

## **TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS**

### **XI. Dioxovanadium(V) complexes with aromatic aldehyde thio- and S-methylisothiosemicarbazones**

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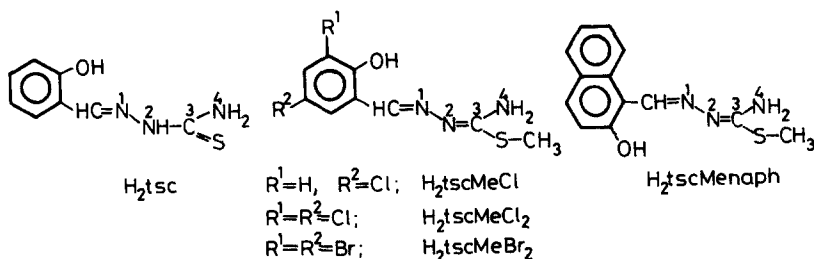
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The thermal decomposition and spectroscopic (reflectance and IR spectra) characterization of the newly synthesized square-pyramidal dioxovanadium(V) complexes of the type  $\text{NH}_4[\text{VO}_2(\text{L})]$  (L is the dianion of the terdentate ligands salicylaldehyde thiosemicarbazone (ONS), halogen-substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde S-methylisothiosemicarbazones (ONN)) are described.

Octahedral bis(ligand) vanadium(III) complexes with terdentate ONS and ONN ligands, salicylaldehyde thio- and S-methylisothiosemicarbazone, respectively, have been described [1, 2]. It has also been shown that in an ammonia-water-ethanol solution of salicylaldehyde S-methylisothiosemicarbazone, V(III) is oxidized to V(V), yielding a square-pyramidal mono(ligand) complex  $\text{NH}_4[\text{VO}_2(\text{L})] \cdot \text{H}_2\text{O}$  [3], where L is the ligand dianion.

The present report describes the synthesis, thermal decomposition, IR and reflectance spectra of some novel dioxovanadium(V) complexes of the general formula  $\text{NH}_4[\text{VO}_2(\text{L})]$ , where L is the dianion of salicylaldehyde thiosemicarbazone, halogen-substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde S-methylisothiosemicarbazones:



## Experimental

### Chemicals and methods

All chemicals used for synthesis were of analytical reagent grade, with the exception of the ligands, which were synthesized according to procedures analogous to those described earlier [4].

The substances for analyses were dried in air. Elemental analysis was carried out by standard micromethods.

IR spectra (KBr pellet) were obtained on a Perkin-Elmer 457 spectrophotometer.

Diffuse-reflection spectra were obtained with an SPM-2 quartz monochromator (VEB Zeiss, Jena) and the reflection cell was of the R-45/0 type. Spectra were taken in the 10000-45000  $\text{cm}^{-1}$  region at room temperature. Samples were prepared to comply with the hypothesis of Kubleka-Munk theory [5], and MgO was used as a white standard.

Thermogravimetric measurements were carried out on a Paulik-Paulik-Erdey derivatograph (MOM, Hungary) in air atmosphere, with  $\alpha\text{-Al}_2\text{O}_3$  as a standard. The mass of the samples was 100 mg. Each sample was heated from room temperature to 1000 $^\circ$ , at a rate of 10 deg/min.

### Synthesis of complexes

#### $\text{NH}_4[\text{VO}_2(\text{tsc})]$

A mixture of 0.80 g (4.0 mmol) of  $\text{H}_2\text{tsc}$  and 0.40 g (4.0 mmol) of  $\text{NH}_4\text{VO}_3$  was treated with 5.0  $\text{cm}^3$  of concentrated aqueous ammonia solution and heated mildly (50 $^\circ$ ) under reflux for 2 h. After filtration, the solution was left to evaporate at room temperature until the volume was reduced to one half. The brown crystals obtained were washed with EtOH and Et $_2$ O. Yield: 0.40 g.

$\text{NH}_4[\text{VO}_2(\text{tscMe})]$  (tscMe = dianion of  $\text{H}_2\text{tscMeCl}$ ,  $\text{H}_2\text{tscMeCl}_2$ ,  $\text{H}_2\text{tscMeBr}_2$  or  $\text{H}_2\text{tscMenaph}$ )

A stoichiometric mixture (2 mmol of each) of  $\text{NH}_4\text{VO}_3$  and the ligand was heated under reflux in 10-15  $\text{cm}^3$  of a  $\text{MeOH} + \text{NH}_3(\text{aq})$  mixture (1:1) for 2-2.5 h. In the cases of  $\text{H}_2\text{tscMeCl}_2$ ,  $\text{H}_2\text{tscMeBr}_2$  and  $\text{H}_2\text{tscMenaph}$ , the dissolution of the reactants was accompanied by the formation of crystals of the complexes, whereas the crystallization of  $\text{NH}_4[\text{VO}_2(\text{tscMeCl})]$  occurred only after cooling of the solution to room temperature. The crystals were washed with  $\text{MeOH}$  and  $\text{Et}_2\text{O}$ . Yields: 50-80 %.

### Results and discussion

It has been shown [1, 6, 7] that in a basic medium salicylaldehyde thiosemicarbazone is coordinated as a dianionic terdentate ON(1)S ligand, formed by deprotonation of the phenolic and thiol groups. Under the same conditions, salicylaldehyde S-methylisothiosemicarbazone is also coordinated as a dianionic terdentate ligand, formed by deprotonation of the phenolic and the N(4)H<sub>2</sub> group, thus having an ON(1)N(4) set of donor atoms [2, 3, 7]. With  $\text{VCl}_3$  or  $\text{NH}_4\text{VO}_3$  in an ammonia-water-ethanol mixture, the latter ligand forms a square-pyramidal cis(dioxo) complex,  $\text{NH}_4[\text{VO}_2(\text{L})] \cdot \text{H}_2\text{O}$  (L = dianion of salicylaldehyde S-methylisothiosemicarbazone); this has been confirmed by X-ray analysis [3, 8]. On the basis of these observations, as well as the results of elemental analysis, molar conductivity measurements (1:1 type of electrolyte [9], Table 1) and other physico-chemical characteristics, it is possible to conclude that in the present case we obtained an analogous cis(dioxo)-vanadate(V) complex of the type  $\text{NH}_4[\text{VO}_2(\text{L})]$ , where L is the ligand dianion (Fig. 1).

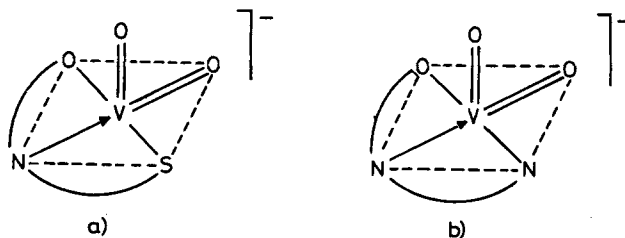


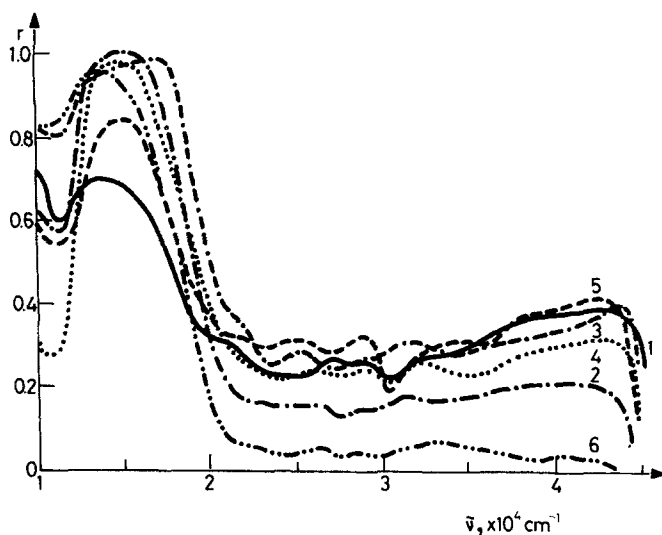
Fig. 1 Square-pyramidal configuration of thiosemicarbazonato (a) and S-methylisothiosemicarbazonato (b) complexes

Table 1 Analytical data and some physical characteristics of the complexes

Complex	Colour	Found (Calcd.), %			N	$\lambda_{M}^*$ , $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	$\nu(\text{VO}_2)$ , $\text{cm}^{-1}$	
		C	H				$\nu_a$	$\nu_s$
$\text{NH}_4[\text{VO}_2(\text{tsc})]$	brown	32.4 (32.6)	3.9 (3.8)		18.7 (19.1)	62.6	920	895
$\text{NH}_4[\text{VO}_2(\text{tscMeCl})]$	orange	31.7 (31.5)	3.5 (3.9)		15.8 (16.3)	58.3	920	900
$\text{NH}_4[\text{VO}_2(\text{tscMeCl}_2)]$	yellow	28.7 (28.6)	3.1 (2.9)		14.6 (14.8)	63.8	935	905
$\text{NH}_4[\text{VO}_2(\text{tscMeBr}_2)]$	orange	23.5 (23.2)	2.4 (2.4)		11.9 (12.0)	63.8	935	895
$\text{NH}_4[\text{VO}_2(\text{tscMenaph})]$	light-brown	44.2 (43.8)	4.4 (4.2)		15.9 (15.6)	62.6	925	885

The presence of the  $\text{VO}_2$  group is indicated by the appearance of the  $\nu_a$  and  $\nu_s$  bands observed in the regions  $935\text{-}920$  and  $905\text{-}885\text{ cm}^{-1}$  of the IR spectrum (Table 1) [3, 8, 10, 11].

It is evident from Fig. 2 that the reflectance curves of all the investigated complexes have a similar pattern. Additionally, these are similar to the re-emission functions observed in studies of the electronic spectra of some similar dioxovanadium(V) compounds [3, 8, 11]. To illustrate this, Fig. 2 shows the  $R(\tilde{\nu})$  for  $[\text{VO}_2(\text{HtscMe})]$ , where HtscMe is the monoanionic form of salicylaldehyde S-methylisothiosemicarbazone [8].



**Fig. 2** Reflection spectra of the complexes:  $\text{NH}_4[\text{VO}_2(\text{tsc})]$  (1),  $\text{NH}_4[\text{VO}_2(\text{tscMeCl})]$  (2),  $\text{NH}_4[\text{VO}_2(\text{tscMeCl}_2)]$  (3),  $\text{NH}_4[\text{VO}_2(\text{tscMeBr}_2)]$  (4),  $\text{NH}_4[\text{VO}_2(\text{tscMenaph})]$  (5) and  $[\text{VO}_2(\text{HtscMe})]$  (6)

As the coordination polyhedra of all these compounds were a deformed square pyramid, the similarity of the re-emission functions suggests the same type of environment in the investigated complexes.

As a consequence of the distortion of the square pyramid, the point group symmetry is lower than  $C_{4v}$ . If it is assumed that the N and O of S-methylisothiosemicarbazone have the same effect on the central ion [8, 11], it can be postulated that the point group is  $C_{2v}$ . Further, as the electronic spectra of  $\text{NH}_4[\text{VO}_2(\text{tsc})]$  are not substantially different from those for the other complexes, it can be assumed that the presence of a sulphur instead of a nitrogen atom does not significantly alter the energy levels

Table 2 Reflection spectral data of the complexes

Complex	Transitions, $\text{cm}^{-1}$						
	$\pi^*_{\text{NO}} \rightarrow a_2$	$\pi^*_{\text{NO}} \rightarrow b_1$	$\pi^*_{\text{NO}} \rightarrow b_2$	IL	$\pi^*_{\text{NO}} \rightarrow 1a_1$	$\pi^*_{\text{NO}} \rightarrow 2a_1$	IL
$\text{NH}_4[\text{VO}_2(\text{tsc})]$	11500	20500	24000	28000	30000	-	45000
$\text{NH}_4[\text{VO}_2(\text{tscMeCl})]$	11200	22000	24000	28000	30000	-	45000
$\text{NH}_4[\text{VO}_2(\text{tscMeCl}_2)]$	11200	21000	24000	28000	30000	34800	45000
$\text{NH}_4[\text{VO}_2(\text{tscMeBr}_2)]$	11000	22000	24000	27500	30000	35000	45000
$\text{NH}_4[\text{VO}_2(\text{tscMenaph})]$	11500	20500	26200	27500	30500	36000	45000

involved in the transitions observed. Hence, the electronic spectra of the all investigated complexes have been interpreted by assuming that the coordination polyhedra have the point group  $C_{2v}$ .

Table 3 The characteristics of thermal decomposition of the complexes

Complex	Effect	Fragment eliminated*	T, K	$\Delta m_{exp}$ , %	$\Delta m_{calc}$ , %
NH <sub>4</sub> [VO <sub>2</sub> (tsc)]	endo	NH <sub>3</sub> + H <sub>2</sub> S	473	16.5	17.4
	exo	Tsc	473-748	22.5	23.1
	exo	Sal + 1/20	748-923	31.5	28.6
		1/2V <sub>2</sub> O <sub>5</sub>	923	29.5	30.9
NH <sub>4</sub> [VO <sub>2</sub> (tscMeCl)]	endo	NH <sub>3</sub> + HCl	383-493	14.5	15.6
	exo	SMe	523	15	13.7
	exo	Tsc	523-793	19	19.6
	exo	Sal + 1/20	793-1000	27	24.6
		1/2V <sub>2</sub> O <sub>5</sub>	1000	24.5	26.5
NH <sub>4</sub> [VO <sub>2</sub> (tscMeCl <sub>2</sub> )]	endo	NH <sub>3</sub> + 2HCl	473	21	23.5
	exo	SMe	553	12	12.3
	exo	Tsc	553-773	18	17.8
	exo	Sal + 1/20	773-973	25	22.3
		1/2V <sub>2</sub> O <sub>5</sub>	973	24	24.1
NH <sub>4</sub> [VO <sub>2</sub> (tscMeBr <sub>2</sub> )]	endo	NH <sub>3</sub>	493	5	3.7
	exo	SMe	553	10	10.1
	exo	Tsc	553-728	15	14.7
	exo	Sal + 1/20 + 2H Br	728-933	49.5	51.9
		1/2V <sub>2</sub> O <sub>5</sub>	933	20.5	19.6
NH <sub>4</sub> [VO <sub>2</sub> (tscMenaph)]	endo	NH <sub>3</sub>	483	5	4.8
	exo	SMe	543	14	13.3
	exo	Tsc	543-748	21	21.2
	exo	Naph	748-978	36	35.3
		1/2V <sub>2</sub> O <sub>5</sub>	978	24	25.4

\*Tsc, Sal and Naph = thiosemicarbazide, salicylaldehyde and naphthalene residue, respectively

Since V(V) is a  $d^0$  system, the spectral bands can be ascribed either to the charge-transfer or to intraligand transitions. The bands appearing in the region 11000-11500  $\text{cm}^{-1}$  (Table 2) can be related to the charge-transfer transition from the ligand  $\pi_{NO}$  orbital to the  $a_2$  vanadium orbital, as observed earlier for other complexes [3, 8, 11]. The probability of this transi-

tion is relatively low and thus the corresponding spectral bands have relatively low intensities.

The broad and very intense spectral band with the saddle in the region 20800-22000  $\text{cm}^{-1}$  corresponds to the transitions from the ligand  $\pi_{\text{NO}}$  orbital to the vanadium  $b_1$  and  $b_2$  orbitals. Its substantial width is a consequence of the relatively poor separation of the  $b_1$  and  $b_2$  orbitals formed by splitting of the  $e$  orbital, accompanied by a decrease in the point group symmetry from  $C_{4v}$  to  $C_{2v}$ .

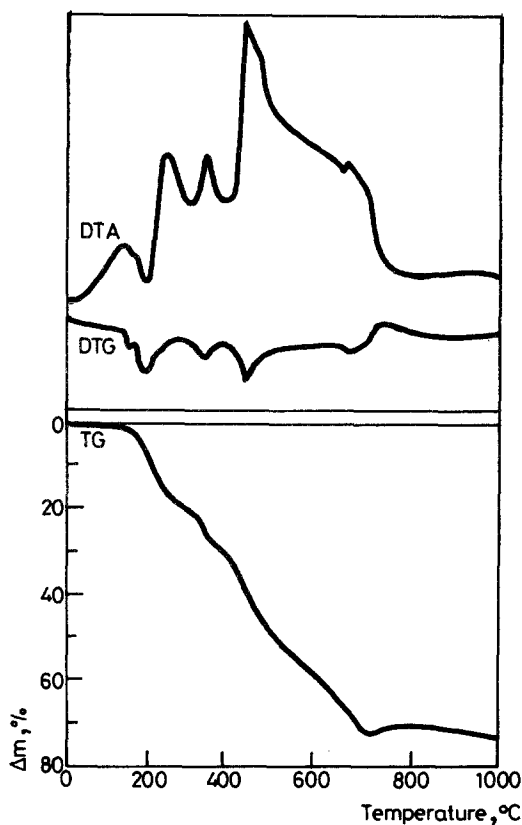


Fig. 3 TG, DTG and DTA curves of  $\text{NH}_4[\text{VO}_2(\text{tsc})]$

The next spectral band in the region 27500-28000  $\text{cm}^{-1}$  is related to intraligand transitions. It should be noted that the position of this band is al-



most the same in the spectra of all the investigated dioxovanadium(V) complexes with similar ligand [3, 8, 11].

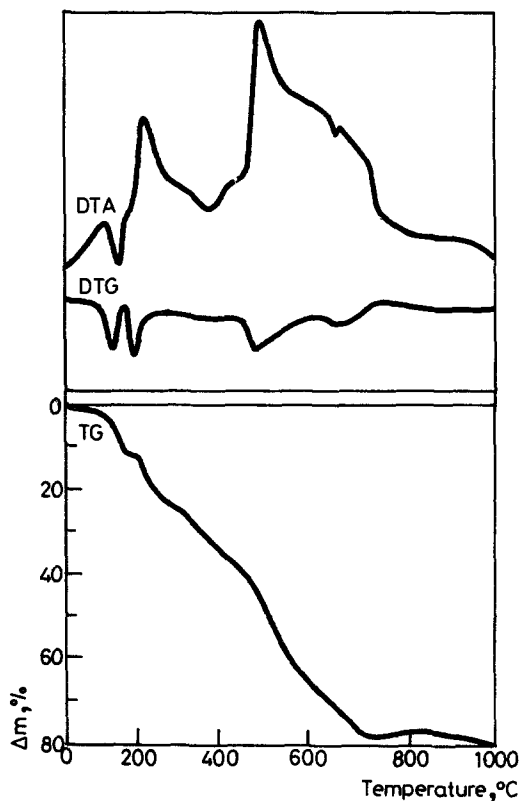


Fig. 4 TG, DTG and DTA curves of  $\text{NH}_4[\text{VO}_2(\text{tscMeCl})]$

The minimum at ca  $30000\text{ cm}^{-1}$  corresponds to the charge transfer  $\pi_{\text{NO}} \rightarrow 1a_1$ .

The band which appears at  $35000\text{--}36000\text{ cm}^{-1}$  in some spectra is probably due to the charge transfer  $\pi_{\text{NO}} \rightarrow 2a_1$ , or to a combination of charge-transfer and intraligand transitions.

The transition observed in the range  $\tilde{\nu} > 45000\text{ cm}^{-1}$  is of the intraligand type.

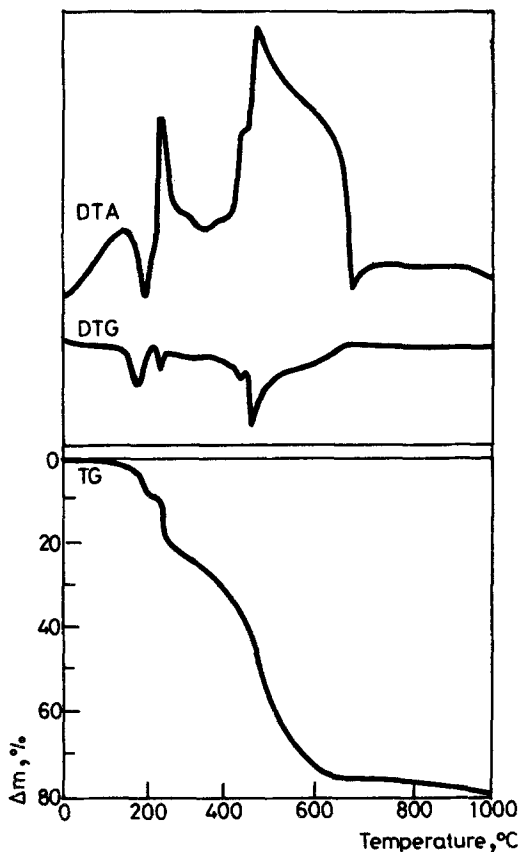


Fig. 5 TG, DTG and DTA curves of  $\text{NH}_4[\text{VO}_2(\text{tscMeCl}_2)]$

### Thermal analysis

The process of thermal decomposition of these compounds is accompanied by several endothermic and exothermic effects (Table 3, Figs 3-7). As can be seen from the DTA curves, the first endothermic peak appears in the range 475-485 K. It can be ascribed either to the elimination of  $\text{NH}_3$  from  $\text{NH}_4[\text{VO}_2(\text{tscMenaph})]$  (Fig. 7) or to the simultaneous evolution of  $\text{NH}_3$  and  $\text{HCl}$  from the complexes containing chlorine (Figs 4 and 5), or of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  from  $\text{NH}_4[\text{VO}_2(\text{tsc})]$  (Fig. 3).

Further heating of the complexes containing the SME group is accompanied by elimination of this group, which is observed as an exothermic

peak in the interval 523-563 K. Exothermic maxima in approximately the same temperature interval have been observed for some other dioxovanadium compounds [8].

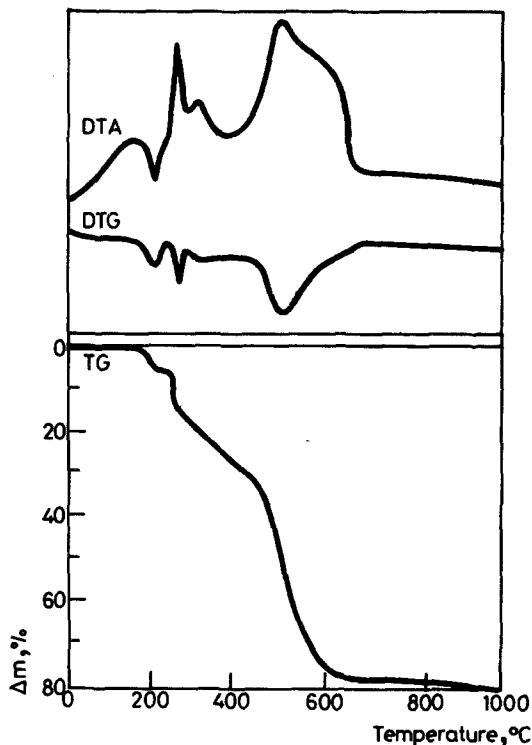


Fig. 6 TG, DTG and DTA curves of  $\text{NH}_4[\text{VO}_2(\text{tscMeBr}_2)]$

The further course of thermal decomposition is accompanied by marked exothermic effects related to elimination of the remaining part of the ligand and oxidation of the vanadium.

It is obvious that the process of thermal decomposition of  $\text{NH}_4[\text{VO}_2(\text{tscMeBr}_2)]$  proceeds in a different way from that of the analogous  $\text{NH}_4[\text{VO}_2(\text{tscMeCl}_2)]$ . The first endothermic effect, at 493 K, is due to the elimination of  $\text{NH}_3$ . The elimination of the SMe group and thiosemicarbazide residue is accompanied by exothermic effects at temperatures close to those observed for the other complexes. However, the two bromine atoms still remain linked to the ligand residue and are eliminated

only the interval 728-933 K. It is possible that in this case two HBr molecules are formed and eliminated, this being accompanied by an endothermic effect, followed by another endothermic effect that is due to elimination of the salicylaldehyde residue and oxidation of the vanadium. The appearance of the subsequent endothermic effect at a decreased content of oxidizing components means that the resulting exothermic effect in this case is lower than for the chlorine-containing complexes.

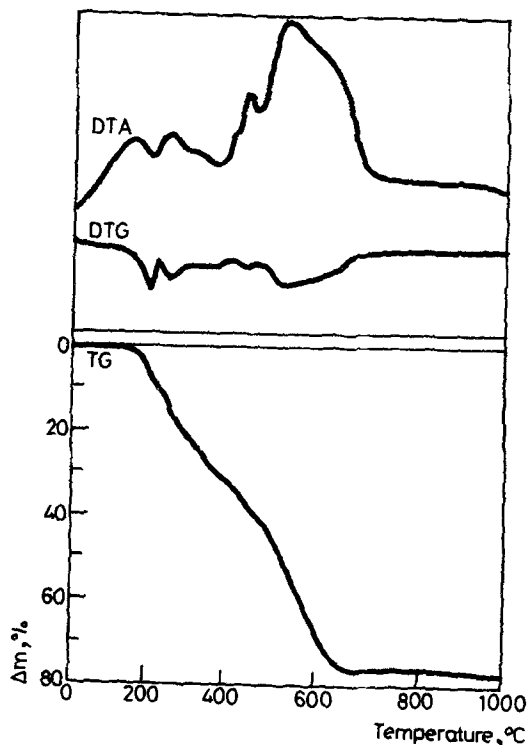


Fig. 7 TG, DTG and DTA curves of  $\text{NH}_4[\text{VO}_2(\text{tscMenaph})]$

The process of thermal decomposition of the complexes is completed at 923 to 1000 K, and the residue is always  $\text{V}_2\text{O}_5$ , as confirmed by X-ray analysis.

## References

- 1 N. V. Gerbeleu, *Zhur. Neorg. Khim.*, 13 (1968) 2467.
- 2 V. M. Leovac, N. V. Gerbeleu and V. D. Canich, *Zhur. Neorg. Khim.*, 27 (1982) 918.
- 3 A. F. Petrovic, B. Ribár, D. M. Petrovic, V. M. Leovac and N. V. Gerbeleu, *J. Coord. Chem.*, 11 (1982) 239.
- 4 Gy. Argay, A. Kálmán, B. Ribár, V. M. Leovac and A. F. Petrovic, *Monatsh. Chem.*, 114 (1983) 1205.
- 5 P. Kubelka and F. Munk, *Z. Tech. Phys.*, 12 (1931) 593.
- 6 M. J. M. Campbell, *Coor. Chem. Rev.*, 15 (1975) 279.
- 7 V. M. Leovac, L. Bjelica and Lj. Jovanovic, *Polyhedron*, 4 (1985) 233.
- 8 A. F. Petrovic, V. M. Leovac, B. Ribár, Gy. Argay and A. Kálmán, *Transition Met. Chem.*, 11 (1986) 207.
- 9 W. J. Geary, *Coord. Chem. Rev.*, 7 (1971) 81.
- 10 W. P. Griffith and T. D. Wickins, *J. Chem. Soc., (A)*, (1968) 400.
- 11 V. M. Leovac and A. F. Petrovic, *Transition Met. Chem.*, 8 (1983) 337.

**Zusammenfassung** — Es wird die thermische Zersetzung und spektroskopische Charakterisierung (Reflexionsvermögen und IR-Spektren) neu synthetisierter Dioxovanadium(V)-Komplexe der allgemeinen Formel  $\text{NH}_4[\text{VO}_2(\text{L})]$  beschrieben, wobei L das Dianion des dreizahnigen Liganden Salicylaldehyd-thiosemicarbazon (ONS), halogensubstituiertes Salicylaldehyd- bzw. 2-Hydroxy-1-naphthaldehyd-S-methyl-isothiosemicarbazon (ONN) ist.