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THERMAL AND SPECTROSCOPIC STUDY OF THE COMPLEXES FORMED BETWEEN *N*-PHENYL-*O*-ACETYL-MANDELOHYDROXAMIC ACID AND VANADIUM(V)

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ABSTRACT

The solid complexes formed between *N*-phenyl-*O*-acetyl-mandelohydroxamic acid (*N*-PAMHA) and vanadium(V) obtained in hydrochloric acid ($10^{-2.3}$ M and 4.8 M) and sulphuric acid (0.9 M in the presence of 10^{-3} M SCN^-) have been studied. The stoichiometries found were HVO_2:2(*N*-PAMHA):HCl (I); VO: 2(*N*-PAMHA):2HCl (II); and VO:2(*N*-PAMHA): SCN (III) respectively. Their thermal behaviour was studied by TG and IR spectroscopic techniques.

INTRODUCTION

Hydroxamic acids form complexes with vanadium(V) in strong and weak acidic media [1–4]. The absorption maxima for these complexes have been found to be about 440 nm for pH values between 1 and 6. The corresponding stoichiometries calculated by UV–VIS spectrophotometric methods are 2R : V(V) in all cases [5,6].

Mixed ligand complexes forming in acidic media between vanadium(V), several hydroxamic acids and some anions, such as Cl^- [7,8], NO_3^- [9], SCN^- [10,11] and $C_2O_4^{2-}$ [12], have been described. *N*-PAMHA forms this kind of complex in solution with vanadium(V), and includes one or two molecules of hydrogen chloride (for solutions with pH 2.3 and 4.8 M HCl

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respectively) or one group of thiocyanate (from a 0.9 M sulphuric acid and 10^{-3} M SCN^- solution).

We have previously [13] studied the solid complexes formed between *N*-PAMHA and several divalent metallic cations. The present work gives the results obtained in the studies of the solid complexes vanadium(V)–*N*-PAMHA prepared by the authors, using TG, DTG and IR spectroscopic techniques, as well as elemental analysis.

EXPERIMENTAL

Materials

All the reagents used were of analytical quality. *N*-PAMHA was synthesized by reaction between acetylmandelic acid chloride and *N*-phenylhydroxylamine in a bicarbonated medium, according to the general method described by Gupta and Tandon [14].

The solid complexes were prepared by mixing 25 ml portions of a 5×10^{-3} M *N*-PAMHA chloroformic solution with 25 ml of each of the following aqueous 2×10^{-2} M solutions of the cation V(V): in $10^{-2.3}$ M HCl (**I**); in 4.8 M HCl (**II**); and in 0.9 M H_2SO_4 in the presence of 10^{-3} M SCN^- (**III**). In every case, the organic layer was separated after shaking for 15 min, the solvent was evaporated at reduced pressure and the solid was dried over anhydrous Na_2SO_4 in vacuum. Analytical data are given in Table 1.

Apparatus

Elemental analyses were carried out at the Instituto de Química Biorgânica de Barcelona.

The thermal studies were carried out on a Mettler TA 3000 System with a Mettler TG 50 thermobalance. TG curves were obtained at a heating rate of

TABLE 1

Elemental analysis data

Compound [a]	C (%)		H (%)		N (%)	
	Calc.	Found	Calc.	Found	Calc.	Found
N-PAMHA	67.35	67.88	5.29	5.34	4.90	4.96
$HVO_2:2R:HCl$	56.07	54.78	4.23	4.47	4.05	3.99
VO:2R:2HCl	54.46	54.01	4.25	4.39	3.94	3.80
VO:2R:SCN	57.35	58.27	4.05	4.13	6.03	5.98

[a] *N*-PAMHA = *N*-Phenyl-*O*-acetyl-mandelohydroxamic acid, $C_{16}H_{15}NO_4$.
R = $C_{16}H_{14}NO_4$.

10 °C min^{-1} in a static air atmosphere, using samples of weights between 8.00 and 13.00 mg. The studied temperature range was from 40 to 600 °C.

IR spectra were made on a Perkin-Elmer 297 Spectrophotometer using KBr pellets prepared with the solid complexes.

RESULTS AND DISCUSSION

The solid *N*-PAMHA-vanadium(V) complexes obtained have stoichiometries 2*N*-PAMHA : VO_2H : HCl (I), 2*N*-PAMHA : VO : 2HCl(II) and 2*N*-PAMHA : VO : SCN (III), as shown in Table 1. The complexes crystallize without any solvent, neither water nor chloroform, molecules of crystallization or coordination.

The complexes are less stable thermally than *N*-PAMHA itself, see Fig. 1 and Table 2.

Complex **I** has its first mass loss between 100 and 160 °C, corresponding to one molecule of HCl (calculated, 5.25%; found, 4.39%). Further mass losses are observed between 160 and 350 °C, and 425 and 525 °C, corresponding to 63.0% and 22.0% respectively. V_2O_5 is formed above 525 °C (calculated, 13.19%; residue found, 10.54%).

Complex **II** is stable below 120 °C and shows a first mass loss between 120 and 150 °C (11.0%), the calculated loss for 2 molecules of HCl being

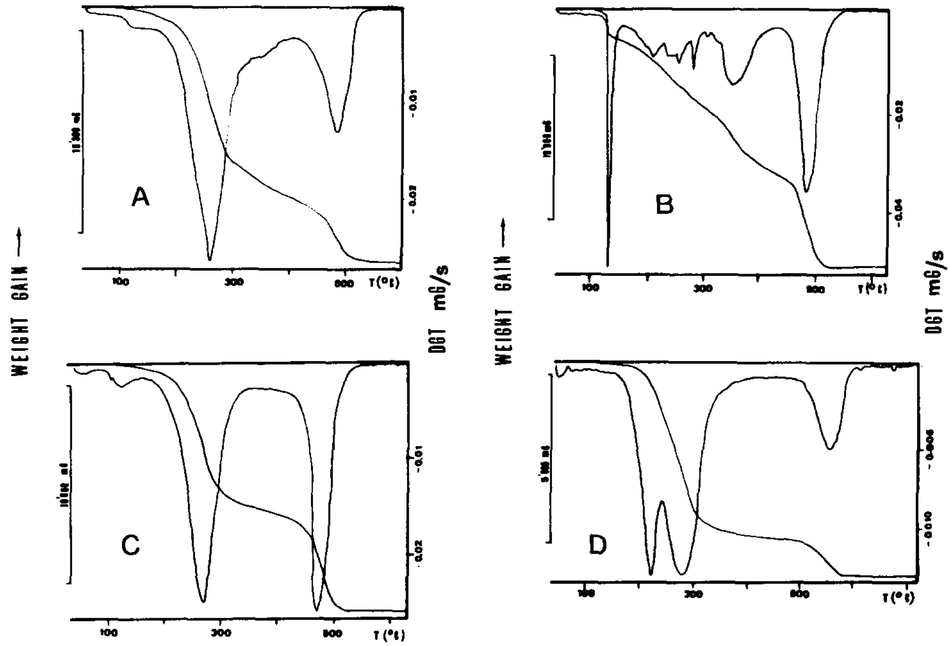


Fig. 1. TG curves of: A, HVO_2:2R:HCl; B, VO:2R:2HCl; C, VO:2R:SCN; and D, *N*-PAMHA.

TABLE 2

TG data

Compound [a]	Temperature range (°C)	Process	Mass loss (%)		Residue (%)	
			Calc.	Found.	Calc.	Found.
I	100–160	-HCl	5.25	4.39		
	160–350		63.03			
	425–525		22.04			
	> 525	V_2O_5			13.19	10.53
II	120–160	-2HCl	10.29	11.00		
	160–425		45.99			
	425–525		31.87			
	> 525	V_2O_5			12.83	11.14
III	100–150		4.45			
	200–350		50.10			
	450–525		35.80			
	> 525	V_2O_5			13.11	9.64

[a] I = HVO_2 : 2R : HCl.
II = VO : 2R:2HCl.
II = VO : 2R:SCN.

10.3%. The complex decomposes at approximately 525 °C. The residual mass corresponds to the formation of V_2O_5 (calculated, 12.83%; found, 11.14%).

Complex **III** decomposes in three steps: 100–150, 200–350 and 450–525 °C, with loss percentages of 4.4, 50.1 and 35.8%. V_2O_5 is formed above 525 °C (calculated, 13.11%; found, 9.64%).

The IR data (Table 3) show a strong absorption at 1640 cm^{-1} for the free acid, this band being assigned to C=O stretching, which shifts toward lower wavelengths in the studied complexes (1670–1690 cm^{-1}). (The band corresponding to C=O of acetate groups appears, as expected, in every case at 1750 cm^{-1}.)

A band between 930 and 950 cm^{-1} assigned to the double bond V=O [15] is observed in all the complexes but does not appear in the free *N*-PAMHA.

TABLE 3

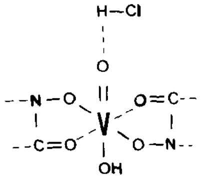
IR absorption bands (cm^{-1})

Compound [a]	O–H	O–H	SCN	C=O acetate	C=O amido	C–N	N–O	V=O
N-PAMHA	–	3180	–	1740	1640	1380	960	–
HVO_2 : 2R : HCl	3350	–	–	1750	1685	1385	980	950
VO : 2R : 2HCl	3350	–	–	1755	1690	1380	980	935
VO : 2R : SCN	–	–	2040	1750	1670	1385	970	935

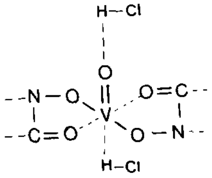
[a] *N*-PAMHA = *N*-Phenyl-*O*-acetyl-mandelohydroxamic acid = $C_{16}H_{15}NO_4$.
R = $C_{16}H_{14}NO_4$.

It can be observed in complex **I** as a sharp medium band at 3350 cm^{-1} assigned to the free -OH vibration (of the V-OH group). In the spectrum of complex **III**, a weak band appears at 2040 cm^{-1} which can be assigned to SCN$^-$ although it is shifted from its usual position (2350 cm^{-1}), probably because it is in an anionic form.

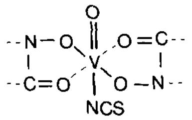
On these bases, we propose the following structural formulae for the complexes.



(I)



(II)



(III)

REFERENCES

1 V.K. Gupta and S.G. Tandon, Anal. Chim. Acta, 66 (1973) 39.
2 U. Tandon and S.G. Tandon, J. Indian Chem. Soc., 46 (1969) 983.
3 D.G. Bhura and S.G. Tandon, Anal. Chim. Acta, 53 (1971) 379.
4 B.S. Chandravanshi and V.K. Gupta, Croatica Chem. Acta, 51 (1978) 107.
5 D.E. Ryan, Analyst, 85 (1960) 569.
6 J.P. Shukla, Rev. Roum. Chim., 27 (1982) 751.
7 I. Kojima and Y. Miwa, Anal. Chim. Acta, 83 (1976) 329.
8 F. Salinas, J.L. Martinez-Vidal and J.L. Pino, Ann. Chim., 77 (1987) 683.
9 F. Freniche, Tesina de Licenciatura, Univ. de Granada, 1989.
10 M. Assefa and B. Chandravanshi, Microchim. Acta, 13 (1983) 255.
11 S. Bag, A. Chatterjee, A. Chakrabarti and D. Chakraborty, Talanta, 29 (1982) 526.
12 J.L. Martinez-Vidal, E. Gonzalez Pradas, M. Villafranca and F. Salinas, Bull. Soc. Chim. Belg., 94 (1985) 401.
13 F. Salinas, J.L. Martinez-Vidal and D. Cervantes Ocaña, Thermochim. Acta, 158 (1990) 277.
14 V.K. Gupta and S.G. Tandon, J. Indian Chem. Soc., 48 (1971) 753.
15 A. Doadrio Lopez and M. Frutos, An. Quim., 74 (1978) 1470.