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Thermal behavior of some vanadyl complexes with flavone derivatives as potential insulin-mimetic agents

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Abstract Two new complexes having general formula $VOL_2 \cdot nH_2O$ [(**1**) L: 5-hydroxyflavone, $n = 1$; (**2**) L: chrysin, $n = 4$] were synthesized and characterized. Based on IR and electronic data we concluded that studied flavones act as bidentate ligands in complexes with metallic ion coordinated in a square-pyramidal stereochemistry. The thermal analysis (TG, DTA) elucidated the composition and also the number and nature of the water molecules. The thermal behavior also indicated strong interactions between oxovanadium (IV) and these oxygen donor ligands.

Keywords Flavone derivative · Vanadyl(IV) complex · Thermal stability

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Introduction

Flavonoids belong to a large group of naturally occurring pigments present in seeds, fruit skin, peel, and bark of plants and represent a common constituent of the human diet [1].

These natural products stimulate or inhibit a wide variety of enzyme and display various biological effects as antioxidant [2–5], antitumor [6–11], anti-inflammatory and anti-allergic [12–17], antibacterial [18, 19], antiviral [20–22], anti-atherosclerotic [23–25], anti-thrombogenic [26, 27], anti-angiogenic [28, 29], and anti-osteoporotic [30, 31].

The flavonoid nucleus (Fig. 1a) consists of benzo-γ-pyrone (an aromatic A-ring fused to a heterocyclic C-ring) attached through a single carbon–carbon bond to an benzene B-ring with hydroxyl, carbonyl, sugar, or methyl groups are attached to this base structure. Flavonoids can be divided into six subclasses depending on the variations in the heterocyclic C-ring: flavones, flavonols, flavanones, flavanols, anthocyanidins, and isoflavones [32]. Flavones show a double bond between C_2 and C_3 and a carbonylic carbon atom at C_4. Unlike flavonols, the flavones do not contain a hydroxyl group at C_3, but may contain hydroxyl groups at C_5 or C_5 and C_7 as in the case of 5-hydroxyflavone (Primuletin) (Fig. 1b) and 5,7-dihydroxyflavone (chrysin) (Fig. 1c). Both molecules possess chelating properties due the 5-hydroxy and the 4-carbonyl groups in the C ring.

The chelating properties of 5-hydroxyflavone in different solutions were studied toward some cations like Al(III) [33–36], Zn(II) [37], and Pb(II) [38]. Few solid complexes with Co(II), Ni(II), Cu(II), V(III), and Fe(III) are reported [39]. For chrysin, the chelation process in solution has been studied also, the cations involved being Al(III) [40, 41],

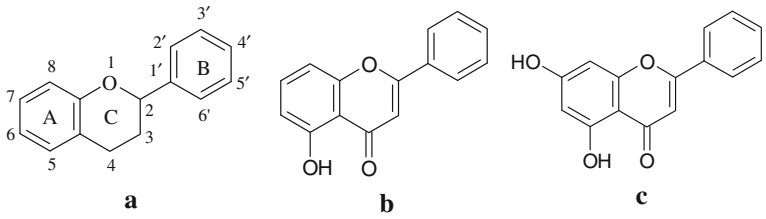


Fig. 1 **a** Base structure of flavonoids; **b** structure of 5-hydroxyflavone; **c** structure of chrysin

and Fe(III) [42, 43]. The interest for isolation of solid complexes of chrysin has greatly increased in view to enhance their anticancer properties. Complexes with Zn(II), Ti(IV), and Zr(IV) [44] have been isolated, but the more studied were the complexes with trivalent cations like Al(III), Ga(III), In(III) [45], and the lanthanides Y(III) [46], La(III) [47], Tb(III), Ho(III), Er(III), and Yb(III) [48].

This article adds to the studies regarding to obtain the new complexes of flavones with potential biological activity. Two new solid compounds of oxovanadium (IV) with 5-hydroxyflavone and chrysin were obtained. The composition of complexes was established by elementary and thermogravimetric analysis and their structures were proposed based on the results of visible and infrared spectroscopy.

Experimental

Materials and methods

All chemicals were purchased from Sigma-Aldrich or Acros Organics, reagent grade and were used without further purification.

The chemical analyses were performed on a Perkin Elmer PE 2400 analyser (for C, H, N, S) and a Shimadzu AA 6300 spectrometer (for V).

The IR spectra were recorded in KBr pellets with a FT-IR VERTEX 70 (Bruker) spectrometer in the range 400–4000 cm^{-1}.

Electronic spectra by diffuse reflectance technique, with Spectralon as standard, were recorded in the range 200–1000 nm on a Jasco V 670 spectrophotometer.

The heating curves (TG and DTA) were recorded using a Labsys 1200 SETARAM instrument, with a sample mass of 12–30 mg over the temperature range of 30–900 °C, using a heating rate of 10 K min^{-1}. The measurements were carried out in synthetic air atmosphere (flow rate 16.66 cm^3 min^{-1}) by using alumina crucibles.

The X-ray powder diffraction patterns were collected on a DRON-3 diffractometer with a nickel filtered Cu K_α radiation ($\lambda = 1.5418$ Å) in a 2θ range of 5–70°, a step width of 0.05° and an acquisition time of 2 s on each step.

Synthesis of the complexes and spectral data

*Synthesis of 5-hydroxyflavone complex (**1**)*

Complex (**1**) was prepared by the addition of a methanolic solution (15 mL) of 5-hydroxyflavone (0.4 mmoles, 113 mg), deprotonated with KOH (0.4 mmoles, 22 mg), to a methanolic solution (10 mL) of $VOSO_4$ (0.2 mmoles, 50.6 mg $VOSO_4 \cdot 5H_2O$). The reaction mixture was refluxed for 3 h. The green product formed was filtered off, washed with methanol, and dried in air. Analysis, found: V, 8.48; C, 59.65; H, 3.40%; calculated for $VC_{30}H_{20}O_8$: V, 8.42; C, 59.56; H, 3.34%.

*Synthesis of chrysin complex (**2**)*

2.23 g (8.2 mmoles) of chrysin monohydrate was dissolved in 50 cm^3 of distilled water containing a few KOH platelets. To the resulting solution, a saturated solution of $VOSO_4 \cdot 5H_2O$ (in the molar ratio VO:ligand 1:2) was added drop wise, under continuous stirring. After the pH was adjusted to ~ 6 with H_2SO_4 1 M, a brown-yellow solid precipitated immediately. The sparingly soluble product was filtered off through a fritted glass funnel, washed several times with water, and dried in desiccator over $CaCl_2$. Analysis, found: V, 7.91; C, 55.53; H, 4.03%; calculated for $VC_{30}H_{26}O_{13}$: V, 7.89; C, 55.82; H, 4.07%.

Results and discussion

Physico-chemical characterization of complexes

In this article, we report the preparation and physico-chemical characterisation of some complexes with flavones as 5-hydroxyflavone ($C_{15}H_9O_3$) (L^1) and chrysin ($C_{15}H_9O_4$) (L^2) (Fig. 1).

The major goal of this article was to evidence the thermal behavior of complexes resulted from the reactions of these flavones with $VO(SO_4) \cdot 5H_2O$. The complexes have been formulated on the basis of chemical analysis, IR, and electronic spectra as follows:

$VO(C_{15}H_9O_3)_2(H_2O)$ or $VO(L^1)_2(H_2O)$ (1)

$VO(C_{15}H_9O_4)_2(H_2O)_4$ or $VO(L^2)_2(H_2O)_4$. (2)

The IR spectra of complexes exhibits the characteristic patterns of flavones (Table 1) that generate bands about 3100 ($\nu(OH)_{phenol}$), 1630 ($\nu(C{=}O)$) and 1270 cm^{-1} ($\nu(C–O–C)$).

The band assigned to the carbonyl group is shifted to lower wavenumbers comparing with that of free ligand as a proof of its coordination. Supplementary bands at 984 cm^{-1} are assigned to the $\nu(V{=}O)$ stretching mode. The presence of water molecule in complexes could be responsible for the appearance of a large band in the 3300–3450 cm^{-1} range assigned to $\nu(OH)$ stretching vibrations [49]. Moreover, the new band that appears around 530 cm^{-1} can be assigned to the $\nu(V–O)$ stretching mode. In Fig. 2, the IR spectra of 5-hydroxyflavone and its oxovanadium (IV) complex are presented comparatively.

The solid-state *d–d* spectra of complexes show the characteristic bands of VO^{2+} in a square-pyramidal environment. It is known that vanadium complexes containing V=O moiety show electronic spectra which are distinct from other vanadium (IV) compounds [50]. The explanation consists in the strong axial perturbation determined by the axial V=O group leading to a lower symmetry of complexes (C_{2v}). As a consequence, the degeneracy of the *e* ($dx^2 - y^2$, dz^2) orbitals is removed leading to supplementary transitions. Table 2 contains the absorption maxima and their assignments based on literature data [50, 51], and Fig. 3 displays UV–Vis spectra of 5-hydroxyflavone and VO(5-hydroxyflavone)$_2(H_2O)$ comparatively.

On the basis of all discussed data the proposed coordination for the complexes is as it follows (Fig. 4):

Table 1 IR data for the free ligands and its oxovanadium (IV) complexes (cm^{-1})

L^1	$VO(L^1)_2(H_2O)$	$L^2 \cdot H_2O$	$VO(L^2)_2(H_2O)_4$	Assignments
–	3435m	3431m	3369br	$\nu(H_2O)$
3059s	–	3085m	3087m	$\nu(OH)_{phenol}$
1654vs	1628vs	1653vs	1634vs	$\nu(C{=}O)$
1587s	1577s	1556s	1533m	$\nu(C{=}C)$
1256s	1271s	1246m	1246m	$\nu(C–O–C)$
–	984s	–	984m	$\nu(V{=}O)$
–	530m	–	522m	$\nu(V–O)$

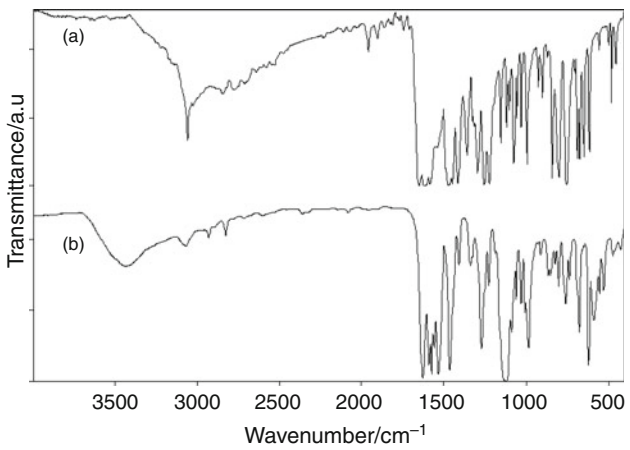


Fig. 2 IR spectra of $C_{15}H_9O_3$ (*a*) and $VO(C_{15}H_9O_3)_2(H_2O)$ (*b*)

Thermal behavior of complexes

The results concerning the thermal decomposition/degradation of the new complexes are presented as it follows.

Thermal decomposition of $VO(C_{15}H_9O_3)_2(H_2O)$

The TG and DTA curves corresponding to the complex (**1**) heated in the 30–900 °C temperature range are presented in Fig. 5.

The thermal decomposition of $VO(C_{15}H_{10}O_3)_2(H_2O)$ (**1**) occurs in three, well-defined steps (Table 3). The first step,

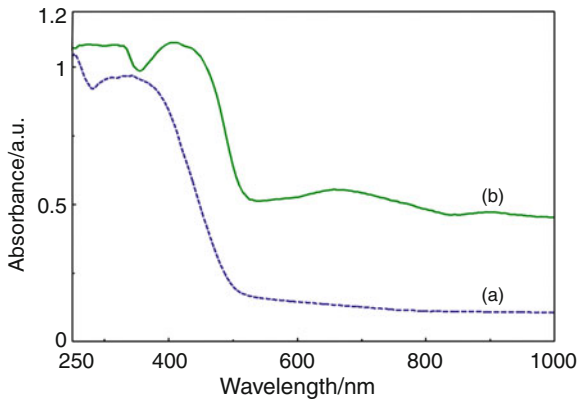
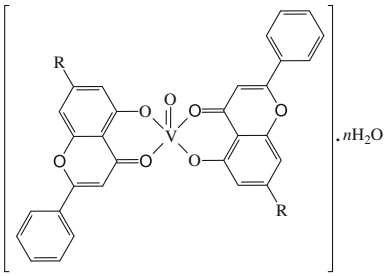


Fig. 3 UV–Vis spectra of $C_{15}H_9O_3$ (*a*) and $VO(C_{15}H_9O_3)_2(H_2O)$ (*b*)

Table 2 Electronic data for complexes (nm)

Complexes	Band I $^2B_2$ (d_{xy}) → ^2E (d_{xz}, d_{yz})	Band II $^2B_2$ (d_{xy}) → $^2B_1$ (dx^2-y^2)	Band III $^2B_2$ (d_{xy}) → $^2A_1$ (dz^2)
1	900	665	410
2	861	679	388



(1) R = H; $n = 1$
(2) R = OH; $n = 4$

Fig. 4 The proposed coordination for complexes

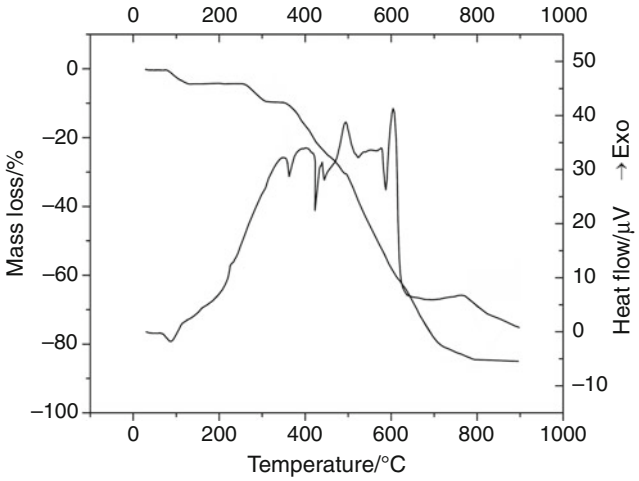


Fig. 5 TG and DTA curves of $VO(C_{15}H_9O_3)_2(H_2O)$

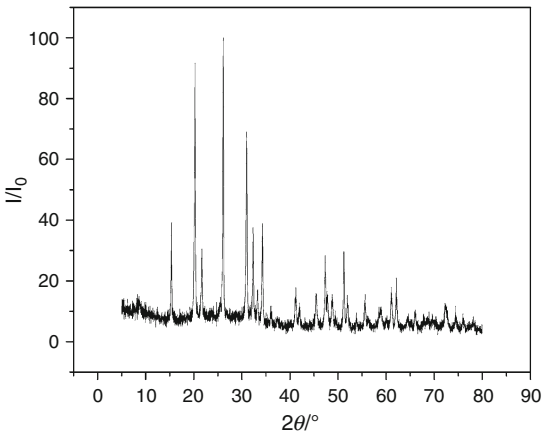


Fig. 6 Powder X-ray diffraction pattern for residue

which is endothermic, corresponds to the loss of water molecule. The reaction proceeds with a maximum rate at 80 °C. Taking in consideration the hard acid nature of VO^{2+} ion and in consequence the existence of strong bonds with hard donors as oxygen atoms the low temperature corresponding to this transformation can be associated with the nature of water as for crystallisation [52–54]. The resulted anhydrous compound is stable in a large area of temperature (130–250 °C), which demonstrates a high bonding strength and a great stability of compound. This decomposes after 250 °C, first losing the benzene molecule from 5-hydroxyflavone (the benzene can be eliminated as it is or its oxidative degradation may occur, its boiling temperature being b.p. 80 °C). This step is a complex one being an overlap of at least two oxidative processes as DTA curve indicates.

The third step, an exothermic one, corresponds to the oxidative degradation of the remaining organic component consisting in two or three processes not well defined (as both TG and DTA indicate). The final product is V_2O_5 shcherbinaite modification (ASTM 41-1426) as XRD reveals (Fig. 6) (found/calcd. overall mass loss: 83.7/83.7).

Thermal decomposition of $VO(C_{15}H_9O_4)_2(H_2O)_4$

Thermal analysis for (**2**) has confirmed the number and the nature of water molecules. Thus, the first step corresponds to the four water molecules elimination in as an endothermic process (Fig. 7). Based on the low temperature corresponding to the dehydration process, it could be assumed that the water molecules are also for crystallisation [52–54].

The second step, which is exothermic, corresponds to oxidative degradation of the organic ligand with benzene molecule elimination. The third step corresponds to the

Table 3 Thermal behavior data (in air atmosphere) for the complexes

Complexes	Steps	Thermal effects	Temperature interval/°C	Δm_{exp}/%	Δm_{calc}/%
$VO(C_{15}H_9O_3)_2(H_2O)$ (**1**)	1.	Endothermic	70–130	3.5	3.2
	2.	Exothermic	250–500	27.7	27.9
	3.	Exothermic	500–900	52.5	52.6
	Residue (V_2O_5)			16.3	16.3
$VO(C_{15}H_9O_4)_2(H_2O)_4$ (**2**)	1.	Endothermic	65–140	11.1	11.2
	2.	Exothermic	170–420	24.3	24.2
	3.	Exothermic	420–900	50.6	50.5
	Residue (V_2O_5)			14.0	14.1

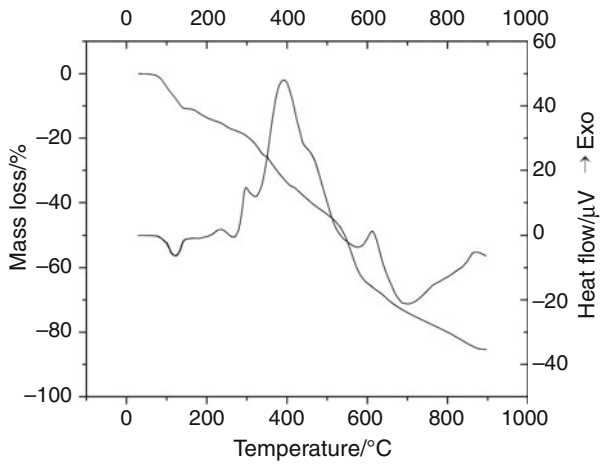


Fig. 7 TG and DTA curves of $VO(C_{15}H_9O_4)_2(H_2O)_4$

oxidative degradation of the remaining intermediate that leads to the V_2O_5 formation as the final product (found/calcd. overall mass loss: 86/85.9). According to both TG and DTA curves profiles this step comprises at least two processes.

Conclusions

The new complexes of oxovanadium (IV) with ligands belong to a class of coordination compounds of current interest for their insulin-mimetic and antitumoral activity have been synthesized and characterized by analytical and spectral investigations. A square-pyramidal stereochemistry for metallic ion was proposed based on the electronic spectra, while the IR spectra features indicated a chelate coordination mode of flavones.

Thermal analysis (TG, DTA) of these complexes elucidated the composition and also the number and nature of the water molecules. It was also evidenced the existence of an intermediate step corresponding to the flavones decomposition with the benzene molecules loss. The final product of thermal decomposition was in all cases V_2O_5 as powder X-ray diffraction indicated.

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