with them. We were unable to prepare such peroxovanadium (V) complexes of HBBMZ due to its insolubility in water causing precipitation of ligand during preparation.

The similar non isolable peroxomolybdenum(VI) or peroxotungsten(VI) species [as peroxovanadium(V)] prepared by the reaction of MoO_3 or $WO_3.H_2O$, respectively, with an excess of 30% H_2O_2 readily react with an aloholic solution of HEBMZ to give the corresponding peroxo complexes. These complexes on crystallisation from ethanol shows the general formula $[MO(O_2)(HEBMZ)_2]$ (where M = Mo or W). These air stable complexes are crystalline in nature, light yellow in colour and soluble in methanol, ethanol, pyridine, DMF and DMSO.

3.1.2 Dioxo Complexes

Reaction of $[MO_2(acac)_2]$ (where M = Mo or W, acacH = acetyl acetone) with 2 equivalents of ligands in methanol leads to the formation of dioxomolybdenum(VI) or dioxotungsten(VI) complexes of the type $[MO_2\ L_2]$ (where LH = ligand). The reaction can be represented as shown below.

$$[MO_2(acac)_2] + 2LH \xrightarrow{MeOH} [MO_2L_2] + 2acacH$$

These colourless complexes have high decomposition temperature, insoluble in methanol and ethanol and soluble in DMF and DMSO.

The analytical and physicochemical data of the peroxo and dioxo complexes are presented in Tables 1 and 2.

3.2 Thermal Study

The TG curve for the solid phase thermal decomposition of the complexes in static air are given in Appendix. The dynamic TGA data with the % weight loss at different steps and their probable assignments are summarized in Table 3.

3.2.1 Peroxo Complexes :

The loss of two water molecules in $K[VO(O_2)(HMBMZ)_2].2H_2O$ and four molecules in $K[VO(O_2)(HEBMZ)_2].4\ H_2O$ in the temperature range 50-135°C clearly indicate that water is not coordinated in these complexes and present as lattice water. Further increment of temperature causes the breaking of the peroxo group with probable loss of one of the peroxo oxygen. The residue obtained at this stage may thus be considered as $K[VO_2(HMBMZ)_2]$ and $K[VO_2(HEBMZ)_2]$

$$2\ K[VO(O_2)L_2] \longrightarrow 2\ K\ [VO_2L_2] + O_2$$

(where LH = ligand)

However, very poor thermal stability of these species did not allow us to isolate such an intermediate. Such intermediate complexes have been isolated and characterised in case of molybdenum and tungsten peroxo complexes. The third step of the thermograms indicate the continuous decomposition of ligands until the formation of oxide, KVO_3 as the end product. The % weight loss of the residue obtained matches well with the theoretical value. It seems that the required oxygen to form oxide at the end is coming from one of the coordinated ligands as the observed % weight loss in step third correspond to the theoretical value calculated considering the above fact (Table 3).

Peroxo complexes of molybdenum and tungsten do not show any weight loss upto 160° and 180°C respectively. The loss of one of the peroxo oxygen and probable dioxo species formation occurs in first step. The second step of thermogram indicates the

Table 1 : Analytical and physicochemical data of peroxo complexes

*Compound/Stoichiometry**	*Colour*	*Yield (%)*	*Decomp. Temp. (°C)*	*Found (calcd) %*			
				C	*H*	*N*	*Metal*
$K[VO(O_2)(HMBMZ)_2].2H_2O$	Yellowish	69	145	41.32	3.53	11.48	18.76
$C_{16}H_{18}N_4O_7KV$	Brown			(41.03)	(3.85)	(11.97)	(19.23)
$K[VO(O_2)(HEBMZ)_2].4H_2O$	Yellowish	62	135	40.26	4.52	10.43	16.58
$C_{18}H_{26}N_4O_9KV$	Brown			(40.60)	(4.89)	(10.53)	(16.92)
$[MoO(O_2)(HEBMZ)_2]$	Cream	40	185	46.27	3.67	12.25	20.84
$C_{18}H_{18}N_4O_5Mo$				(46.35)	(3.86)	(12.02)	(20.60)
$[WO(O_2)(HEBMZ)_2]$	Cream	38	160	39.15	3.36	10.15	32.98
$C_{18}H_{18}N_4O_5W$				(39.00)	(3.37)	(10.11)	(33.19)

* Abbreviations as under Table 2.

Table 2 : Analytical and physicochemical data of dioxo complexes

*Compound/Stoichiometry**	*Colour*	*Yield (%)*	*Decomp. Temp. (^oC)*	*Found (Calcd) %*			
				C	*H*	*N*	*Metal*
$[MoO_2(HMBMZ)_2]$ $C_{16}H_{14}N_4O_4Mo$	White	71	133	45.47 (45.50)	3.35 (3.32)	13.14 (13.27)	22.89 (22.74)
$[WO_2(HMBMZ)_2]$ $C_{16}H_{14}N_4O_4W$	Cream	62	140	37.43 (37.66)	2.79 (2.75)	10.90 (10.98)	36.35 (36.06)
$[MoO_2(HEBMZ)_2].2H_2O$ $C_{18}H_{22}N_4O_6Mo$	White	69	192	44.23 (44.45)	4.45 (4.53)	11.58 (11.52)	19.43 (19.74)
$[WO_2(HEBMZ)_2]$ $C_{18}H_{18}N_4O_4W$	Cream	41	180	40.02 (40.16)	3.15 (3.35)	10.19 (10.41)	33.98 (34.18)
$[MoO_2(HBBMZ)_2]$ $C_{28}H_{22}N_4O_4Mo$	White	48	130	58.67 (58.54)	3.80 (3.83)	9.53 (9.76)	16.53 (16.72)
$[WO_2(HBBMZ)_2]$ $C_{28}H_{22}N_4O_4W$	Cream	40	120	50.49 (50.77)	3.39 (3.32)	8.27 (8.46)	27.89 (27.78)

* **Abbreviations :**

HMBMZ = 2-(α-hydroxylmethyl) benzimidazole monoanion

HEBMZ = 2-(α-hydroxyethyl) benzimidazole monoanion

HBBMZ = 2-(α-hydroxybenzyl) benzimidazole monoanion

probable loss of two methyl groups from two ligands followed by complete decomposition of ligands untill the formation of respective metal trioxide, MoO_3. The loss of such methyl group as a distinct step in $K[VO(O_2)(HEBMZ)_2]$ could not be located due to continuous weight loss during thermolysis at this stage.

$$2\ [MO(O_2)L_2] \longrightarrow 2\ [MO_2L_2] + O_2$$

(where M = Mo or W)

3.2.2 Dioxo Complexes :

The decomposition pattern of dioxo complexes of molybdenum and tungsten with ligand HEBMZ and HBBMZ are interesting as these follow the loss of two methyl or two phenyl groups, respectively in their first step of thermolysis except in the complex $[MoO_2(HEBMZ)_2].2H_2O$ which accompanied the loss of two water molecules also alongwith two methyl groups. The loss of water at higher temperature than the expected for the lattice water may be due to hydrogen bonding between oxygen of the molecule and imino hydrogen. Loss of methyl or phenyl group is expected to abstract one hydrogen each to release as methane or benzene gas. The readily available hydrogen for such purpose would be the hydrogen on –NH group. If one considers such possibility then negative charge produced after removal of proton would force the ligand to undergo rearrangement. Such rearrangement would result the migration of negative charge on the tertiery nitrogen causing its mononegative behaviour and leaving alcoholic oxygen to behave as aldehydic. Due to aldehydic behaviour of oxygen, stability of the resulting dioxo species would be rather poor than the dioxo species before loosing methyl or benzyl groups. In fact, this assumption is true as thermograms show the loss of another group immediately after loosing R group on further increment of temperature.

Rest thermograms are very similar to that observed in peroxo complexes after second step, i.e. removal of one oxygen and two methyl groups, thus the whole process of decomposition at various stages in peroxo and the corresponding dioxo complexes of molybdenum and tungsten may be summarised as follows (scheme 7).

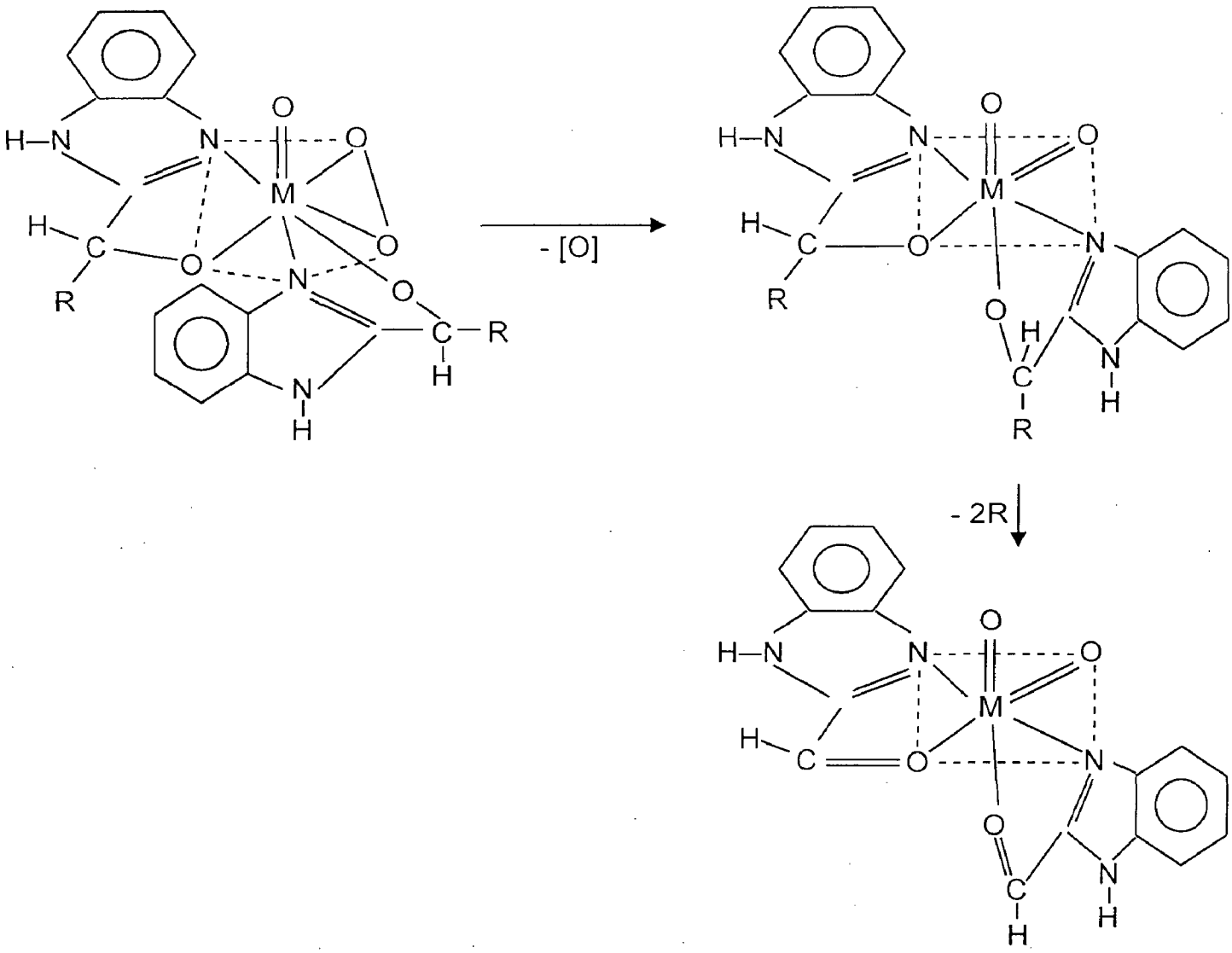
$[MoO_2(HMBMZ)_2]$ is stable upto 250°C and then decomposition of ligand starts and continues until the formation of MoO_3 at 520°C. The loss of various group(s) with their respective temperature range are presented in Tables 3 and 4.

Table 3 : Thermogravimetric data of peroxocomplexes

Complex	*Temp. Range*	*Observed % wt. loss*	*Calculated % wt. loss*	*Expected loss of group*	*Expected residue*
$K[VO(O_2)(HMBMZ)_2].2H_2O$	51-130	7.8	7.7	$2H_2O$	$K[VO(O_2)(HMBMZ)_2]$
$C_{16}H_{18}N_4O_7KV$	145-200	3.6	3.4	O-from peroxo	$K[VO_2(HMBMZ)_2]$
	200-530	60.0	59.4	2 ligand-1 oxygen	KVO_3
$K[VO(O_2)(HEBMZ)_2].4H_2O$	18-135	12.9	13.5	$4.H_2O$	$K[VO(O_2)(HEBMZ)_2]$
$C_{16}H_{26}N_4O_9KV$	135-190	2.9	3.0	O-from peroxo	$K[VO_2(HEBMZ)_2]$
	205-760	57.3	57.5	2 ligand-1 oxygen	KVO_3
$[MoO(O_2)(HEBMZ)_2]$	185-205	4.0	3.4	O-from peroxo	$[MoO_2(HEBMZ)_2]$
$C_{18}H_{18}N_4O_5Mo$	205-226	6.0	6.4	2 CH_3 group	$[MoO_2(HEBMZ)_2]$-2.CH_3
	226-590	60.0	59.3	2 ligand - 1 oxygen - 2 CH_3	MoO_3
$[WO(O_2)(HEBMZ)_2]$	160-215	3.0	2.9	O-from peroxo	$[WO_2(HEBMZ)_2]$
$C_{18}H_{18}N_4O_5W$	225-255	5.2	5.4	2 CH_3 group	$[WO_2(HEBMZ)]$-2CH_3
	255-610	50.8	49.8	2 ligand-1oxygen - 2 CH_3	WO_3

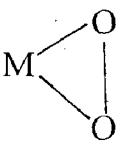
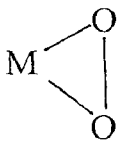
Table 4 : Thermogravimetric data of dioxocomplexes

Complex	*Temp. range (°C)*	*Observed loss %*	*Calculated loss %*	*Expected loss of group*	*Expected residue*
$[MoO_2(HMBMZ)_2]$	250-520	66.0	66.0	2 ligand – 1 oxygen	MoO_3
$C_{16}H_{14}N_4O_4Mo$					
$[MoO_2(HEBMZ)_2].2H_2O$	190-226	14.0	13.6	$2.H_2O + 2\ CH_3$ group	$[MoO_2(HEBMZ)_2]-2\ CH_3$
$C_{18}H_{22}N_4O_6Mo$	226-540	57.0	56.8	2 ligand $-2\ CH_3$ - 1 oxygen	MoO_3
$[WO_2(HEBMZ)_2]$	180-250	6.0	5.6	$2\ CH_3$ group	$[WO_2(HEBMZ)_2] - 2\ CH_3$
$C_{18}H_{18}N_4O_4W$	250-620	51.0	51.3	2 ligand $- 2\ CH_3 -$ 1 oxygen	WO_3
$[MoO_2(HBBMZ)_2]$	181-341	27.0	26.8	$2\ C_6H_5$ group	$[MoO_2(HBBMZ)_2]$-2 C_6H_6
$C_{28}H_{22}N_4O_4Mo$	341-654	48.0	48.3	2 ligand $- 2\ C_6H_5 -$ 1 oxygen	MoO_3
$[WO_2(HBBMZ)_2]$	120-250	23.0	23.3	$2\ C_6H_5$ group	$[WO_2(HBBMZ)_2]$-2 C_6H_6
$C_{28}H_{22}N_4O_4W$	250-320				
	320-620	41.0	41.7	2 ligand $- 2\ C_6H_5 -$ 1 oxygen	WO_3



Scheme 7

3.3 IR Spectral Studies

A partial listing of the IR spectra of the complexes is given in Table 5. The IR spectra of the peroxo complexes show three vibrational modes at 862-872 cm^{-1} (at 901-908 in vanadium complexes), 752-760 cm^{-1} and 582-628 cm^{-1} which are assigned to the O-O intra-stretching (ν_1) mode, the antisymmetric  stretch (ν_3) and the symmetric  stretch (ν_2), respectively (86). These bands confirm the η^2 –coordination of the peroxo group. An additional sharp band which appears at 908-962 cm^{-1} is diagnostic of ν (M = O) bond. Thus IR spectra confirm the presence of [$MO(O_2)$] moiety in these complexes.

The IR spectra of the $[MO_2]^{2+}$ complexes are dominated by the presence of two sharp bands ~ 900 cm^{-1} region due to ν_{sym} (O=M=O) and ν_{asym}(O=M=O) modes; the range for ν_{sym} (O=M=O) and ν_{asym} (O=M=O) being 850-915 cm^{-1} and 870-950 cm^{-1}, respectively (87).

The NH stretching band of the ligands occurs at 2630-3325 cm^{-1} as a broad band which indicate the presence of strong inter-molecular hydrogen bonding possibly between hydrogen of the NH group and oxygen of the alcohol (88). O'Sullivan and Wallis (88) have shown that only substitution of α-hydrogen by bulky group such as methyl or phenyl can either prevent such hydrogen bonding or make such bonding extremely weak. The additional broad band at ~3400 cm^{-1} indicate the presence of free hydroxyl group in the ligand. The broad band due to hydroxyl group disappears in the complexes indicating the deprotonation of hydroxyl group followed by coordination of the oxygen to the metal. However in the peroxo complexes of vanadium and $[MoO_2(HEBMZ)_2].2H_2O$, such a broad band which is still present may be due to lattice water associated with them. The –NH stretching band usually sharpens in the complexes and concentrates around 3300 cm^{-1}, suggests the breaking of hydrogen bond and thus its existence as free NH. However, hydrated complexes still shows such broad band which may be due to the involvement of NH group in hydrogen bonding with lattice water. This is supported by the fact that removal of lattice water in these complexes requires relatively higher temperature as indicated by their thermograms.

The non-involvement of N_1 in bonding is further supported by the unperturbed NH bending vibration of the ligands which appears at ~1450 cm^{-1} (89). The bonding of N_2 (i.e. ring nitrogen) with metal ion is confirmed as a sharp band owing to ν (C=N) ring vibration appears at ~1600 cm^{-1}. Such ν (C=N) vibration in free ligands appears as a weak band at relatively higher position (89). However in some cases this band is seen either at lower position or at the same position as in complexes but always as a weak band. Thus, these ligands behaves as mono basic ON bidentate chelate.

3.4 Electronic Spectra

Table 7 presents the electronic spectral data of the ligands and complexes. The UV-visible spectra of all the ligands exhibit two intense bands at nearly the same

positions, 276 nm and 283 nm. The high molar absorptivity (2970-3450 $lmol^{-1}$ cm^{-1}) of these bands assigns these to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$transitions, respectively. In the peroxo complexes these bands appear at nearly the same positions.

A poorly resolved broad absorption of much smaller intensity between 420-425 nm also appears in peroxovanadium(V) complexes which can be assigned to the peroxo-metal charge-transfer (LMCT) bands [64]. However, such LMCT band in peroxomolybdenum(VI) and tungsten(VI) seems to be appearing ~ 360 nm and 310 nm, respectively, with very poor resolution. In dioxo molybdenum(VI) and dioxotungsten(VI) complexes, the band due to ligand to metal charge transfer between the highest occupied ligand molecular orbital to the lowest empty d-orbital of the metal, could not be located due to low molar absorptivity of the spectra in the expected region of 400-500 nm. The optical density values in all the complexes are extremely low in the lower energy region (500-750 nm) and there was no evidence of any d-d transition. This is consistent with the presence of a d^0 system.

Table 5 : IR spectral data (in cm^{-1}) of peroxo complexes

Compound	ν (NH)	ν(C=N),(C=C)	ν (O-O)	ν_{asym} M(O)(O)	ν_{sym} M(O)(O)	ν (M=O)
$K[VO(O_2)(HMBMZ)_2].2H_2O$	3200	1622, 1595	908	760	615	924
$K[VO(O_2)(HEBMZ)_2].4H_2O$	3150	1620, 1601	901	752	628	928
$[MoO(O_2)(HEBMZ)_2]$	3200	1628, 1593	862	752	582	962
$[WO(O_2)(HEBMZ)_2]$	3384	1622, 1596	872	756	594	908

Table 6 : IR spectral data (in cm^{-1}) of dioxo complexes

Compound	ν (NH)	ν(C=N),(C=C)	ν_{asym}(O=M=O)	ν_{sym}(O=M=O)
HMBMZ	2656-3260	1620, 1589		
$[MoO_2(HMBMZ)_2]$	3325	1622, 1593	916	878
$[WO_2(HMBMZ)_2]$	3200	1624, 1595	920	880
HEBMZ	2554-3200	1622, 1591		
$[MoO_2(HEBMZ)_2].2H_2O$	2630-3340	1622, 1595	926	893
$[WO_2(HEBMZ)_2]$	3300	1597	908	870
HBBMZ	2640-3230	1622, 1591		
$[MoO_2(HBBMZ)_2]$	3100	1634, 1599	926	910
$[WO_2(HBBMZ)_2]$	300	1634, 1598	941	912

Table 7 : Electronic spectral data (in nm) of ligands and complexes.

Compounds	λ_{max}[a]
HMBMZ	276 (3354), 283(3100)
HEBMZ	276(3454), 283(3252)
HBBMZ	278(3182), 284(2970)
$K[VO(O_2)(HMBMZ)_2]$	279, 283, 420
$K[VO(O_2)(HEBMZ)_2]$	276, 279, 425
$[MoO(O_2)(HEBMZ)_2]$	278, 283, 360
$[WO(O_2)(HEBMZ)_2]$	275, 283, 310
$[MoO_2(HMBMZ)_2]$	276, 283
$[MoO_2(HEBMZ)_2]$	276, 281
$[WO_2(HEBMZ)_2]$	278, 288
$[MoO_2(HBBMZ)_2]$	276, 284
$[WO_2(HBBMZ)_2]$	276, 285

a) Figures in the paranthesis indicate molar extinction coefficient values in litre mol^{-1} cm^{-1}.

CONCLUSION

4. CONCLUSIONS

From the physico-chemical and spectral evidences discussed above peroxo complexes are proposed to be pentagonal bipyramidal while dioxo complexes to be octahedral. As such complexes are reported to have potential applications in the field of catalyst, the complexes reported here may be tested for their catalytic activity.

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5. REFERENCES

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APPENDIX

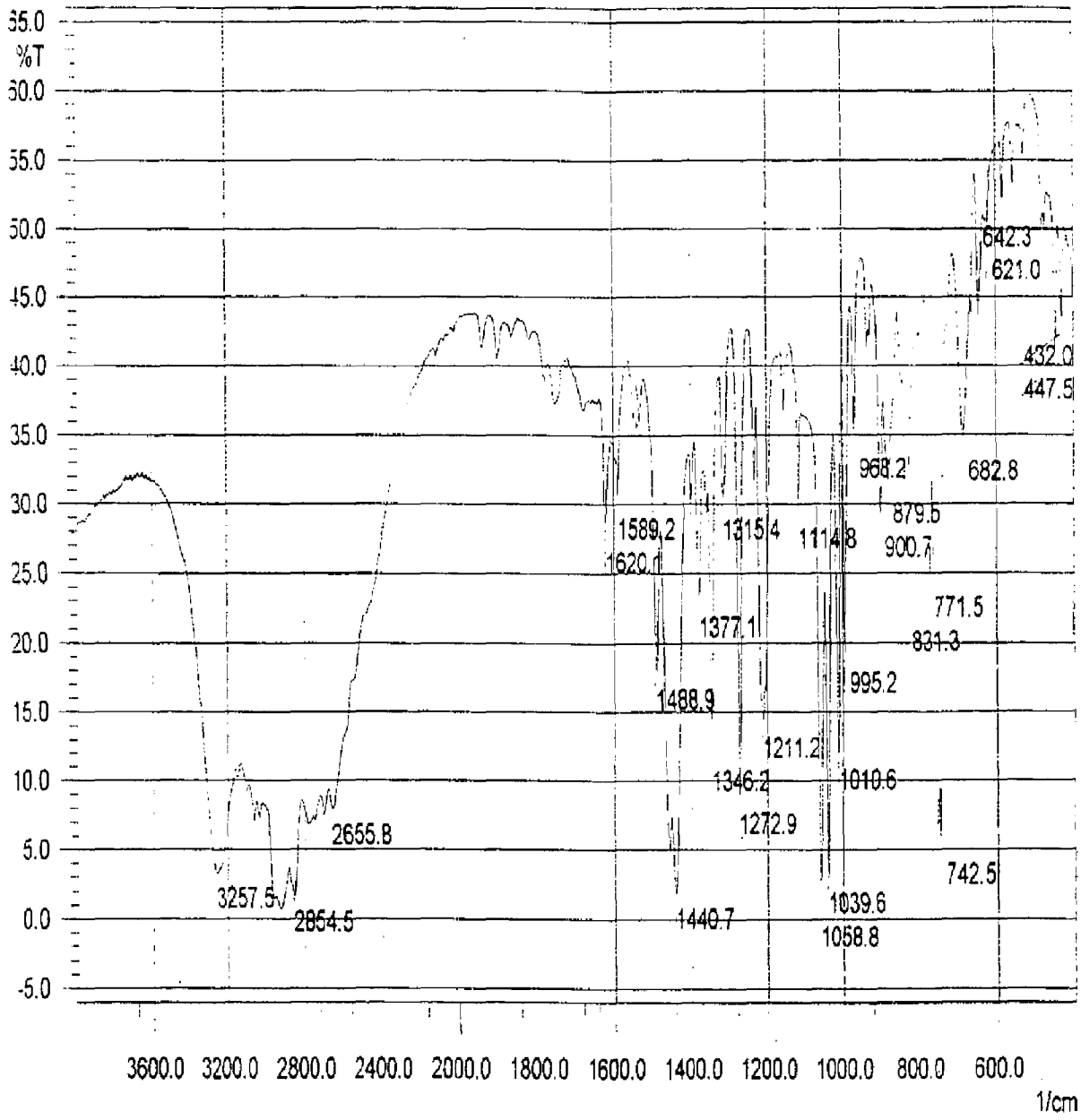

Fig. 8 : IR Spectrum of HMBMZ

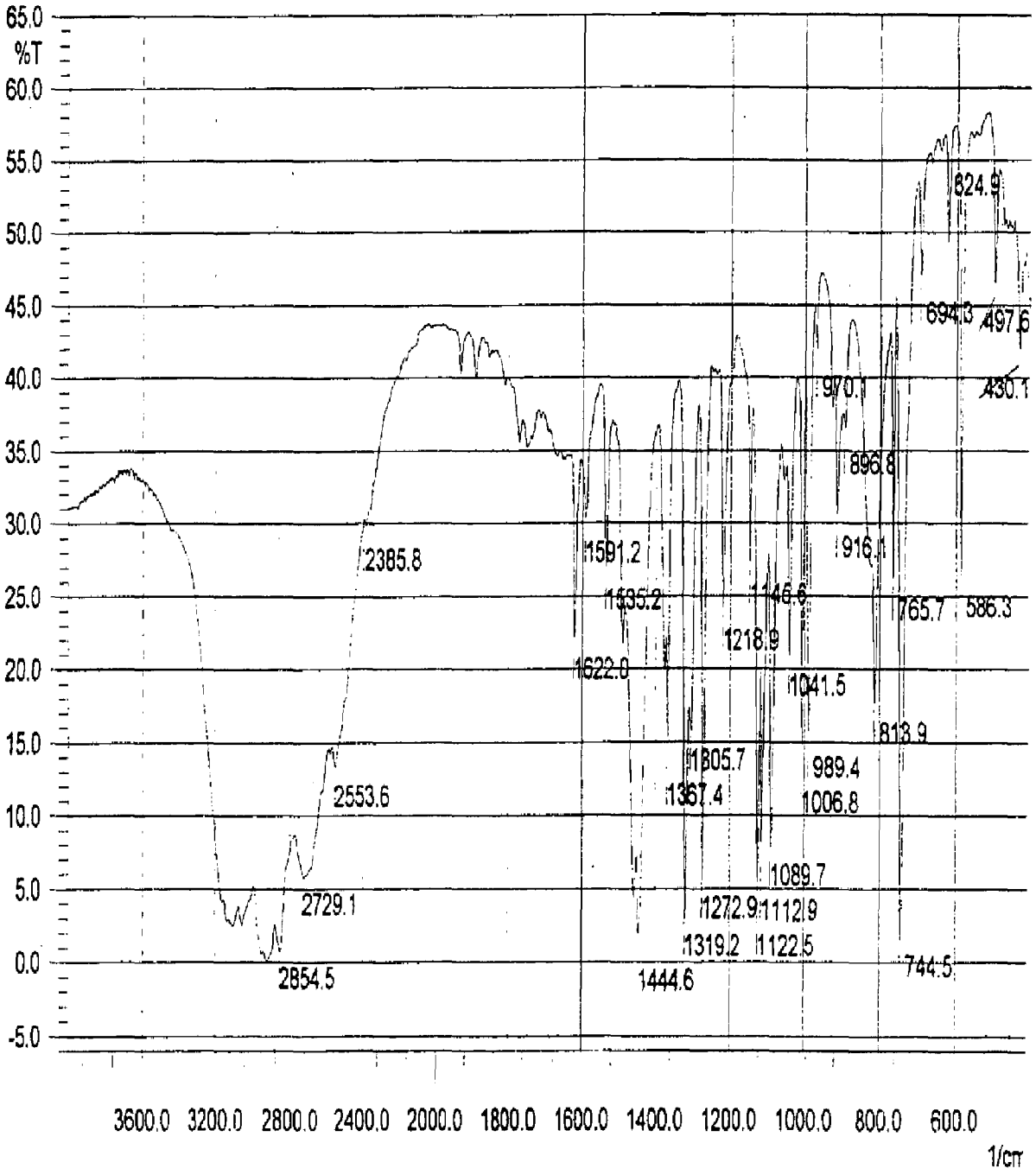

Fig. 9 : IR Spectrum of HEBMZ

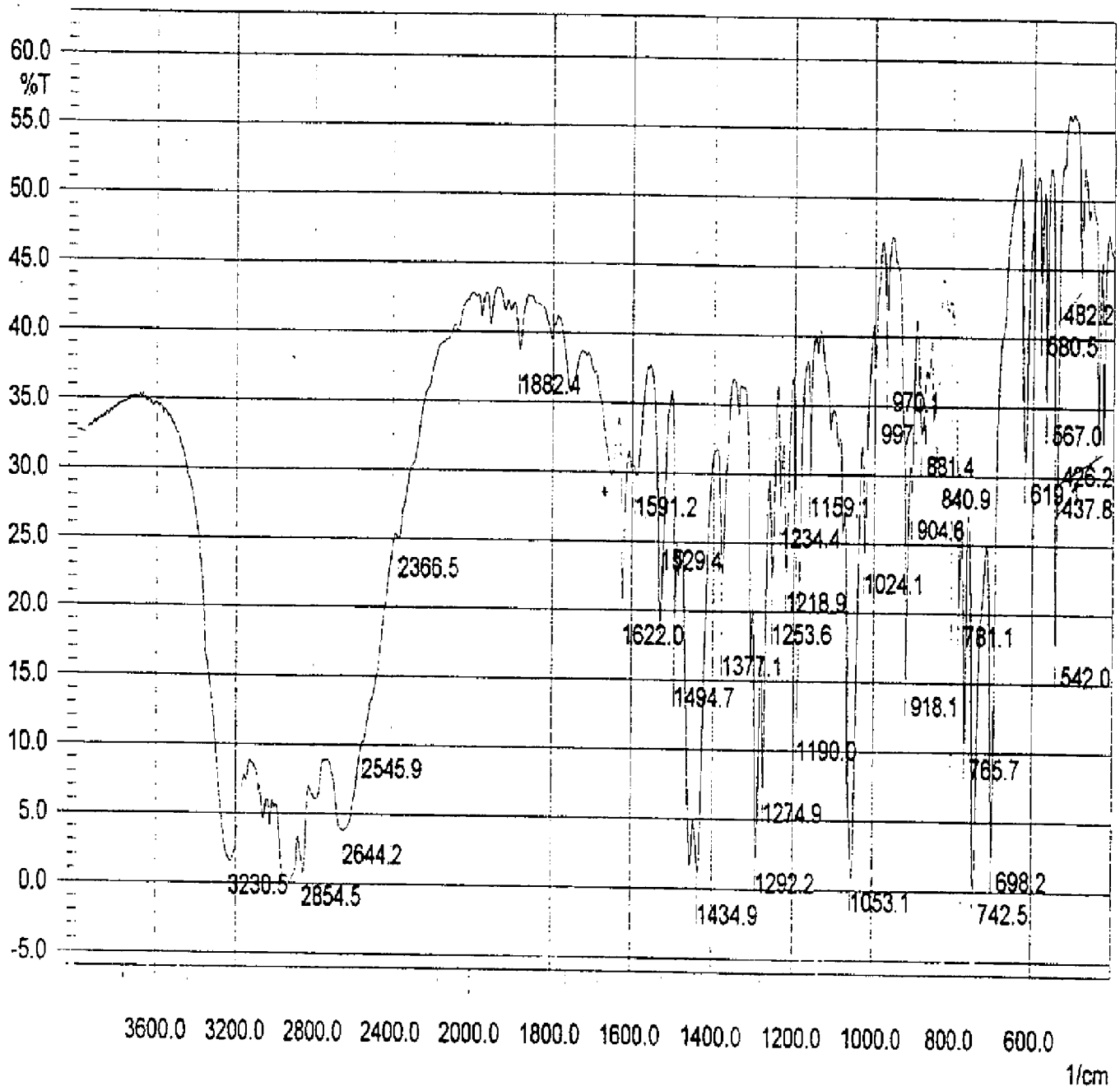

Fig. 10 : IR Spectrum of HBBMZ

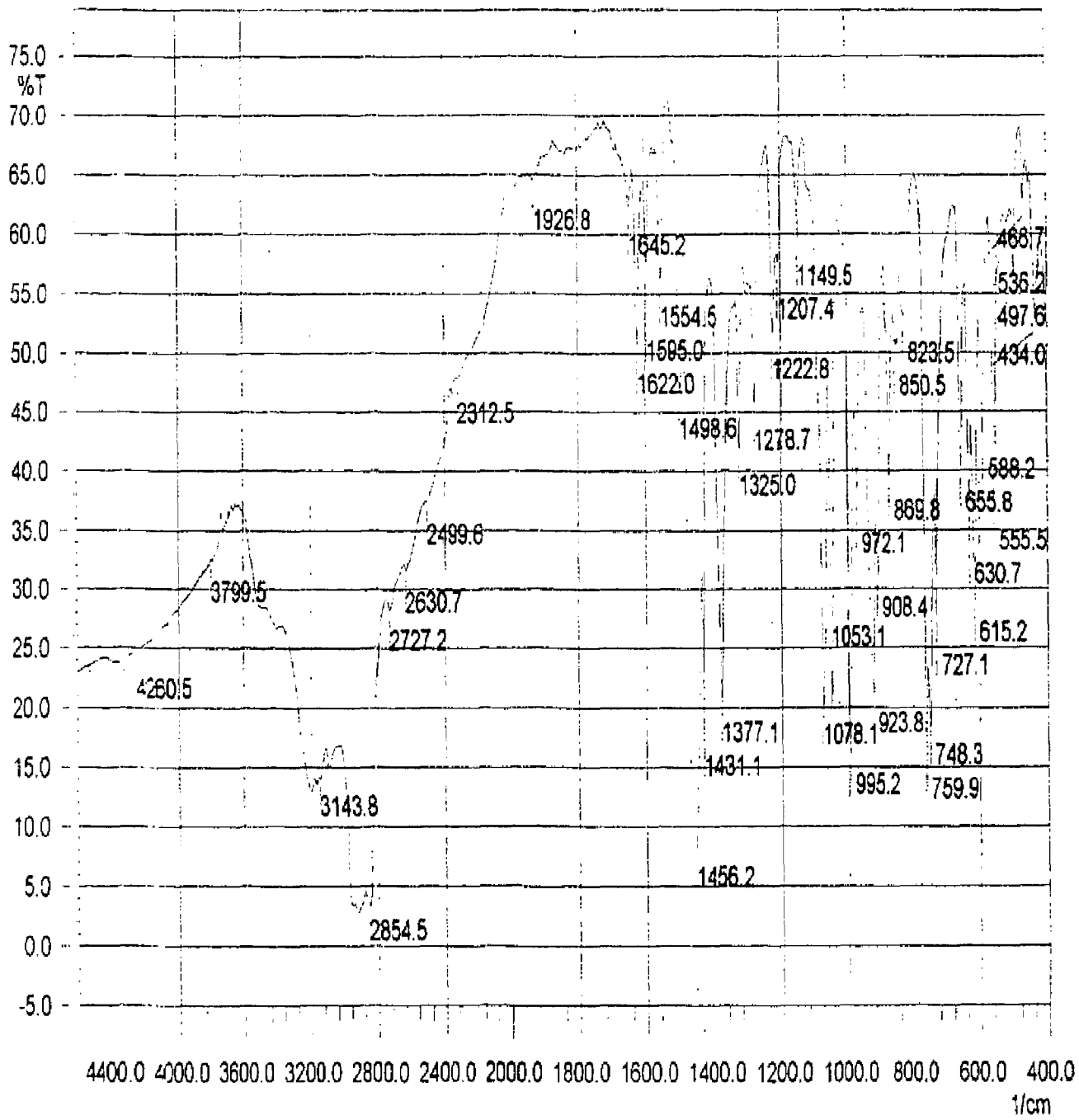

Fig. 11 : IR Spectrum of $K[VO(O_2)(HMBMZ)_2]$

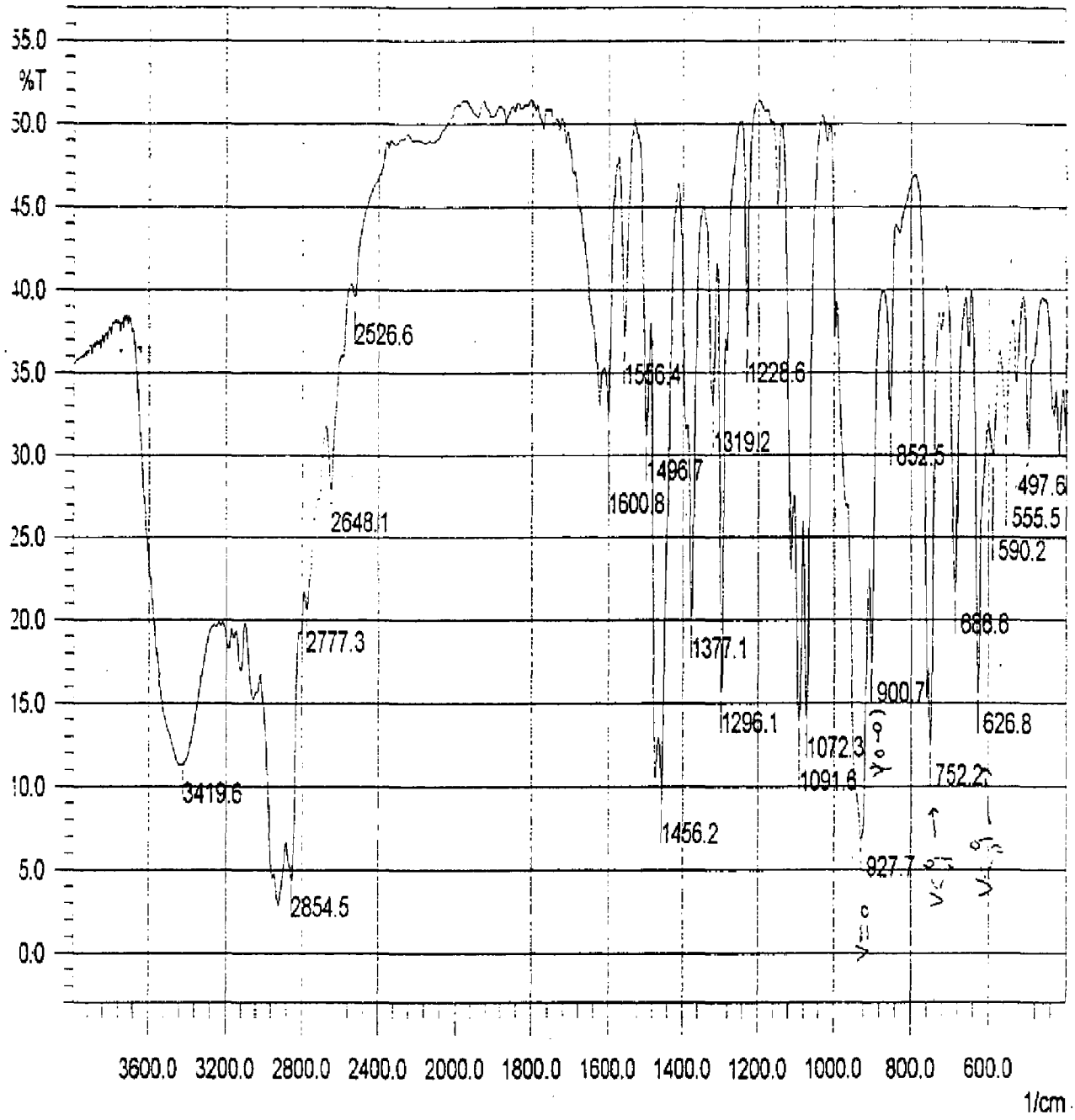

Fig. 12 : IR Spectrum of $K[VO(O_2)(HEBMZ)_2]$

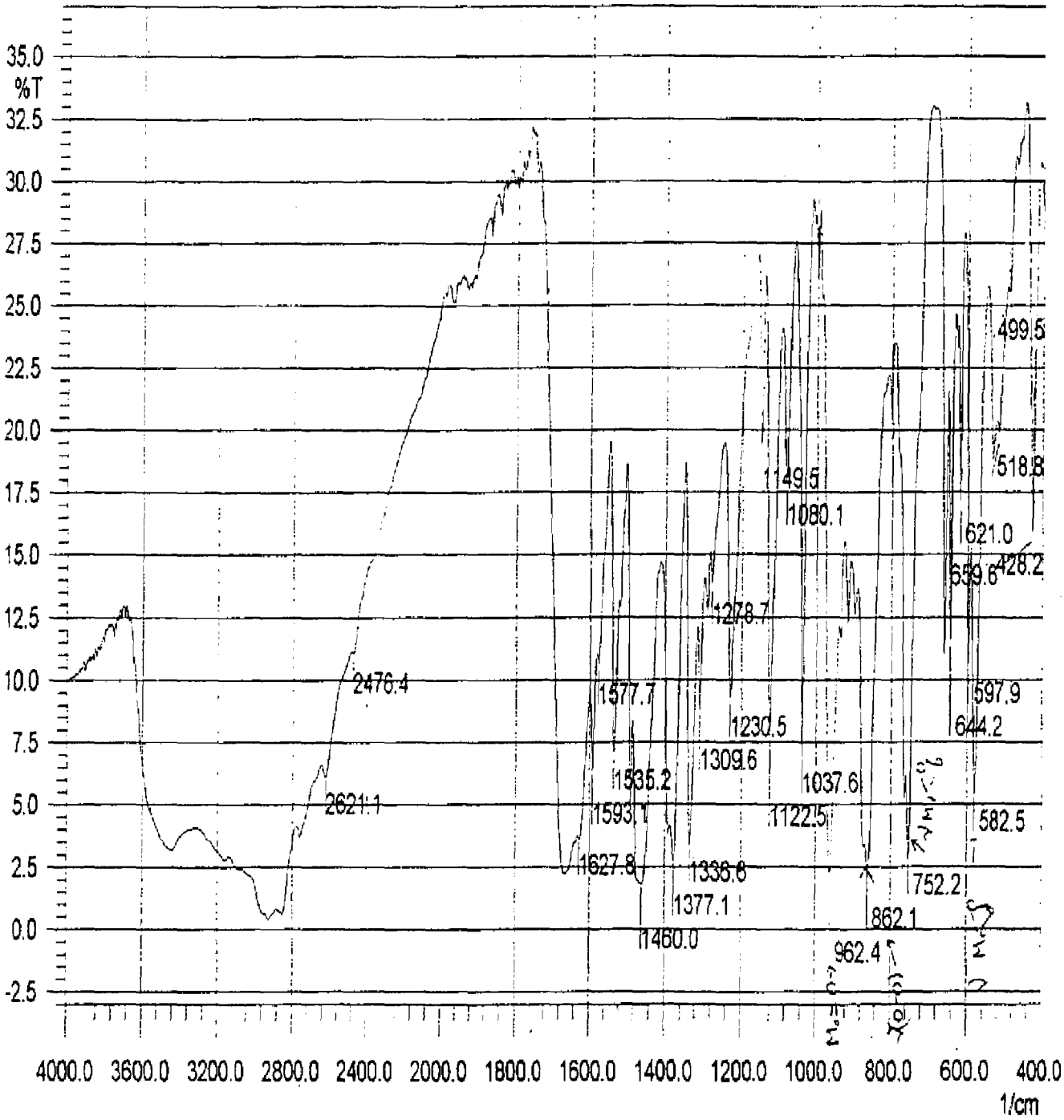

Fig. 13 : IR Spectrum of $[MoO(O_2)(HEBMZ)_2]$

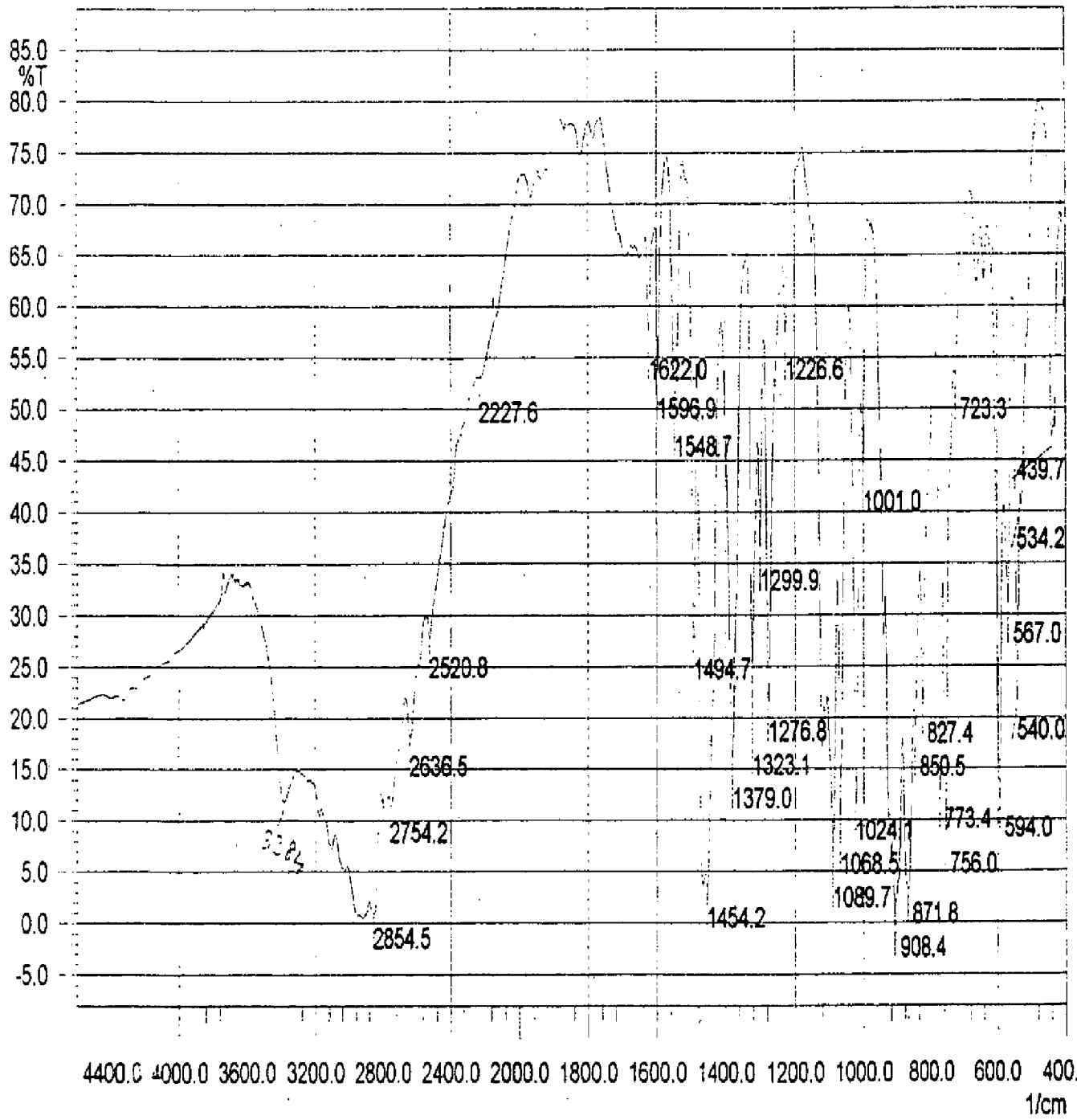

Fig. 14 : IR Spectrum of $[WO(O_2)(HEBMZ)_2]$

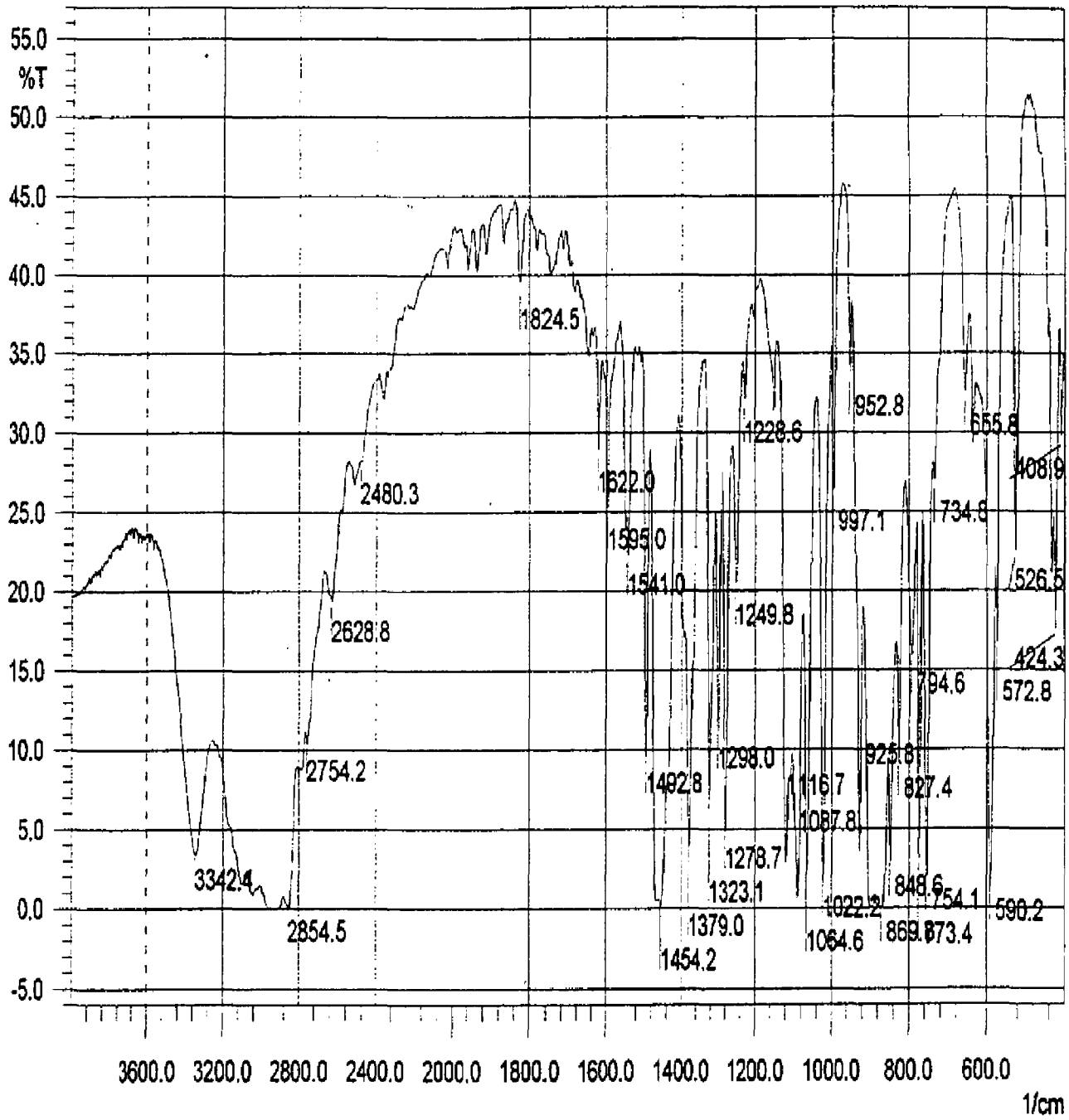

Fig. 16 : IR Spectrum of $[MoO_2(HEBMZ)_2]$

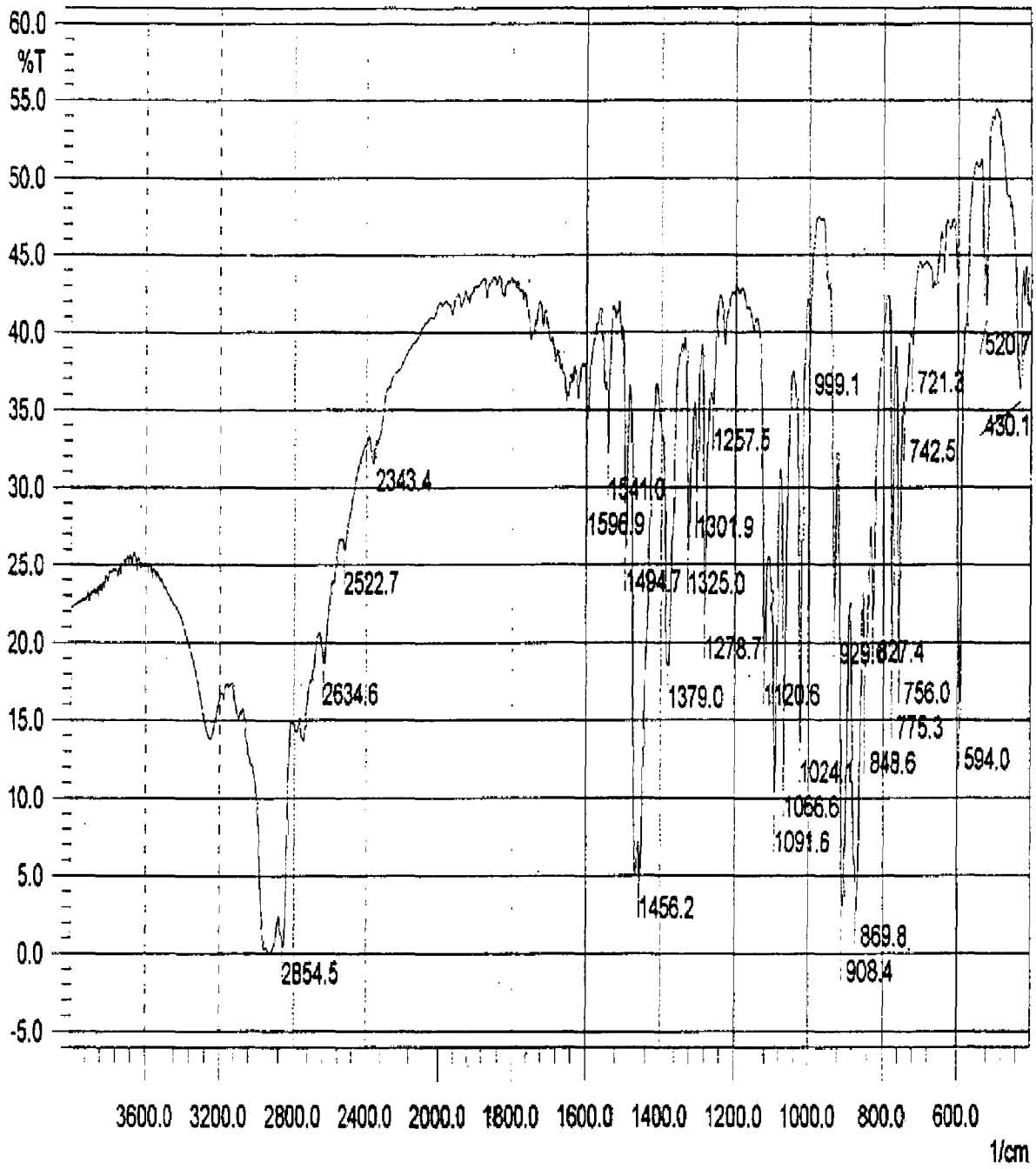

Fig. 17 : IR Spectrum of $[WO_2(HEBMZ)_2]$

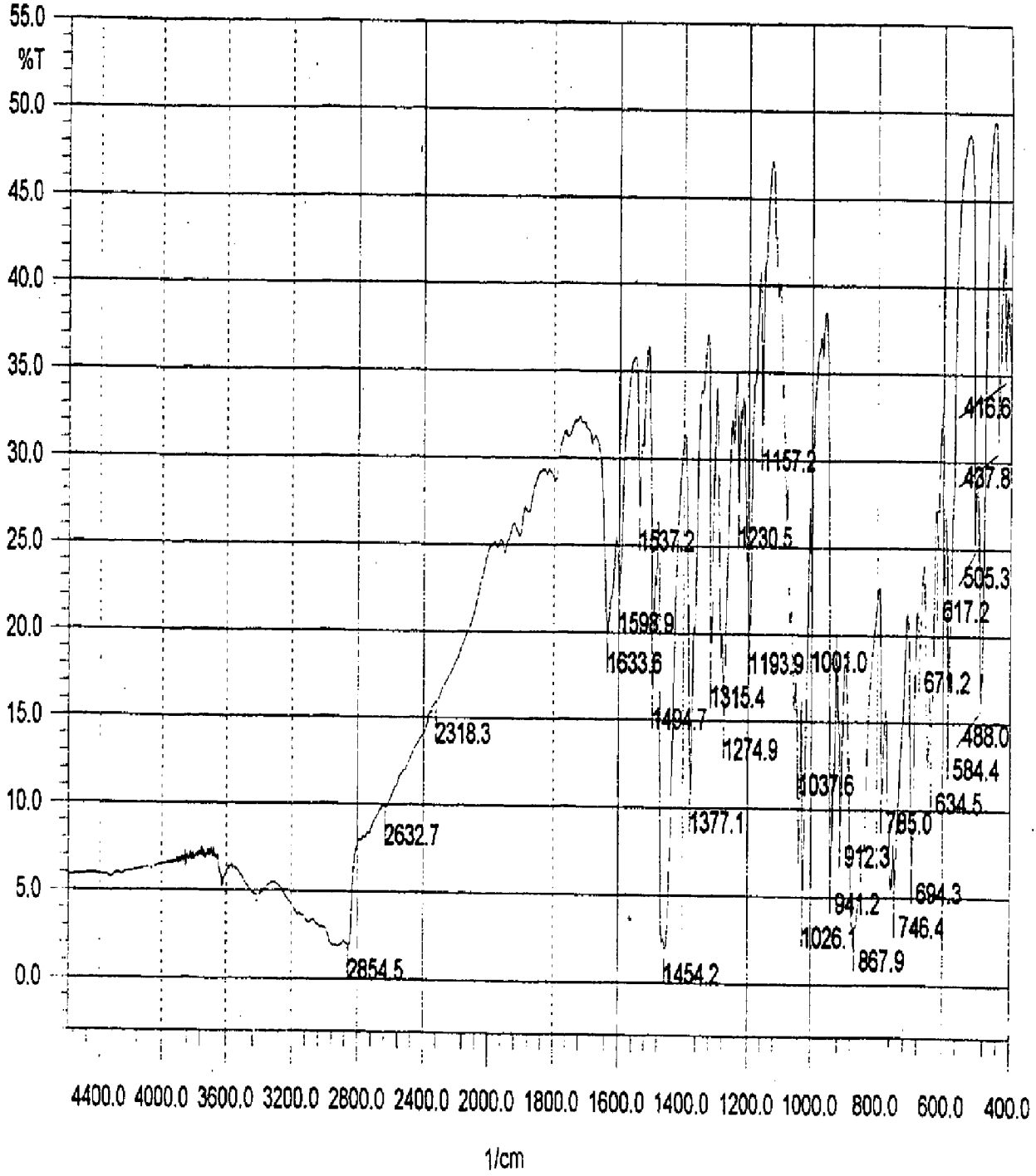

Fig. 19 : IR Spectrum of $[WO_2(HBBMZ)_2]$

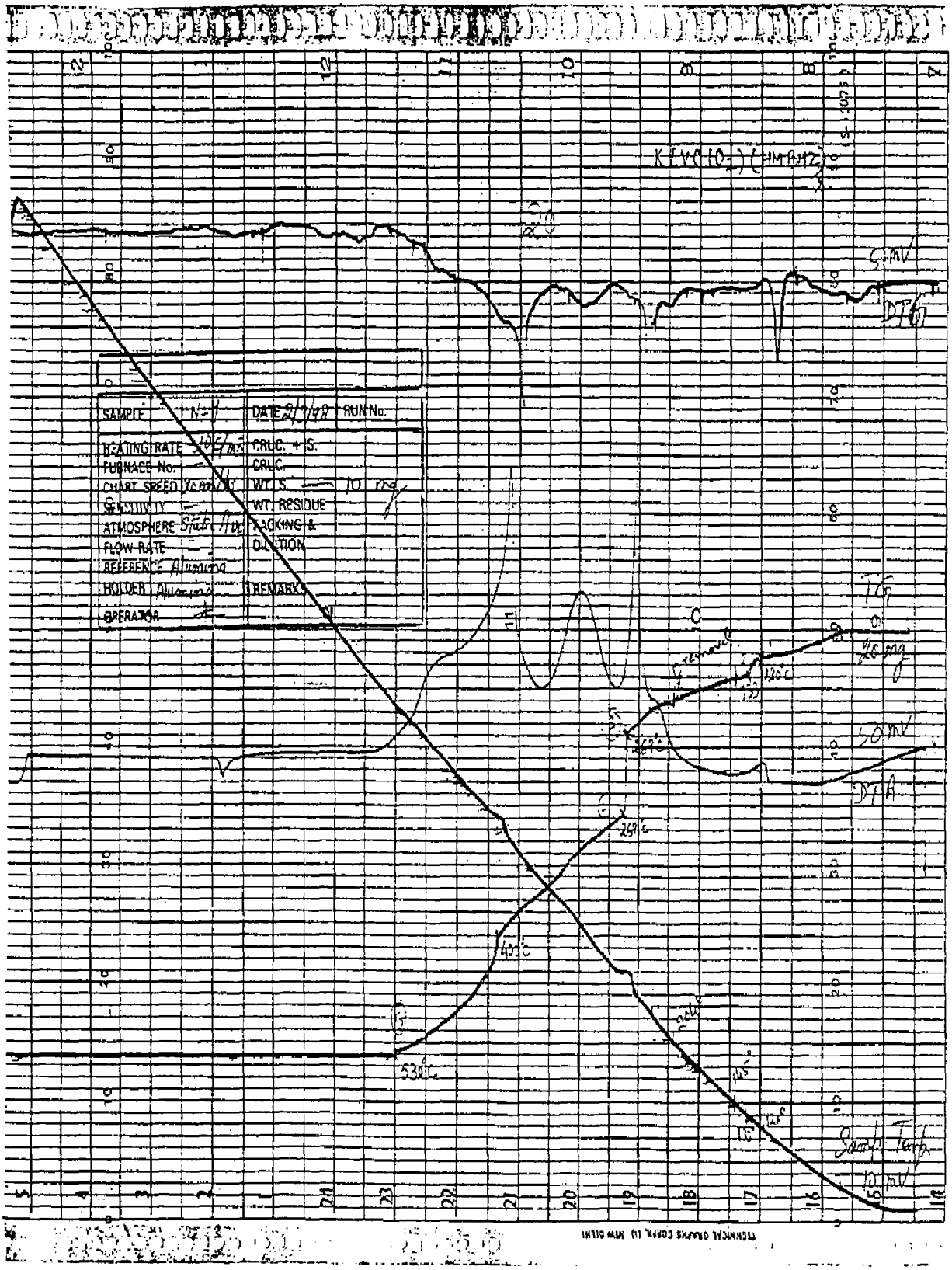

Fig. 20 : Thermogram of $K[VO(O_2)(HMBMZ)_2]$

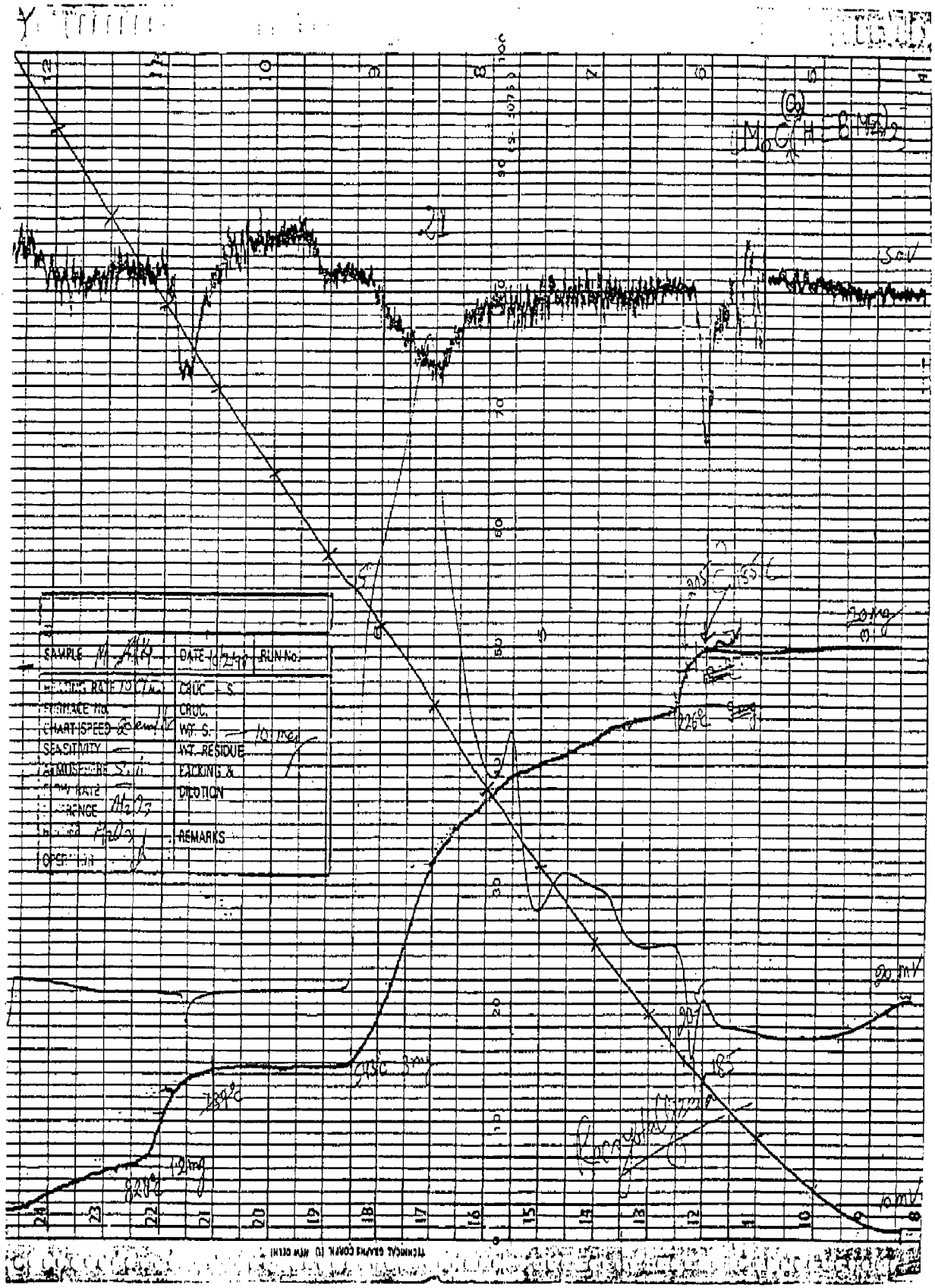

Fig. 21 : Thermogram of $[MoO(O_2)(HEBMZ)_2]$

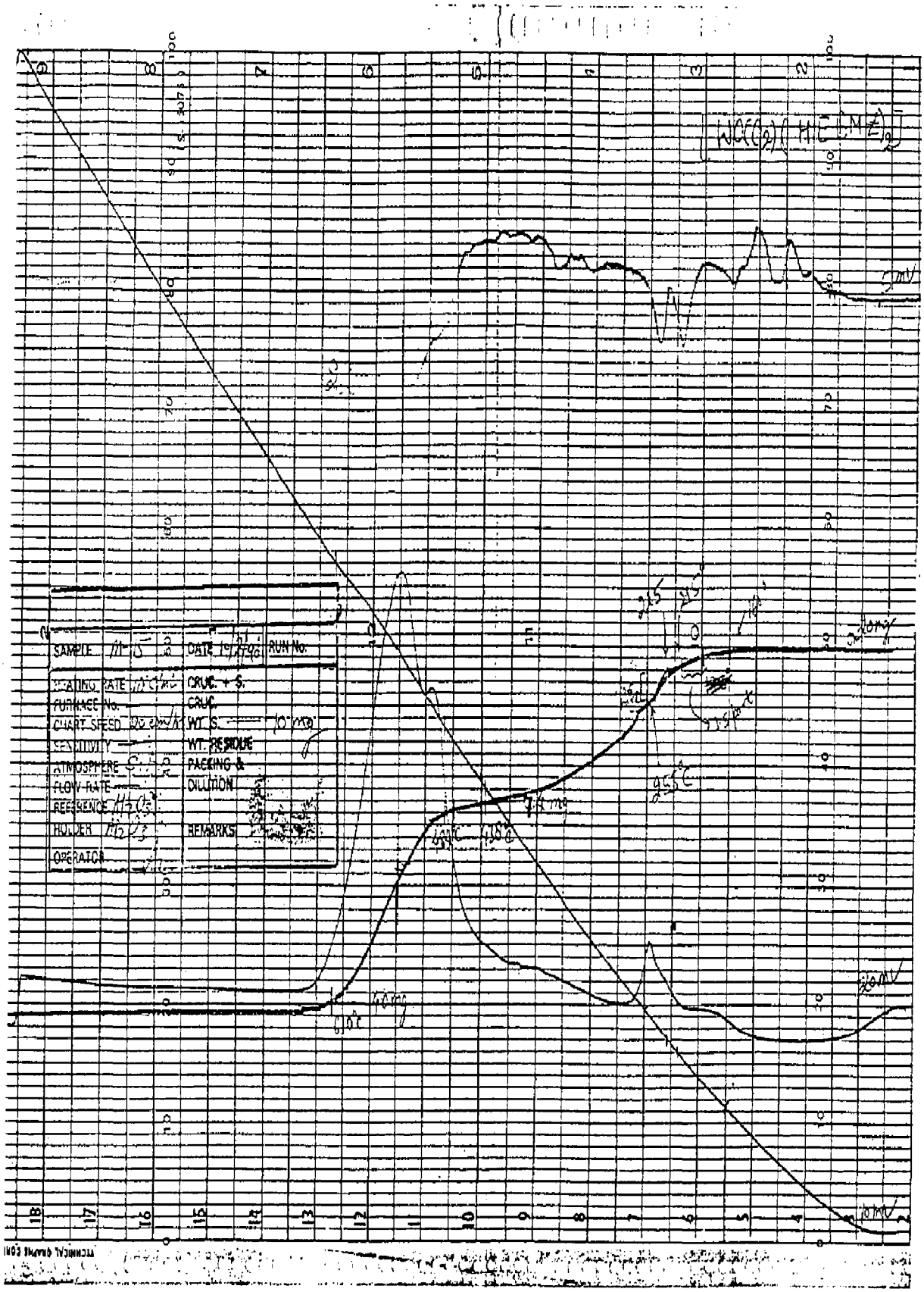

Fig. 22 : Thermogram of $[WO(O_2)(HEBMZ)_2]$

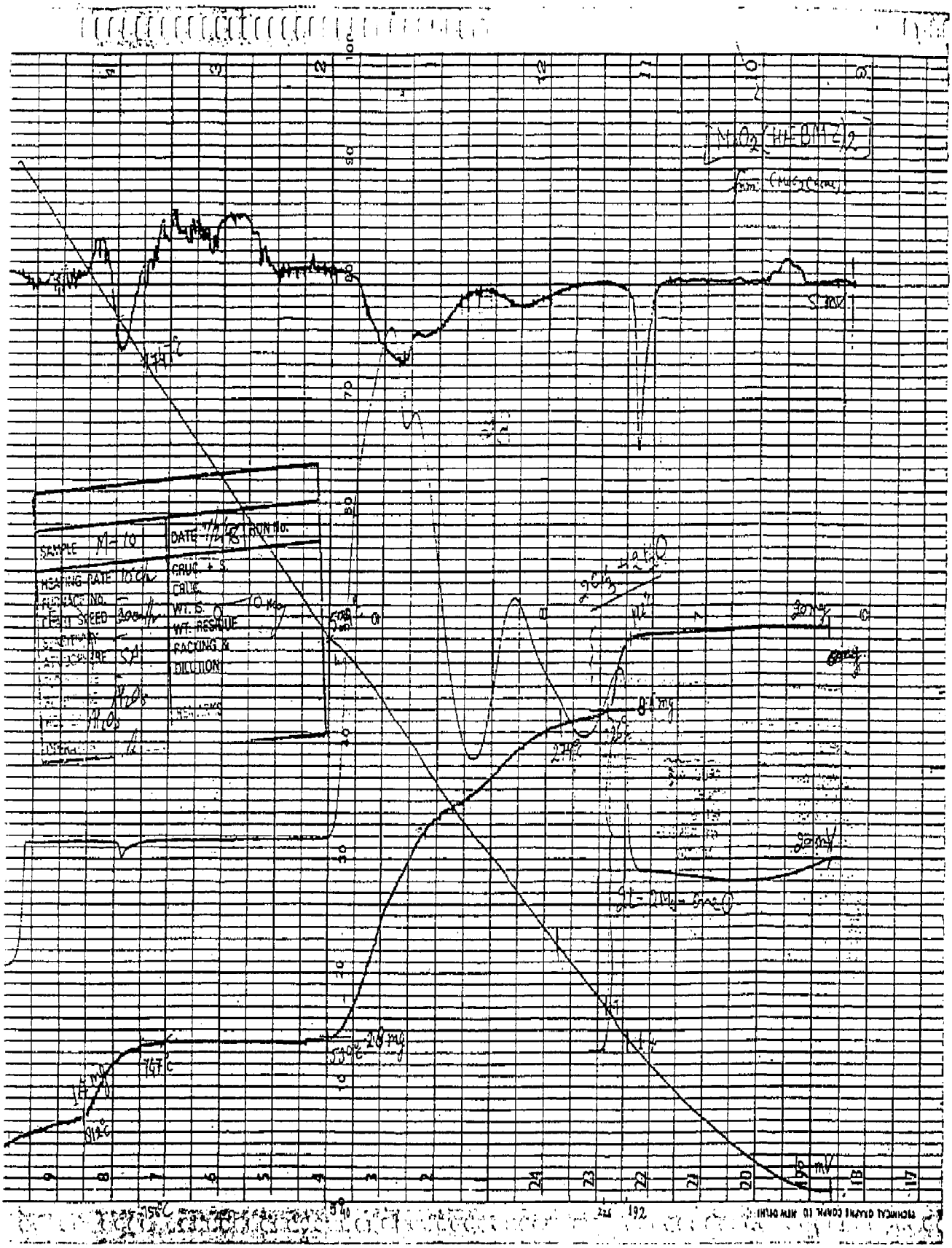

Fig. 23 : Thermogram of $[MoO_2(HEBMZ)_2]$

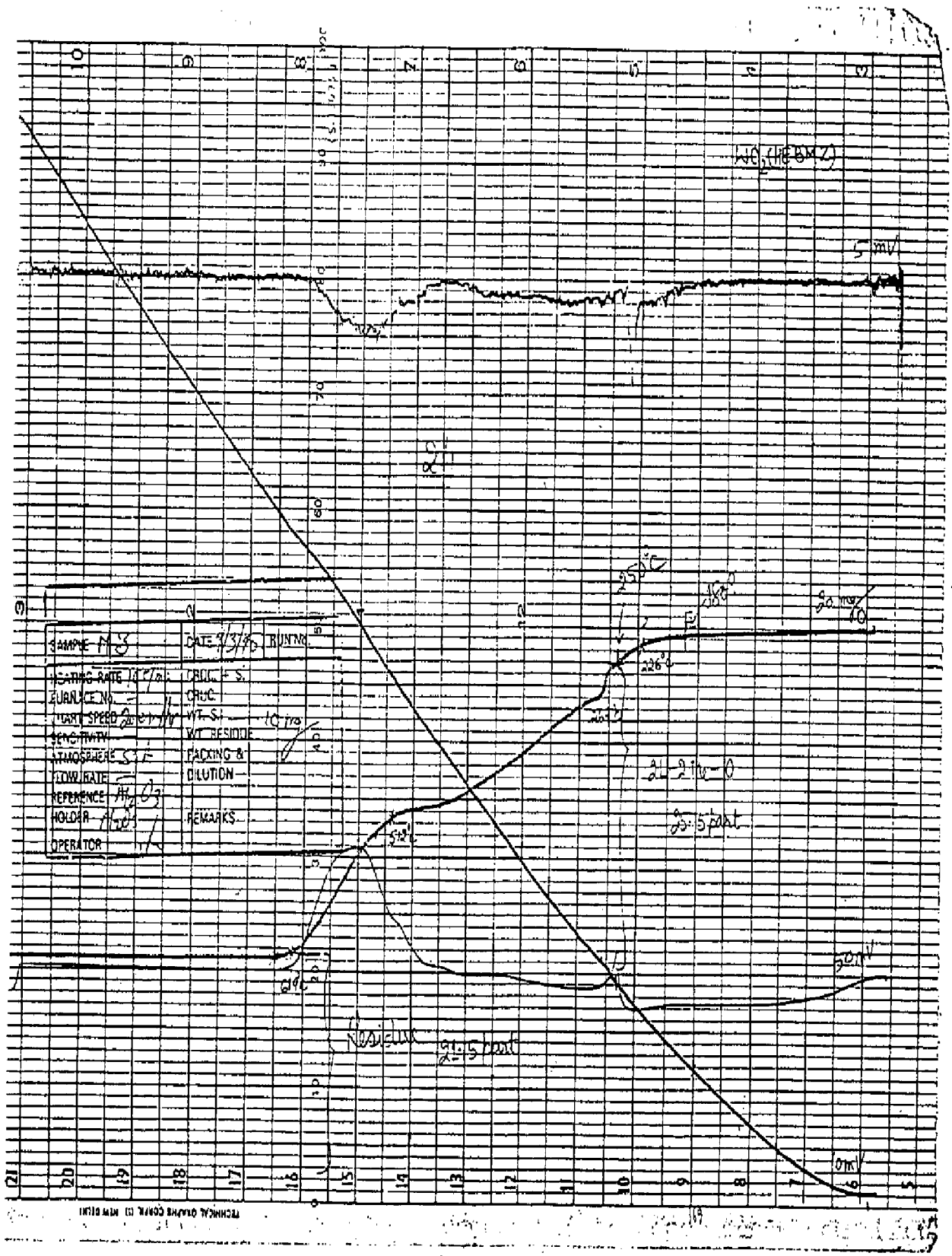

Fig. 24 : Thermogram of $[WO_2(HEBMZ)_2]$

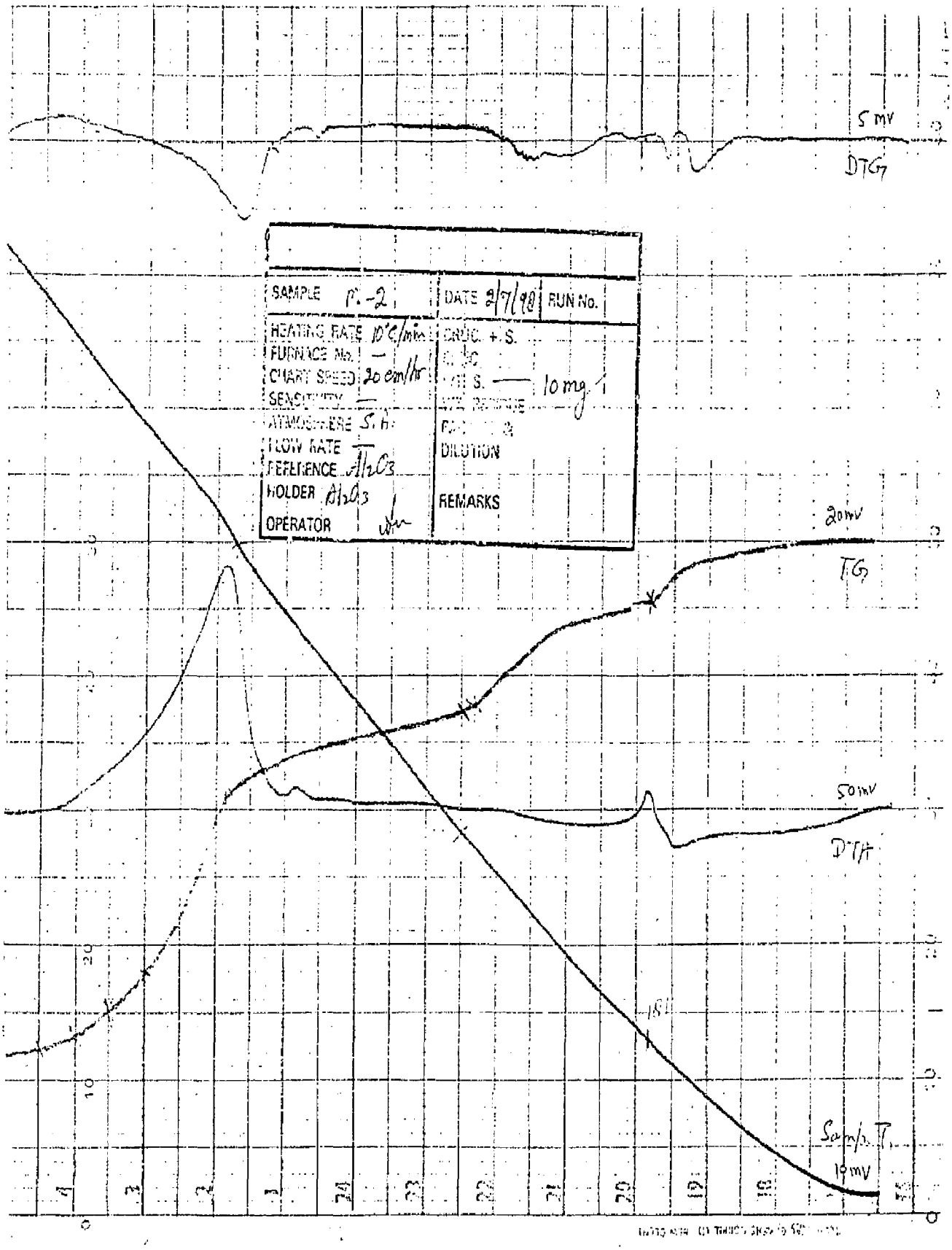

Fig. 25 : Thermogram of $[MoO_2(HBBMZ)_2]$

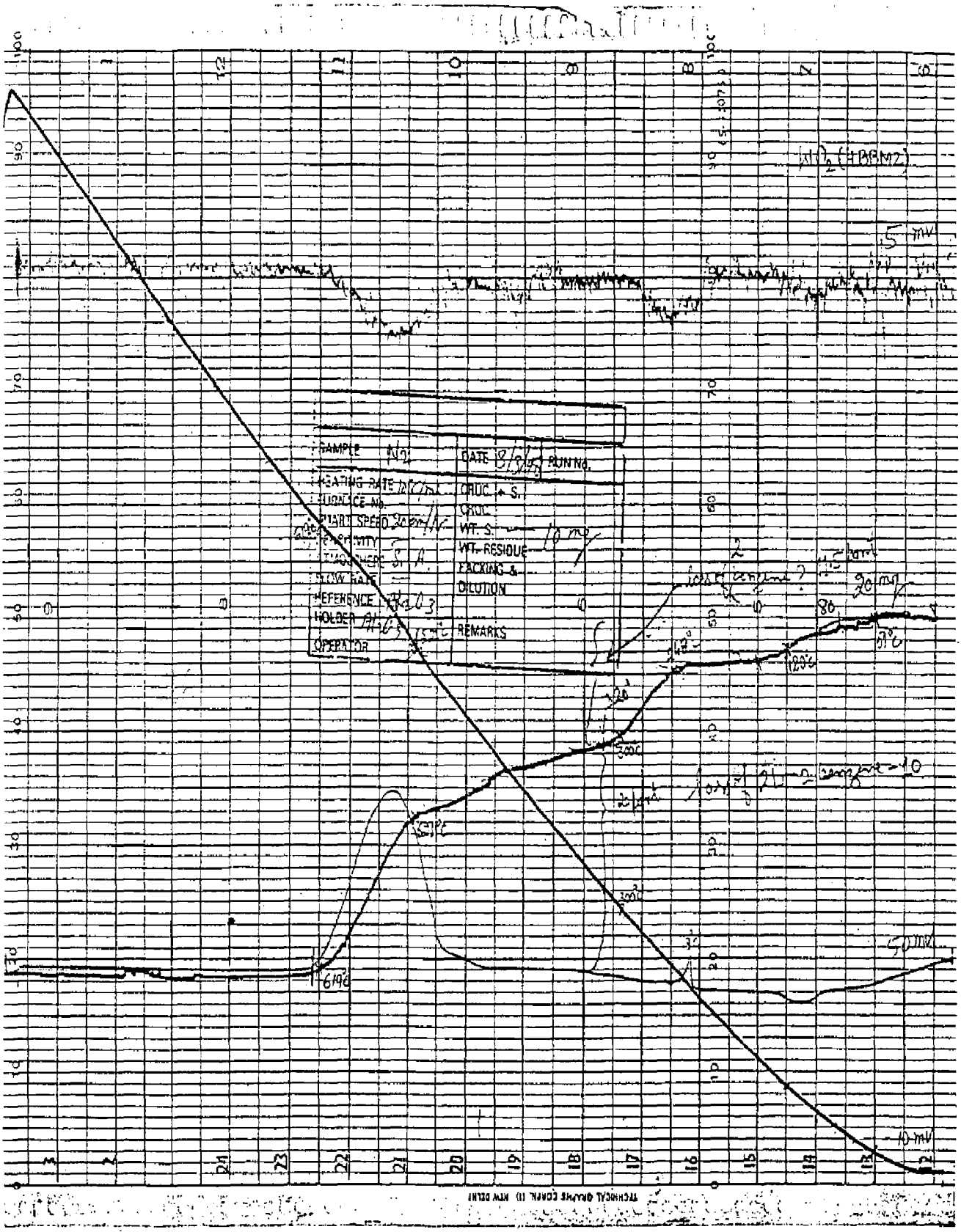

Fig. 26 : Thermogram of $[WO_2(HBBMZ)_2]$

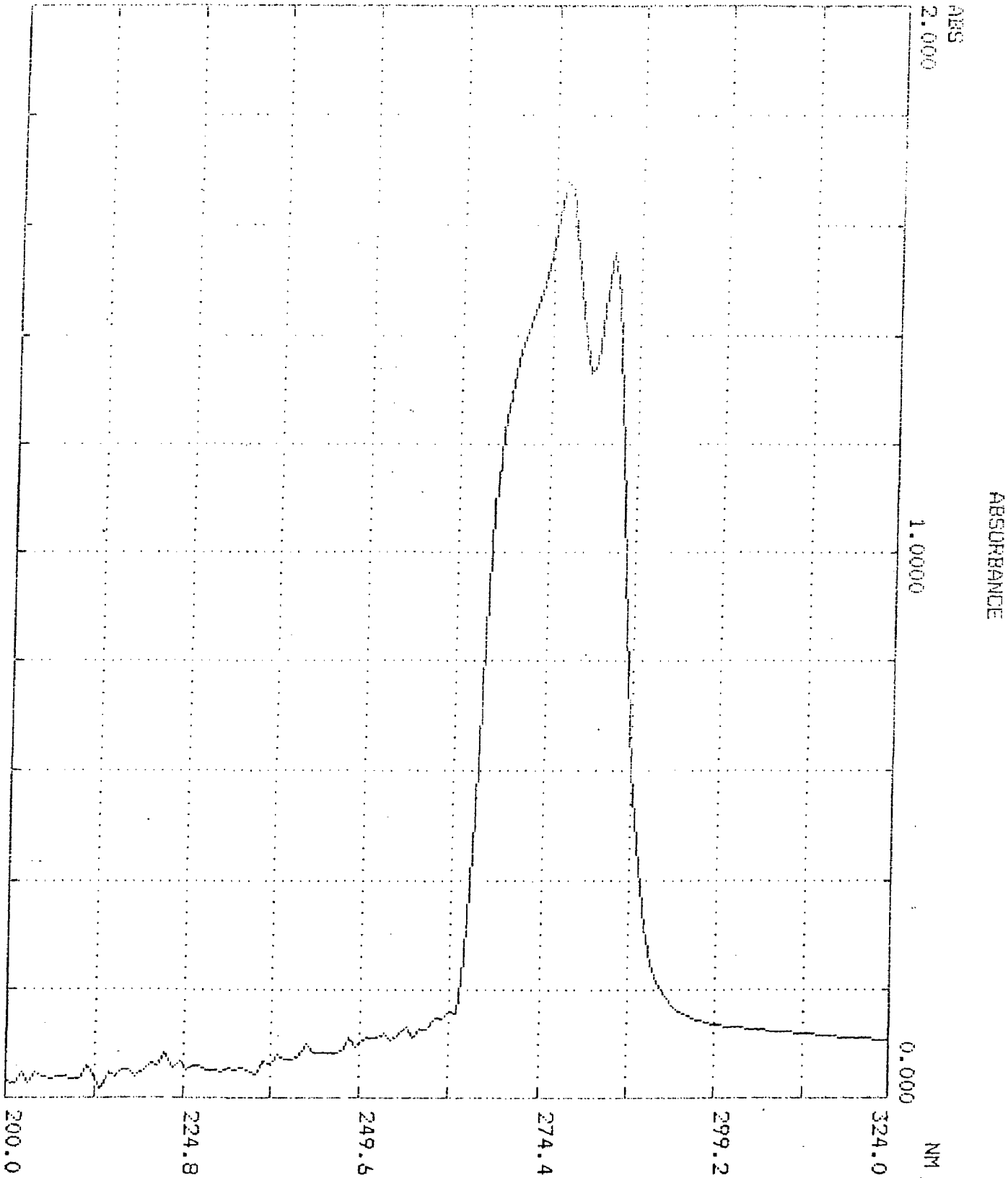

Fig. 27 : Electronic Spectrum of HMBMZ

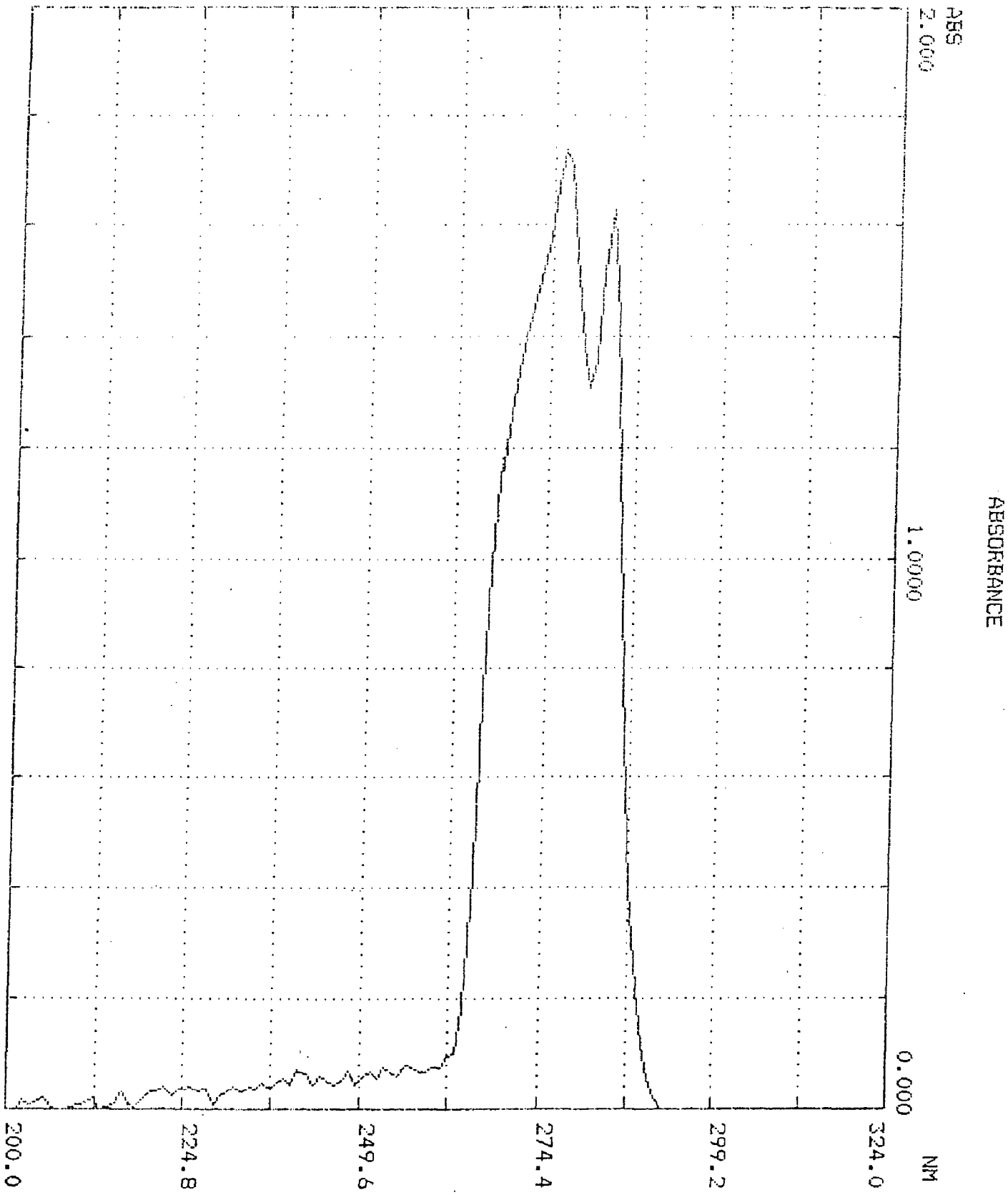

Fig. 28 : Electronic Spectrum of HEBMZ

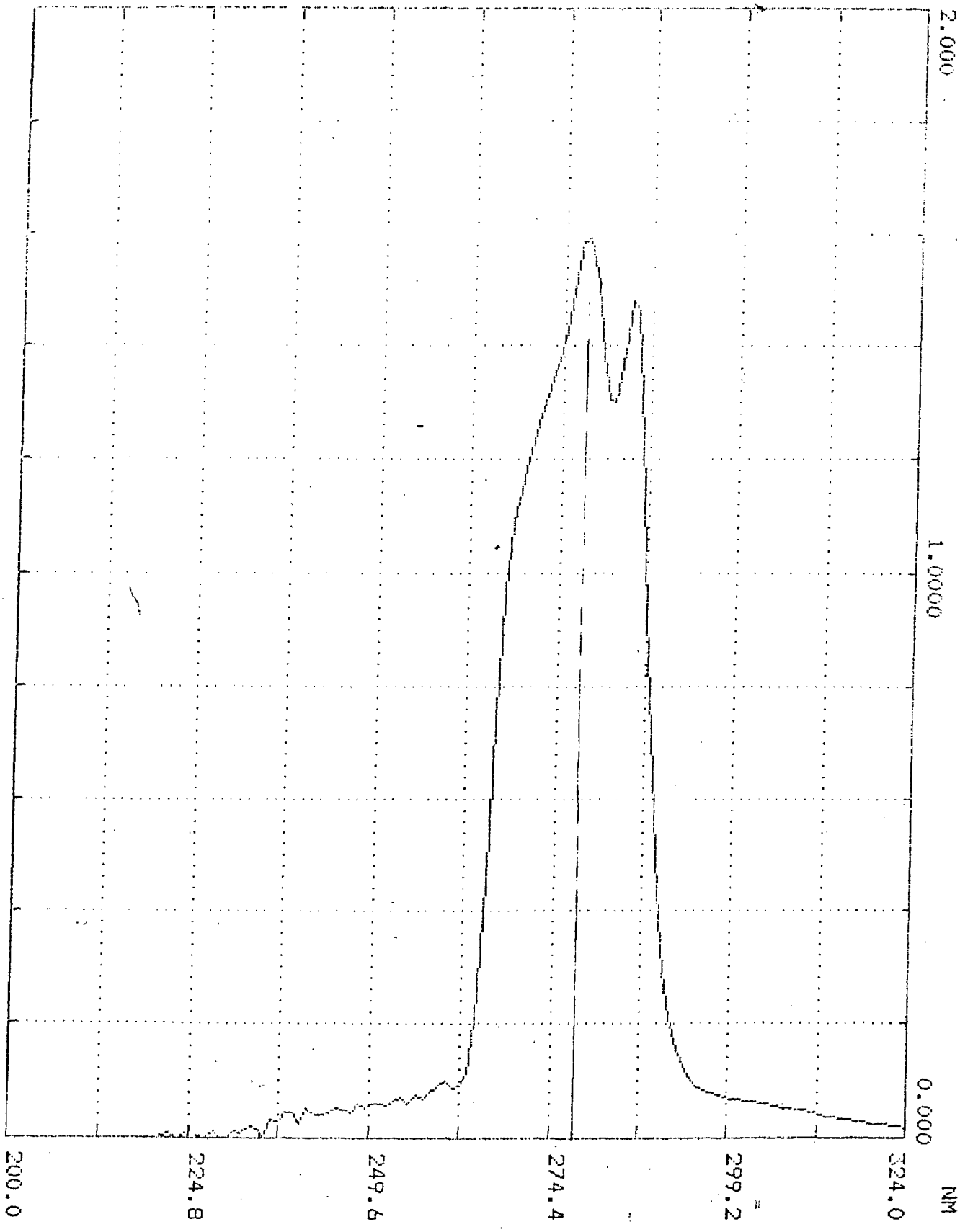

Fig. 29 : Electronic Spectrum of HBBMZ

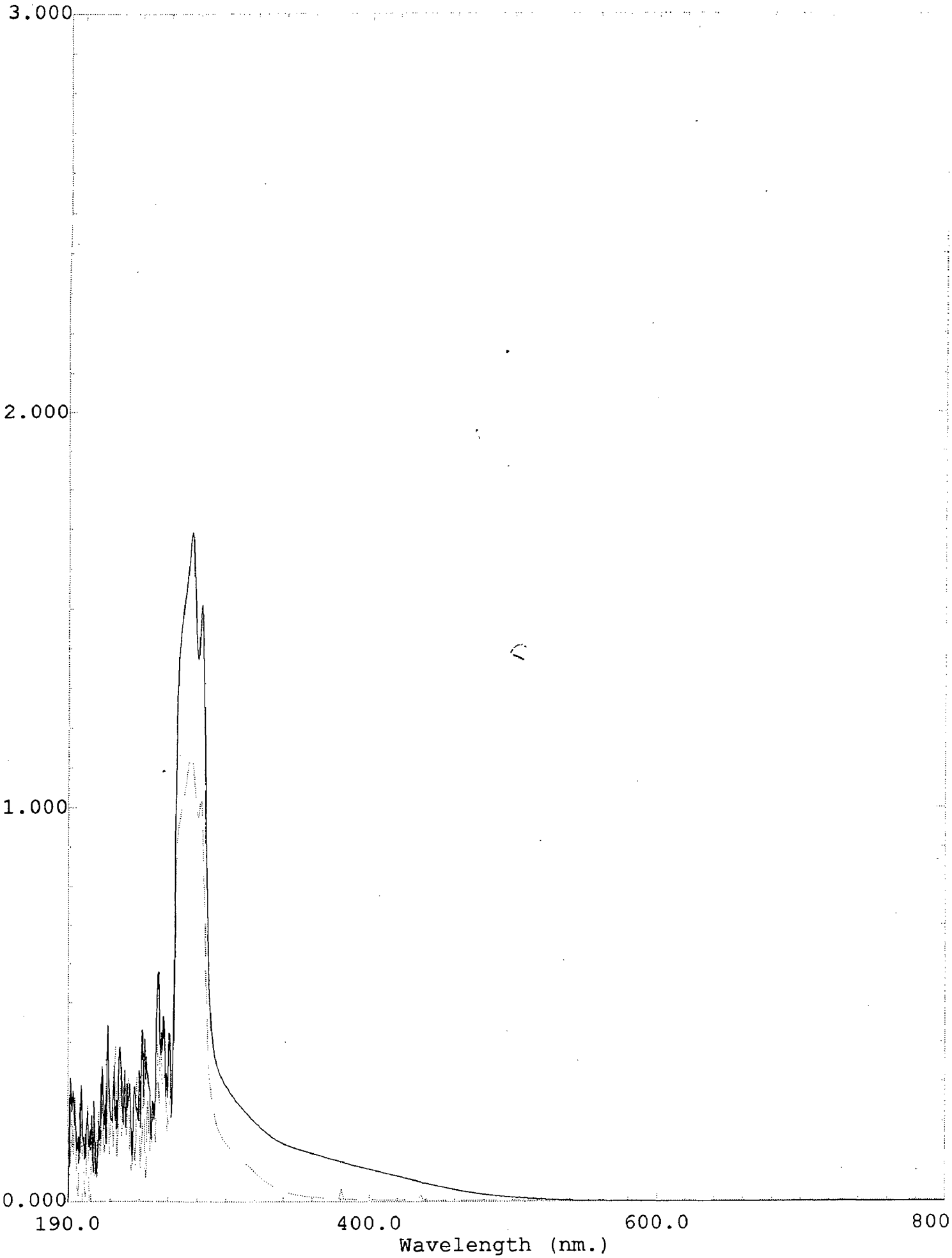

Fig. 30 : Electronic Spectrum of $K[VO(O_2)(HMBMZ)_2]$

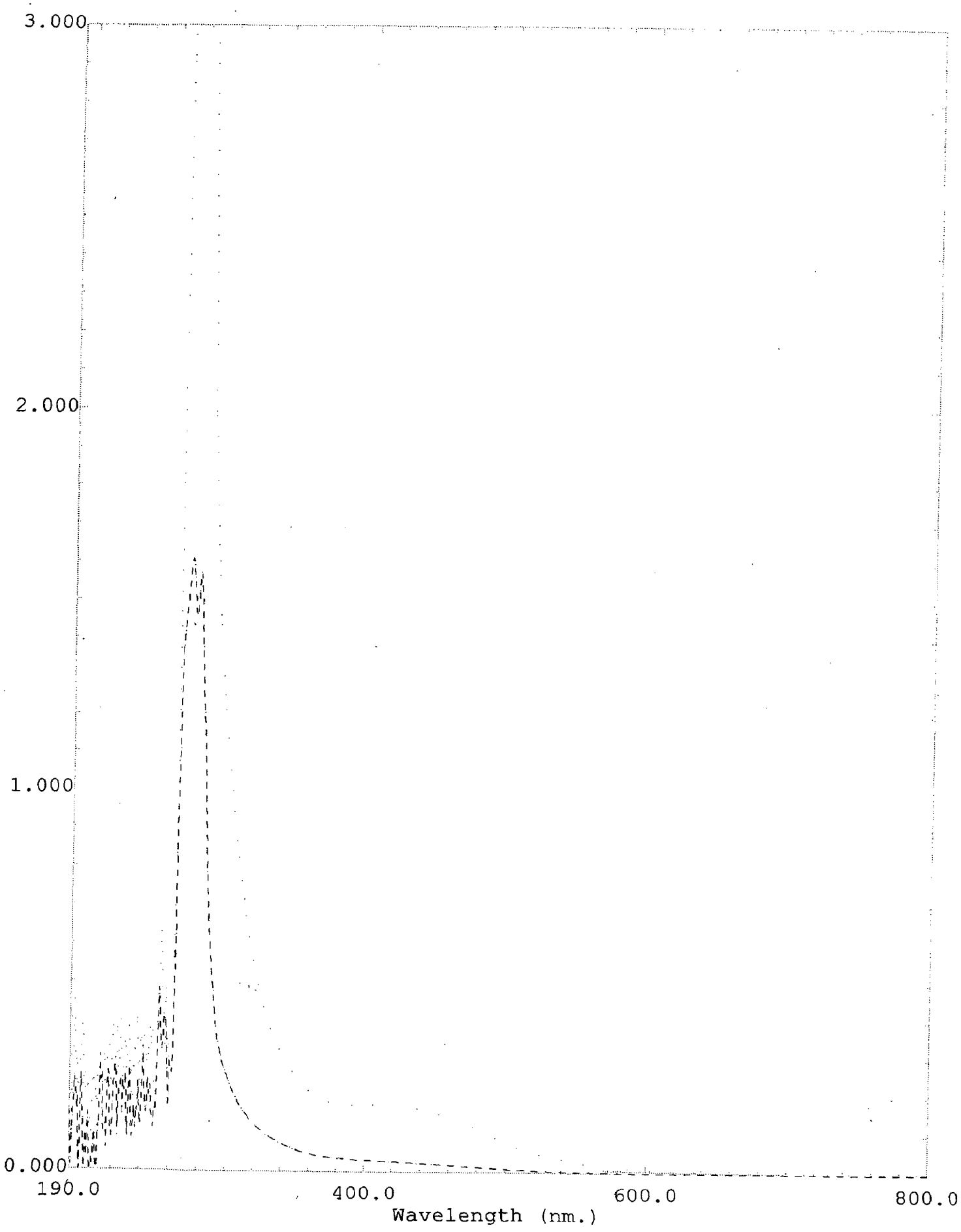

Fig. 31 : Electronic Spectrum of $K[VO(O_2)(HEBMZ)_2]$

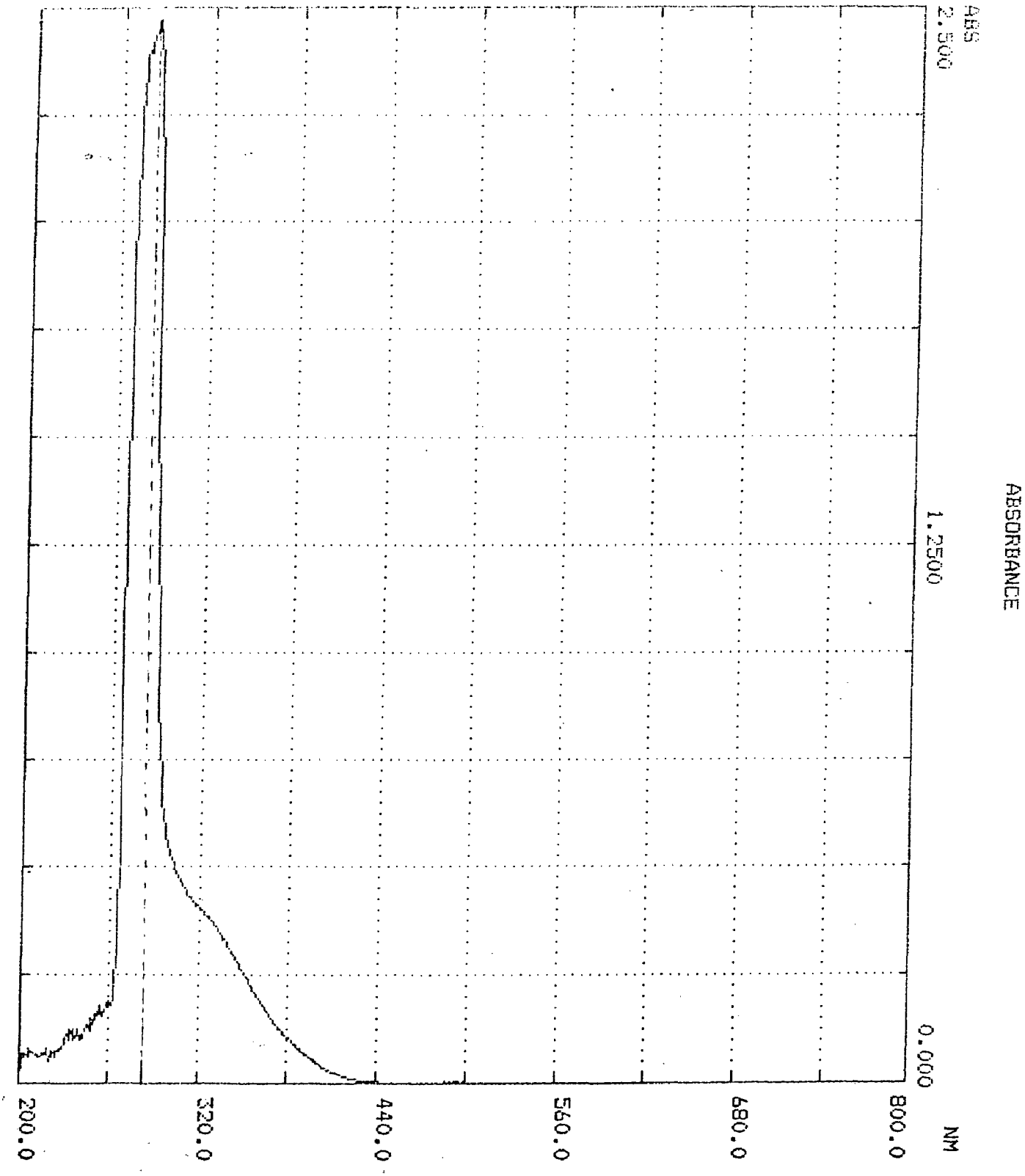

Fig. 32 : Electronic Spectrum of $[MoO_2(HEBMZ)_2]$

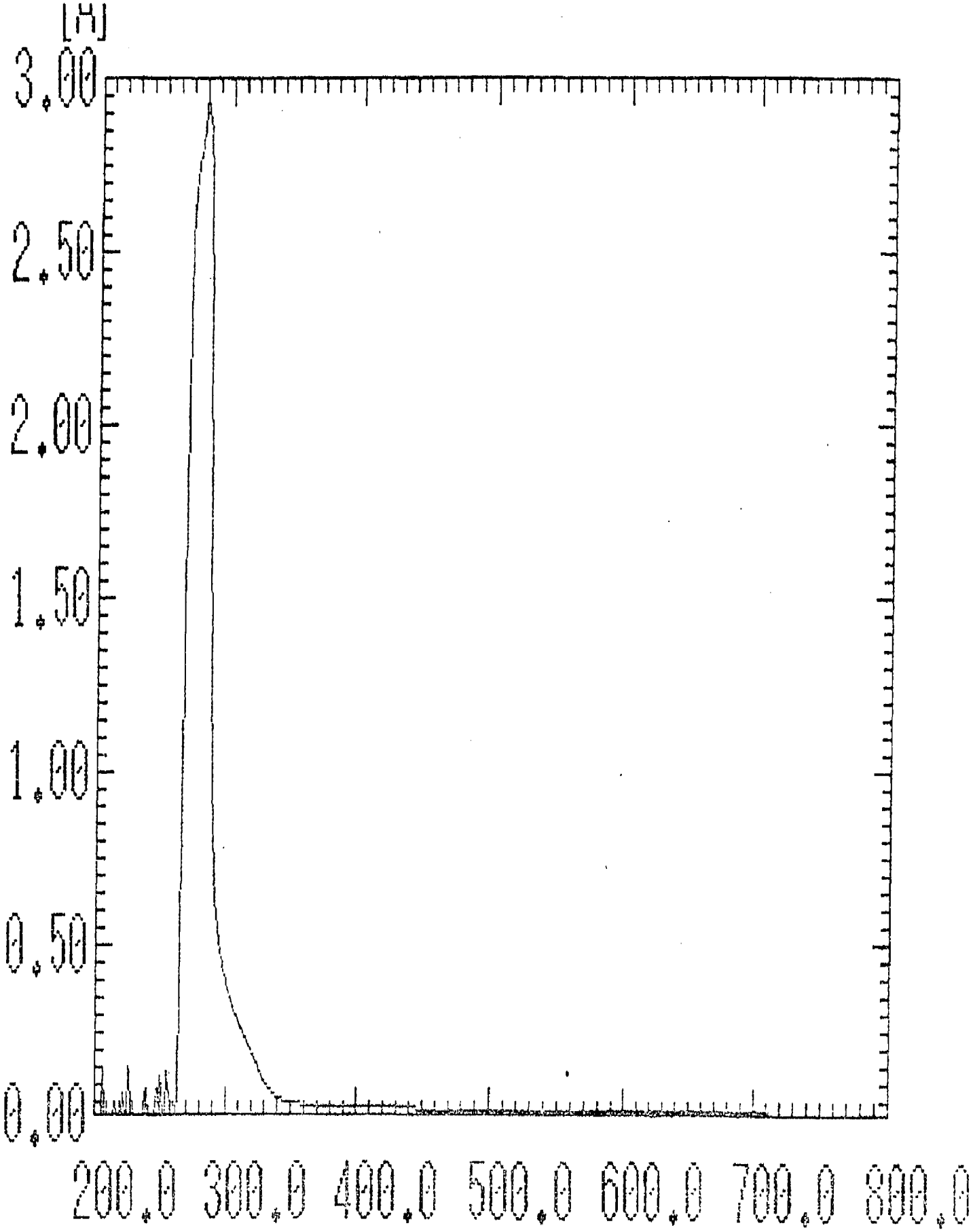

Fig. 33 : Electronic Spectrum of $[WO_2(HEBMZ)_2]$

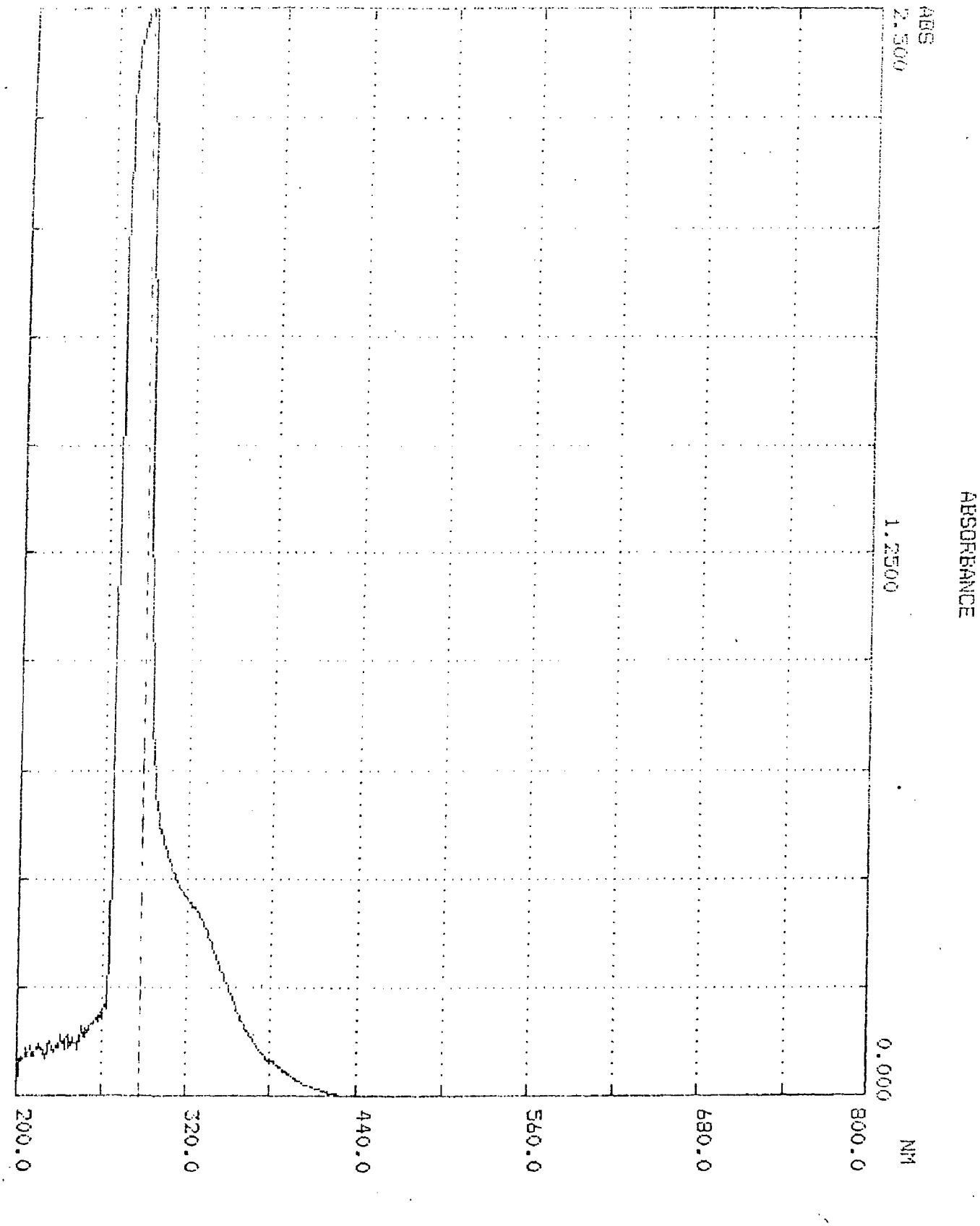

Fig. 34 : Electronic Spectrum of $[MoO_2(HBBMZ)_2]$