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THERMAL, X-RAY, AND NEUTRON-ACTIVATION INVESTIGATIONS OF COMPOUNDS OF NIOBIUM AND TANTALUM*

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ABSTRACT

The thermography of the sodium and potassium salts of metaniobate and metatantalate as well as the dichelate of niobium with n-propyl-3,4,5-trihydroxybenzoate (PTB) is investigated in atmospheres of air, nitrogen, and carbon dioxide; and their thermal decomposition products are identified. The niobyl dichelate (dichelate (I)) is isolated and its structure has been shown to be $K[NbO(C_6H_2(OH)(O_2)(COO)C_3H_7)_2]2(PTB)\cdot 3H_2O$.

INTRODUCTION

The uses of crystals of potassium metaniobate and potassium metatantalate in solid state physics are growing; the synthesis of organometallic compounds of these elements may lead to advances in the fields of catalytic reactions and polymer chemistry.

The preparation, thermal decomposition, and characterization of some oxysalts and organometallic compounds of niobium and tantalum in atmospheres of air, nitrogen and carbon dioxide are investigated. The compounds so formed and their heating products have been identified, wherever possible, by chemical, X-ray, neutron-activation, and atomic absorption methods. Results concerning the mode of preparation, oxidation states, and structures of various compounds of the two elements are obtained.

EXPERIMENTAL

Reagents

All reagents and chemicals were analytical grade.

Method of analysis

Differential thermal analyses (DTA)

The DTA of all substances used throughout this work were carried out on a

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Perkin–Elmer differential thermal analyser. Since particle size has an effect on the shape of the DTA curve, that of 50 mesh/in was used throughout. Ignited alumina was used both as diluent and reference. A heating rate of 10° and sometimes 4°C/min was used for the DTA run and was repeated in dry air, nitrogen, or carbon dioxide. In each run 0.5 g of a mixture of the substance (5% b.w.) in alumina and 0.5 g of the alumina were gently tapped down the respective holders. The apparatus was calibrated each time it was used with calcium carbonate and silver nitrate.

Thermogravimetric analysis (TG)

A Stanton thermorecording balance was used to record time, temperature and weight changes. In all cases the 0.5 g sample, contained in a micro platinum crucible, was placed on the lower pan. The balance was calibrated by placing a known weight on the pan. Furnace temperature and weight change were followed simultaneously on a twin pen electronic recorder, at a heating rate of 10°C/min. The flow rate of controlled gases was 30–40 ml/min. Effluent gases and decomposition products were evaluated as necessary by gas chromatography.

Differential thermogravimetry (DTG)

To pinpoint ambiguous positions on the heating curve, DTG was usually constructed to try to clarify the situation.

Neutron-activation analysis

This technique was used for the quantitative evaluation of the decomposition residues of niobium and tantalum and the compounds themselves. In each determination 100 mg of sample was weighed in a polythene container, sealed and transferred to the core of the nuclear reactor using a high-speed pneumatic system. The irradiation, decay, and counting times were all recorded on the pneumatic system. An IRT-2000 swimming pool nuclear reactor with 2000 kW power was employed. The neutron flux at the irradiation position was 2.8×10^{12} n/cm^2 sec. A Ge (Li) semi-conductor detector and 2048 Channel Nuclear Data multichannel analyser were employed as a counting system. Standards of the various elements present in the investigated compounds and their residues were prepared and their areas were measured. The samples were then irradiated under identical conditions and the unknown weight of the element was calculated from the area measurements. Standards were subjected to similar sample temperatures before activation.

X-ray spectra

All X-ray spectra were taken with a Philips X-ray spectrometer. The identity of a compound was then evaluated by direct comparison with standard spectra of known compounds and whenever possible checked against ASTM results.

Atomic absorption analysis

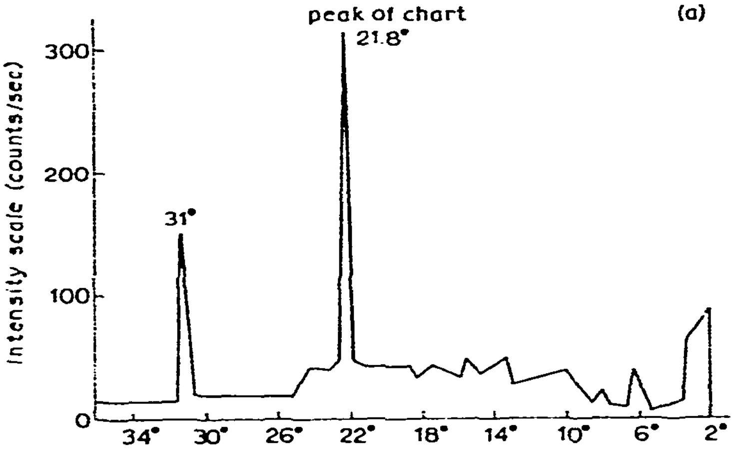
Analyses were carried out with a Beckman Atomic Absorption System with a DB-G model spectrometer using a Techtron Burner Kit-W186100.

Chemical analysis

Elemental analyses for carbon and hydrogen were run on a homemade microcombustion electrical burner using suitable microtrains. Other elements were analysed according to standard procedures.

Preparation and identification

The potassium and sodium salts of orthoniobate, orthotantalate, metaniobate and metatantalate were prepared. The ortho salts were prepared by fusion of their acidic oxides with excess alkali carbonate and their formulae evaluated; the corresponding meta salts were obtained by thermal decomposition of the ortho salts[1-4].



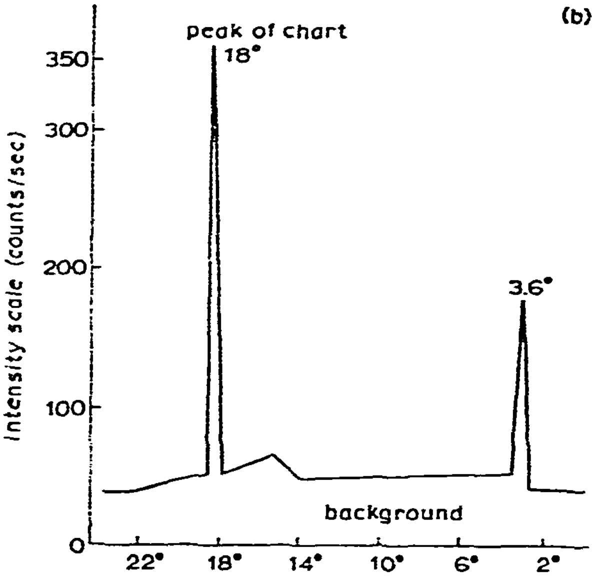


Fig. 1. Diffraction pattern of (a) potassium metaniobate powder and (b) metatantalate powder prepared with a Philips X-ray spectrometer adjusted for high resolution.

Cross checks between these salts and similar salts obtained from B.D.H. were made using various techniques. In Fig. 1 are given the X-ray spectrograms of the metaniobate and metatantalate. In contrast the ortho compounds showed sharp diffracted beams at 31.3 and 27.5° for the niobate and tantalate respectively on plotting the intensity of the diffracted beam against the angle of diffraction, 2θ. In spite of the structures developed[4,5] solutions of the ortho and meta salts of niobium and tantalum were stoichiometrically followed by atomic absorption and spectrophotometry and calibration curves could be constructed.

The procedure, developed for the preparation of the tentatively proposed structure previously published[6] was now extended to isolate the dichelate (I), $K[NbO(PTB)_2]2(PTB)\cdot 3H_2O$. The deep orange solution was slowly cooled to almost 0°C. The excess PTB was crystallized out and centrifuged. The orange centrifuged solution obtained was then evaporated under vacuum at 0°C. The orange prism-like crystals were kept under vacuum for further investigation.

The compounds investigated were mainly the sodium and potassium salts of metaniobate and metatantalate: and the dichelate (I) of niobium with PTB.

RESULTS AND DISCUSSION

Sodium metaniobate hydrate

The heating curves of the investigated salts are shown in Fig. 2. At 80°C the air-dried sodium metaniobate crystals started to lose water. Complete dehydration occured at 225°C with 35.14% weight loss of the original sample (Theory gives a 35.43% weight loss). This corresponded to elimination of $5H_2O$. The DTG, shown in Fig. 4, showed some peculiarities during the dehydration stage. The anhydrous niobate being stable between 225 and 750°C suggested a gravimetric determination of Nb(V) in $NaNbO_3$ as the most suitable. Repetition of the thermogram verified the stoichiometry of the compound from an analytical viewpoint notwithstanding its discrete nature[4,5]. Just after this temperature the anhydrous metaniobate became unstable and 41.44% loss weight was recorded between 750 and 900°C. The loss in weight has due to the evolution of oxygen. The changes might hypothetically be represented by:

$$4NaNbO_3 \rightarrow 4NaNbO_2 + 2O_2$$
$$4NaNbO_2 \rightarrow 2Na_2O + 2Nb_2O_3$$

However a horizontal line could be constructed between 900 and 1100°C on the thermogram. Up to 1250°C the weight loss was 53.25% due to the removal of 11.81% Na_2O. Finally at 1950°C the pyrolysis curve assumed a horizontal line with 46.30% weight loss of the original sample in the microcrucible. To elucidate the structural changes of the compounds at elevated temperatures, DTA runs were made under the three different gaseous atmospheres. The corrugated dehydration endotherm exhibited two continuous stages of dissociation of water of hydration molecules. It was concluded that the first dissociation was due to the coordination of four water groups to

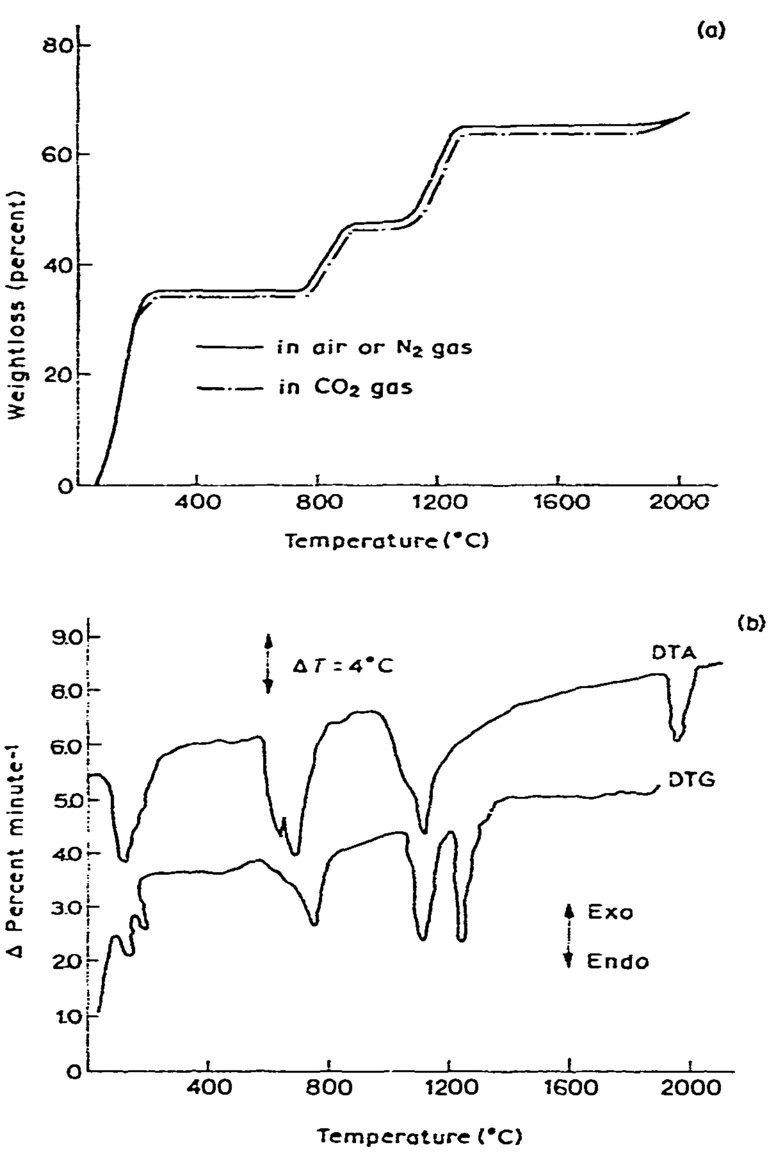


Fig. 2. (a) Thermogram and (b) differential thermogravimetric curves of $NaNbO_3 \cdot 5H_2O$.

the sodium ion and the second dissociation due to the fifth water group coordinated to the metaniobate ion. Therefore the structural formula of the hydrated salt could be written as $[Na(H_2O)_4]^+[NbO_3 \cdot H_2O]^-$. The discrete molecule of hydrated metaniobate was presumed. The levelling out of the curve after 1950°C in air could be explained by the re-oxidation of trivalent to pentavalent niobium

$$2Nb_2O_3 + O_2 \rightleftharpoons 2Nb_2O_4 \rightleftharpoons Nb_2O_3 + Nb_2O_5$$

and therefore the endotherm dip on the DTA might indicate the thermal dissociation of Nb_2O_4 into Nb_2O_3 and Nb_2O_5—a process which absorbs energy. Decomposition products were obtained on different plateaux of the thermogram.

Figure 2a shows the thermogram of $NaNbO_3 \cdot 5H_2O$. The residue obtained at 225°C produced X-ray spectra that could match the ASTM standard diffraction data of $NaNbO_3$. Therefore dehydration did not disrupt the metaniobate ion and therefore a coordinate bond might be excluded. Activation analysis[7] yielded the same composition formula of the compound. The yellowish white residue formed at 900°C was free from soluble substances. Its X-ray diffraction pattern was different from that of the metaniobate (Fig. 1a). Its composition, as determined by neutron-activation analysis (Table 1) and by the amount of oxygen evolved, was found to be $NaNbO_2$. It could be dissolved in both boiling 25% alkali carbonate or hydroxide, and a mixture of nitric and hydrofluoric acids. The solutions gave positive Ca-cotheline[8] tests of trivalent niobium. The R_F values on Whatmann chromatographic paper were different from those of $NaNbO_3$ in a similar solvent. However, a.c. polarography could not result in a steady $E_{\frac{1}{2}}$ of the $NaNbO_2$ solution in either the HNO_3–HF mixture or the alkali mixture. The black powder residue, heated at 1250°C in atmospheres of nitrogen and carbon dioxide, gave on activation analysis an approximate niobium-to-oxygen ratio of 2/3 (Table 2). The X-ray diffraction pattern for it is shown in Table 3; the powder obtained in air was of unsteady composition.

TABLE 1

ANALYSIS OF RESIDUES OBTAINED FROM THERMAL DECOMPOSITION OF SODIUM METANIOBATE HYDRATE

Temp. (°C)	*Weight loss (%)*	*Purity of substances formed at stated temperature (%)*				
		$NaNbO_3$	$NaNbO_2$	Na_2O	Nb_2O_3	O_2
225	35.14	99.5	0.00	0.00	00.0	00.0
900	41.44	00.0	99.8	00.0	00.0	99.0
1100	53.25	00.0	00.0	19.8	79.0	0.08

At higher temperatures and different gaseous atmospheres lower oxides or states of niobium were not identified[9]. Nevertheless near 1950°C there was a comparative gain in % weight of the sample. To reveal the nature of the unknown black residue, the (*d*) values of its strongest three lines did not match that of niobium(III) oxide, niobium(IV) oxide, niobium(V) oxide, nor even the free niobium metal. Activation analysis could not supply a definite composition for it. The residue was perhaps a mixture of oxides and nitrides of the element. Extracts of the residue with water or oxygen containing organic solvents were devoid of any soluble substance.

Potassium metaniobate hydrate

Similar procedures were followed for the thermal decomposition of both potassium metaniobate hydrate and the already discussed sodium metaniobate hydrate. Their heating curves (Fig. 3 and Tables 1 and 4) were almost identical. Moreover experiments showed that the metaniobate of potassium decomposed at lower temper-

TABLE 2

NEUTRON-ACTIVATION ANALYSIS OF STANDARDS AND RESIDUES OBTAINED AT THE VARIOUS HEATING TEMPERATURES OF POTASSIUM METANIOBATE

Sample, irradiated	*Area (counts)*			*Weight (mg)*			*Weight/at.wt. (mg)*			*Atomic ratio K/Nb/O*	*Inference*
	K	*Nb*	*O*	*K*	*Nb*	*O*	*K*	*Nb*	*O*		
K + Nb (standard)	19100	185000		48.0	51.2						
Nb_2O_5 (standard)		250000	12500		62.0	29.6		0.74	1.82	–/2/5	Nb_2O_5
Residue (195 °C)	8627	185000	11580	22.0	51.2	26.6	0.55	0.56	1.66	1/1/3	$KNbO_3$
Residue (870 °C)	9469	205296	8239	22.8	51.3	19.6	0.58	0.57	1.20	1/1/2	$KNbO_2$
Residue (1180 °C)		287146	8680		79.2	20.5		0.85	1.30	1/2/3	Nb_2O_3

TABLE 3

X-RAY DIFFRACTION PATTERN OF $NaNbO_2$ PREPARED AT 900°C IN NITROGEN AND CARBON DIOXIDE GASES

d (Å)	I/I_1	d (Å)	I/I_1
2.34	25	1.18	15
2.30	30	1.15	10
2.27	100	1.10	10
1.50	40	1.01	8
1.27	35	0.93	20
1.22	20	0.860	5
1.20	30	0.820	4

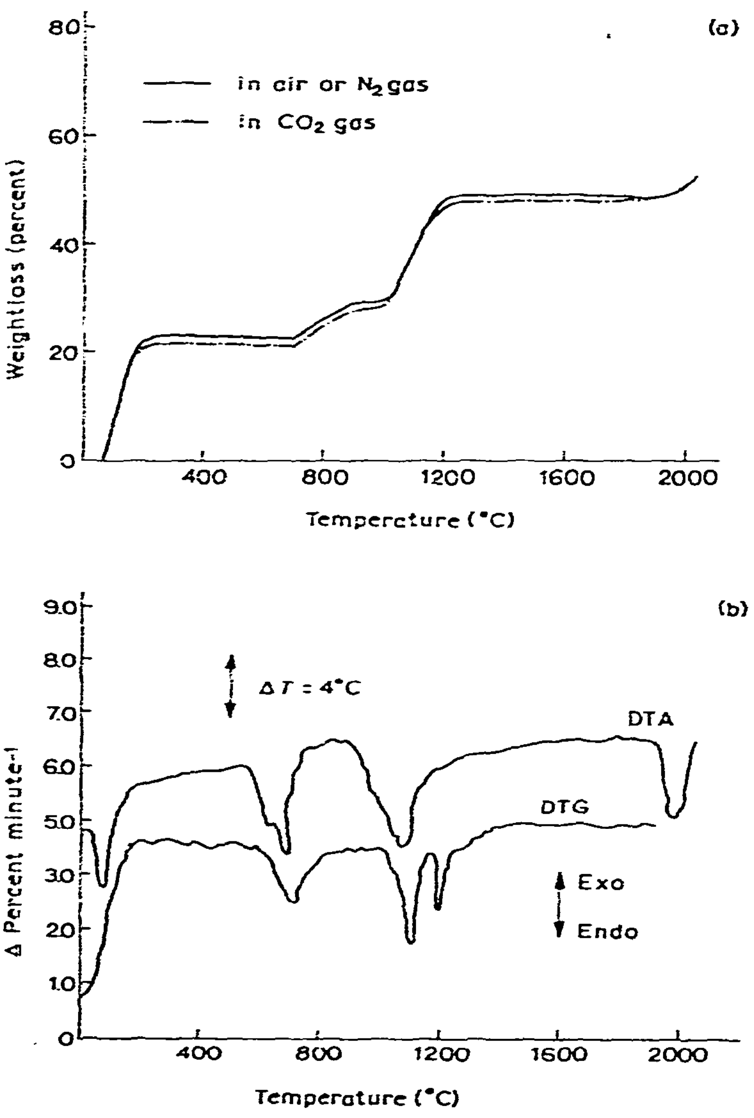


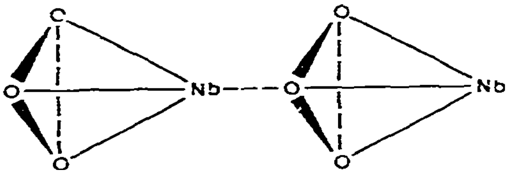
Fig. 3. (a) thermogram and (b) differential thermogravimetric curves of $KNbO_3 \cdot 3H_2O$.

TABLE 4

ANALYSIS OF RESIDUES OBTAINED FROM THERMAL DECOMPOSITION OF POTASSIUM METANIOBATE HYDRATE

Temp. (°C)	*Weight loss (%)*	*Purity of substances formed at stated temperature (%)*				
		$KNbO_3$	*$KNbO_2$*	*K_2O*	*Nb_2O_3*	*O_2*
195	23.0	99.6	00.0	00.0	00.0	00.0
870	29.8	00.0	99.1	00.0	00.0	98.0
1180	49.9	00.0	00.0	19.6	80.0	0.1

atures than that of sodium; whence it was concluded, with little reservation, that the percentage ionic character of the bond between potassium and the oxygen atoms in metaniobate or in water of hydration is lower than that of the sodium salt despite potassium being more electropositive and having a larger ionic radius than sodium, which perhaps could have conferred more stability on the anion and water of hydration through lattice energy effects. However, the pyrolysis curve (Fig. 5) shows the presence of three groups of water of hydration bound to the salt molecule, $[K \cdot 2H_2O]^+$ $[NbO_3 \cdot H_2O]^-$. Meanwhile thermogravimetric calculations indicate, but not conclusively establish, the dimeric structure of the metaniobates, that was speculatively written as the tetrahedral bi-pyramidal



cf. the octahedral perovskite structures of the mixed oxides. Therefore the sodium and potassium niobates were isostructural. Expulsion of water of hydration at temperatures lower than those necessary for the collapse of the metaniobate ion might ascertain that the metal-to-oxygen bond between the metal and the group of water was not operating and instead the two were linked through the more easily breakable ion–dipole bond. No evidence was found for interstitial waters of hydration.

Potassium metatantalate hydrate

The thermolysis curve of that crystalline salt is shown in Figs. 4 and 5. The analyses of various residues are given in Tables 5 and 6. There were four water groups per molecule of the hydrated salt, which could be depicted as $[K \cdot 4H_2O]^+$ $[TaO_3 \cdot H_2O]^-$. In atmospheres of nitrogen or carbon dioxide, the thermal disruption of the tantalite ion into tantalum(V) oxide was a major difference from that of the niobite ion. To account for this behaviour it was thought that the oxygen-to-metal coordinate link in the tantalite (metatantalate) was more stabilized and shielded by arrays of multi-dimeric, of some sort, of non-distorted octahedral structure. At a temperature slightly higher than 900 °C it was shown that the electric conductance of the salt increased; therefore polarization of the octahedral crystal, due to the presence of large holes in it and at the oxo-bridge region between the alkali metal and the central atom, was more likely to occur and consequently splitting of the alkali metal monoxide from the octahedral tantalum(V) oxide was possible in that temperature region.

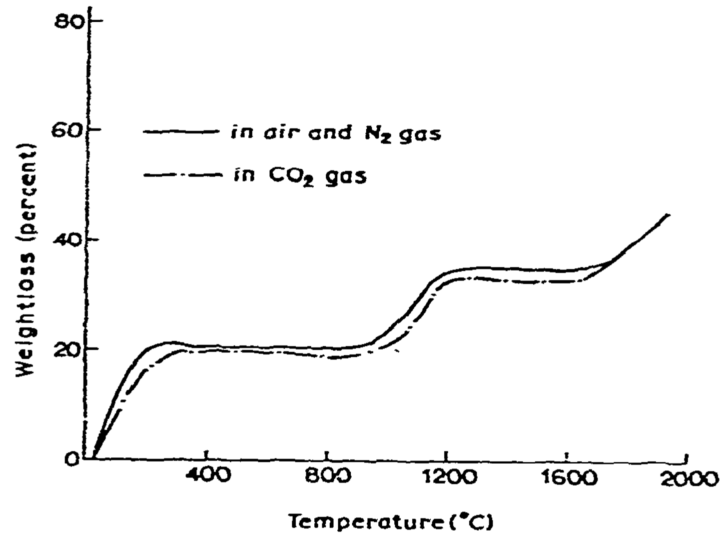


Fig. 4. Thermogram of $KTaO_3 \cdot 4H_2O$.

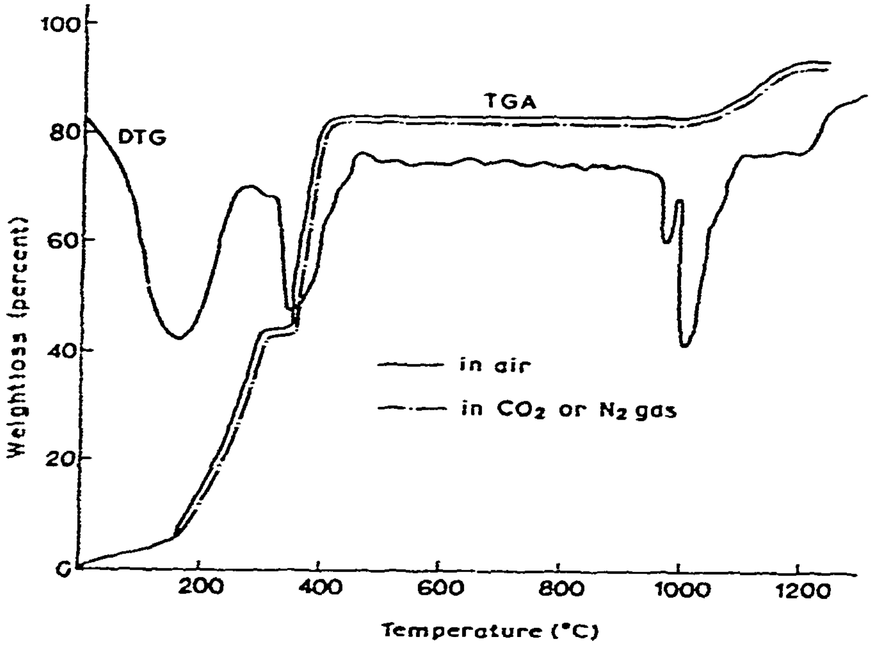


Fig. 5. Relation between TGA and DTG curves for the pyrolysis of Nb–PTB chelate.

TABLE 5

ANALYSIS OF RESIDUES OBTAINED FROM THERMAL DECOMPOSITION OF POTASSIUM METATANTALATE HYDRATE

Temp. (°C)	*Weight loss (%)*	*Purity of substances formed at stated temperature (%)*				
		$KTaO_3$	*K_2O*	*Ta_2O_5*	*Ta*	*O_2*
208	21.1	99.0	00.0	00.0	00.0	00.0
1150	34.9	00.0	17.5	82.4	00.0	00.0
1935	46.7	00.0	00.0	00.0	63.8	17.8

Dichelate (I) $K[NbO(C_6H_2(OH)(O_2)(COO)C_3H_7)_2]2(PTB)\cdot 3H_2O$

The above structure of dichelate (I) resulted from elemental and functional group analyses as well as other analytical procedures. Thermal analyses (Fig. 6) showed the presence of three water groups of hydration and two PTB's of crystallization. Dislocation of the waters of hydration and PTB's of crystallization without breaking down of the binuclear chelate might be a good evidence for their being interstitially present as lattice molecules uncoordinated to the central atom.

Like its congeners in the transition series, niobium formed the oxoniobium radical. The ability of that radical to form coordinate bonds with ligands could be accounted for through the stretchable double bond. It was shown that NbO had infrared bonds around 1000 cm^{-1}. This property of the Nb=O structure and accordingly the flow of electron density from $p\pi$ of oxygen to $d\pi$ of niobium (niobium has a partially filled 4*d* orbital) might create a π-bond capable of taking up ligands and forming a maximum valence of six and in the case of PTB, having an octahedral geometry.

However, at 356 °C the dichelate (I) decomposed into potassium monoxide, niobium(V) oxide and colourless crystals of unknown sublimate which could not be identified.

The X-ray diffraction pattern of dichelate (I) is given in Fig. 7. The three (*d*) strongest lines for it were 2.60, 2.46, 2.36 Å respectively (Table 8). On plotting the intensity of the diffracted beam as a function of the angle of diffraction a chart peak at 37.7° was obtained (see Fig. 11).

It was worthwhile to see if the dichelate (I) causes any shift in absorption in the niobium atomic spectra. Experiments showed that maximum atomic absorption of the dichelate occurred at 298.3 nm, Fig. 8, whereas equivalent amounts of atomized niobium without chelation absorbed at 290.2 nm. That shift of wavelength could be used for the determination of the metal in the presence of other metals that might interfere before chelation. That was really the case since the interference of tantalum, rhenium, molybdenum, and manganese were avoided because of the different maxima of their absorption wavelength.

Moreover, microcrystalloscopic examinations showed rhombic prismlike crystals. The deep orange colour could be due to the occurrence of moderately strong

TABLE 6

NEUTRON-ACTIVATION ANALYSIS OF STANDARDS AND RESIDUES OBTAINED AT THE VARIOUS HEATING TEMPERATURES OF POTASSIUM METATANTALATE

Sample, irradiated	*Area (counts)*			*Weight (mg)*			*Weight/at.wt. (mg)*			*Atomic ratio K/Ta/O*	*Inference*
	K	*Ta*	*O*	*K*	*Ta*	*O*	*K*	*Ta*	*O*		
K+Ta (standard)	8600	7000		50.0	50.0						
Ta_2O_5 (standard)		11200	5000		80.0	18.20		0.44	1.11	–/2/5	Ta_2O_5
Residue (208 °C)	2503	9403	1658	14.55	67.54	17.88	0.37	0.37	1.11	1/1/3	$KTaO_3$
Residue (1156 °C)		11200	5000		80.00	18.10		0.44	1.10	–/2/5	Ta_2O_5

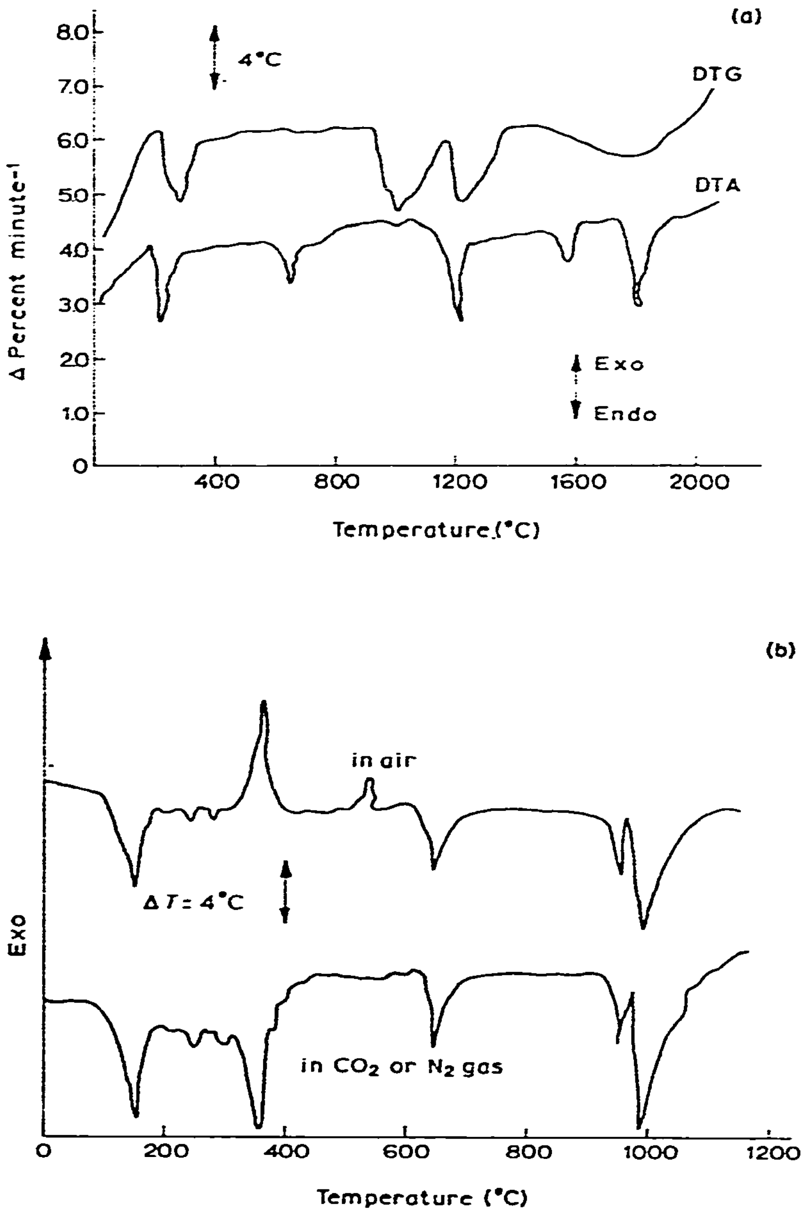


Fig. 6. Differential thermal curves of Nb–PTB.

charge transfer bands within the double bond of the oxoniobium group. A hypothetical explanation for the solubility of dichelate (I) could be as follows. The long chelate molecule folds up in such a way that its negative charge is buried under PTB's of crystallization. Resulting from that distortion Van der Waals forces arise and solvation of the chelate occurs. Strong acid solutions decomposed the chelate; but no hydrogel of niobium(V) oxide was detected. Perhaps the decomposition products contained the acid resistant soluble oxoniobium radical.

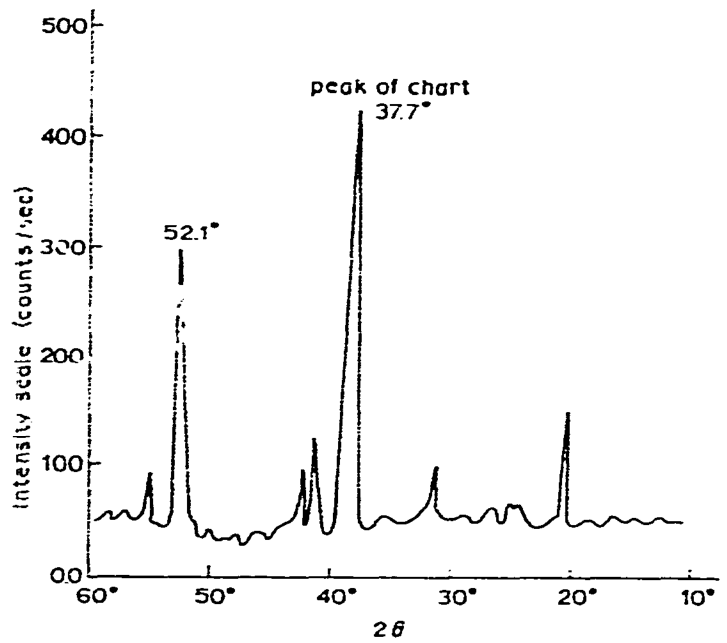


Fig. 7. X-ray emission spectrum of K[NbO(PTB)$_2$]2(PTB)·3H$_2$O.

TABLE 7

X-RAY DIFFRACTION PATTERN OF Nb$_2$O$_3$ PREPARED AT 1100°C IN NITROGEN AND CARBON DIOXIDE GASES

d (Å)	I/I_1	d (Å)	I/I_1
2.17	50	1.09	20
2.15	100	1.03	15
2.02	35	1.01	5
1.85	45	0.950	5
1.75	30	0.910	4
1.37	35	0.812	10
1.34	40		
1.22	10	0.781	14

TABLE 8

X-RAY DIFFRACTION PATTERN OF THE DICHELATE (I)

d (Å)	I/I_1	d (Å)	I/I_1
2.60	28	1.05	7
2.46	34	0.991	19
2.36	100	0.931	15
1.27	23	0.893	8
1.20	13	0.811	8
1.18	5	0.798	9
1.09	6	0.714	5
1.07	3		

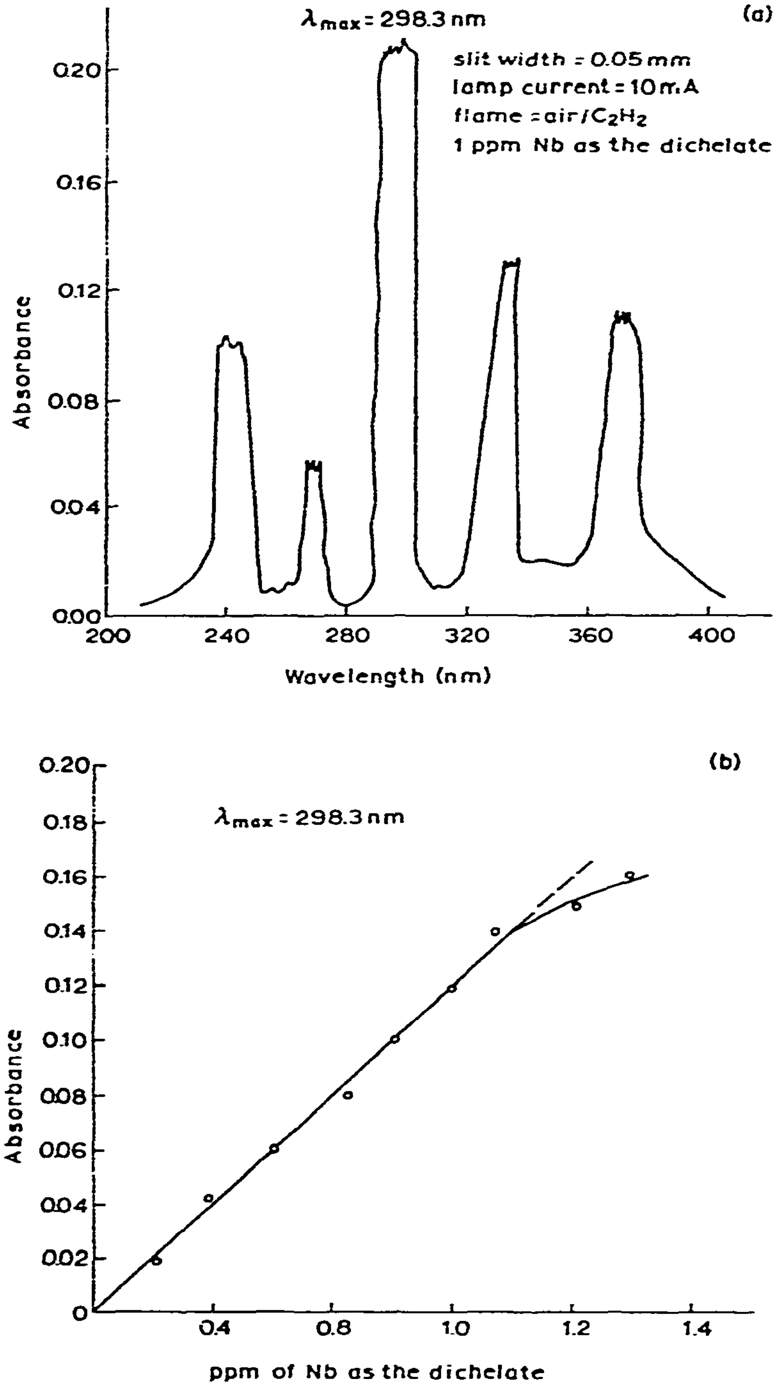


Fig. 8. (a) Atomic absorption spectrum of $K[NbO(PTB)_2]2(PTB)\cdot 3H_2O$ in water–acetone solution, and (b) calibration curve.

It may be said with some certainty that the absence of niobium-to-niobium interaction meant the molecule had a magnetic moment corresponding to one unpaired electron.

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