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THERMAL AND STRUCTURAL STUDIES ON THE ADDUCTS OF BIS(β-DIKETONATE) OXOVANADIUM(IV) COMPLEXES WITH ORGANIC BASES

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ABSTRACT

Some new bis(β-diketonate) oxovanadium(IV) adducts with organic bases were prepared and characterized. The structural properties of these compounds were studied using electronic and IR spectroscopies, magnetic susceptibility measurements and analytical data.

Using DTA and TG techniques the degree of thermal stability of these compounds was determined and the loss of one mole of coordinated base was observed in the initial endothermic process. The activation energy and enthalpy of the endothermic process were calculated using DSC techniques.

INTRODUCTION

A thermal and structural study of some bis(β-diketonate) oxovanadium-(IV) adducts with various organic bases is reported. A series of bis(β-diketonate) oxovanadium(IV) adducts with pyridine and monosubstituted or bisubstituted pyridines as base has previously been reported [1–4]. In these studies a relationship was established between the strength of bonding of the base with the vanadium atom and the activation energy, basic character, thermal stability and frequency of vibration ν (V=O) of the IR spectra.

In this work the synthesis of a new series of adducts obtained from 1,3-diphenylpropanedione (dbm) and 1-phenyl-1,3-butanedione (bza) with heterocyclic nitrogen donors possessing different steric requirements is described. The study of these complexes using IR and electronic spectroscopies, magnetic susceptibility measurements and analytical data shows that the stoichiometry of the complex is 2 : 1 (ligand : metal) and that of the adducts is 1 : 1 (base : complex).

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In the thermal study the DTA curves corresponding to the decomposition of the adducts show only a single endothermic peak. The mass loss accompanying the endothermic transition corresponds to the loss of one molecule of the base on the TG curve. By studying the endothermic process using DSC techniques the activation energy and enthalpy were calculated.

The principal objective of this work is to establish a relationship between the basic character of the organic base and the strength of its bonding with the vanadium atom in the adduct formed. This was achieved using IR spectroscopy (which shows a decrease in the ν(V=O) and ν(N $\rightarrow$ V) values of the adducts compared with the complexes) and the activation energy values of the initial endothermic process calculated from the DSC curves.

EXPERIMENTAL

Preparation of compounds

$VO(bza)_2$ and $VO(dbm)_2$ complexes were prepared following the method described previously [5,6].

The adducts were prepared by dissolving 1 g of the $VO(bza)_2$ or $VO(dbm)_2$ complex in 2 ml of organic base. This mixture was heated for 15 min and a brown solid was formed after 24 h at room temperature. This solid was filtered in vacuo, washed with a water and ethanol mixture (1 : 1) and dried over P_4O_{10}.

Materials

1,3-Diphenylpropanedione (dbm), 1-phenyl-1,3-butanedione (bza) and the organic bases were obtained from Merck. The solvents used to prepare the complexes were obtained from Carlo Erba or Merck.

Analytical procedure

Elemental analyses were performed using a Perkin–Elmer model 240B. Vanadium was determined by atomic absorption using a Perkin–Elmer model 430 atomic absorption spectrophotometer after decomposing the compounds with a mixture of concentrated HNO_3 and H_2SO_4 (1 : 1) [7]. The analytical data for the compounds are shown in Table 1.

Magnetic susceptibility

Magnetic susceptibilities were measured by the Gouy [8] method at room temperature using a Mettler H-51 AR balance and a type C Oxford electromagnet. Molar susceptibilities were corrected for the diamagnetism of

TABLE 1

Analytical and magnetic data

Compound	Calculated (%)				Found (%)				μ (BM)
	C	H	N	V	C	H	N	V	
$VO(dbm)_2$	70.11	4.28	–	9.92	70.09	4.25	–	9.89	1.75
$VO(dbm)_2 \cdot$morpholine	67.93	5.16	2.33	8.48	67.89	5.19	2.39	8.48	1.69
$VO(dbm)_2 \cdot$cyclohexylamine	70.51	5.71	2.28	8.31	70.44	5.74	2.32	8.37	1.70
$VO(dbm)_2 \cdot$ethylamine	68.74	5.19	2.50	9.12	68.67	5.11	2.49	9.07	1.71
$VO(dbm)_2 \cdot$piperidine	70.16	5.51	2.33	8.50	70.20	5.55	2.30	8.57	1.73
$VO(dbm)_2 \cdot$pyrrolidine	69.79	5.30	2.39	8.71	69.82	5.35	2.44	8.77	1.69
$VO(bza)_2$	61.64	4.62	–	13.08	61.68	4.67	–	13.12	1.72
$VO(bza)_2 \cdot$morpholine	60.44	5.66	2.93	10.69	60.47	5.69	2.89	10.74	1.73
$VO(bza)_2 \cdot$piperazine	60.57	5.88	5.88	10.71	60.54	5.82	5.90	10.75	1.70
$VO(bza)_2 \cdot$piperidine	63.22	6.11	2.95	10.73	63.18	6.05	3.00	10.77	1.69
$VO(bza)_2 \cdot$pyrrolidine	62.54	5.86	3.04	11.06	62.60	5.90	3.14	11.09	1.71

TABLE 2

IR absorption maxima (cm^{-1}) of compounds

Compound	ν(V=O)	ν_a(V–O)	ν_s(V–O)	δ(O–V–O)	ν(C=C)+ν(C=O)	ν(C–O–V)	ν(N → V)
$VO(dbm)_2$	996	558	373	469	1530	1370	–
$VO(dbm)_2$·morpholine	947	580–565	385	465	1530–1540	1380–1400	340–350
$VO(dbm)_2$·cyclohexylamine	942	560	373	460	1535	1375	335
$VO(dbm)_2$·ethylamine	945	560	375	465	1530–1540	1370	330–340
$VO(dbm)_2$·piperidine	940	570–555	370	465	1530	1370–1390	340
$VO(dbm)_2$·pyrrolidine	945	560	370	465	1528	1372	335
$VO(bza)_2$	1000	574	380	453	1550–1520	1375–1355	–
$VO(bza)_2$·morpholine	955	565	375	445	1500	1320–1330	330
$VO(bza)_2$·piperazine	950	560	366	460	1530	1360	340
$VO(bza)_2$·piperidine	945	560	360	460	1530	1380	340
$VO(bza)_2$·pyrrolidine	925	570–590	380	475	1535	1350	320

the constituent molecules [9,10]. The magnetic moments were calculated according to the formula $\mu = 2.84(\chi'_M T)^{0.5}$ BM, where χ'_M is the corrected molar susceptibility. The values of the magnetic moments are given in Table 1.

IR spectra

The IR spectra were recorded on a Perkin–Elmer recording spectrophotometer (model 283). The samples were run as KBr pellets. The IR absorption peaks for the compounds prepared in this study are listed in Table 2.

Electronic spectra

The electronic spectra of the compounds were recorded in the range 220–1000 nm on a Beckman 5240 recording spectrophotometer using solutions of the complexes in dichloromethane. The results obtained are given in Table 3.

Thermogravimetric analysis

Thermogravimetric measurements were performed using a Mettler HE 20 thermobalance. The analytical constants were as follows: heating rate, 5 °C min^{-1}; TG range, 20 mV; record rate, 20 cm^{-1} h; reference, Al_2O_3; sample mass, 20 mg; thermocouple Pt/Pt–Rh.

The instrument was calibrated using indium as a standard. The analyses were performed in a dynamic nitrogen atmosphere to 300 °C and then in an oxygen atmosphere to 600 °C.

The temperatures of the thermal transitions and the mass loss determinations are shown in Table 4.

Differential scanning calorimetry

Thermal measurements were recorded using a Mettler TA 3000 system with a Mettler differential scanning calorimeter (model DSC 20). Samples of about 5 mg were used to render the degree of temperature non-uniformity within the sample insignificant. An aluminium pan was used under a dry nitrogen atmosphere. The scanning rate was 2 °C min^{-1}. The instrument calibration was checked periodically with standard samples of indium. In all cases several runs were performed and the results are shown in Table 5.

The activation energies were calculated using the procedure of Thomas and Clarke [11,12]. A plot of $\log(dH/dt)$ vs. $1/T$ was obtained from the

TABLE 3

Electronic spectral data

Compound	Solvent	Assignment: ν (cm^{-1}) (ϵ)				
		$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$	Intraligand	
$VO(dbm)_2$	CH_2Cl_2	14705 (75)	16051 (80)	20408 (137)	29850 (84535);	37174 (38401)
$VO(dbm)_2 \cdot$ morpholine	CH_2Cl_2	14601 (84)	16614 (98)	20904 (175)	29897 (49705);	36905 (38040)
$VO(dbm)_2 \cdot$ cyclohexylamine	CH_2Cl_2	14587 (93)	16714 (118)	21040 (184)	29734 (55794);	37410 (40718)
$VO(dbm)_2 \cdot$ ethylamine	CH_2Cl_2	14579 (98)	16975 (123)	21037 (187)	29843 (49237);	37495 (39437)
$VO(dbm)_2 \cdot$ piperidine	CH_2Cl_2	14598 (64)	16556 (82)	20865 (140)	29637 (56704);	37210 (39437)
$VO(dbm)_2 \cdot$ pyrrolidine	CH_2Cl_2	14593 (89)	16794 (117)	29873 (193)	29408 (48687);	37093 (32255)
$VO(bza)_2$	CH_2Cl_2	14815 (66)	16806 (67)	23255 (140)	30303 (51576);	38911 (26531)
$VO(bza)_2 \cdot$ morpholine	CH_2Cl_2	14567 (87)	16998 (123)	22940 (148)	32291 (50497);	36987 (28976)
$VO(bza)_2 \cdot$ piperazine	CH_2Cl_2	14698 (78)	16949 (87)	22988 (223)	33820 (51498);	38979 (34689)
$VO(bza)_2 \cdot$ piperidine	CH_2Cl_2	14643 (89)	16947 (103)	23149 (153)	32348 (51341);	35947 (28743)
$VO(bza)_2 \cdot$ pyrrolidine	CH_2Cl_2	14498 (98)	17048 (115)	23289 (203)	29543 (52567);	37009 (32347)

TABLE 4

Thermal data for the decomposition of $VO(bza)_2$ and $VO(dbm)_2$ adducts

Compound	Temperature (°C)	$\Delta m/m$		Process	Identified compound
		Calculated (%)	Found (%)		
$VO(dbm)_2$	220–500	82.28	81.95	Exothermic	V_2O_5
$VO(dbm)_2 \cdot$ morpholine	106–179	14.50	14.46	Endothermic	$VO(C_{15}H_{11}O_2)_2$
	205–565	82.28	82.10	Exothermic	V_2O_5
$VO(dbm)_2 \cdot$ cyclohexylamine	102–162	16.18	16.02	Endothermic	$VO(C_{15}H_{11}O_2)_2$
	210–560	82.28	81.98	Exothermic	V_2O_5
$VO(dbm)_2 \cdot$ ethylamine	112–177	8.07	8.12	Endothermic	$VO(C_{15}H_{11}O_2)_2$
	215–545	82.28	82.38	Exothermic	V_2O_5
$VO(dbm)_2 \cdot$ piperidine	98–157	14.22	14.17	Endothermic	$VO(C_{15}H_{11}O_2)_2$
	200–540	82.28	81.99	Exothermic	V_2O_5
$VO(dbm)_2 \cdot$ pyrrolidine	105–167	12.16	12.08	Endothermic	$VO(C_{15}H_{11}O_2)_2$
	200–530	82.28	82.23	Exothermic	V_2O_5
$VO(bza)_2$	240–575	76.64	76.57	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ morpholine	104–174	18.28	18.21	Endothermic	$VO(C_{10}H_9O_2)_2$
	235–560	76.64	76.60	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ piperazine	94–158	18.11	18.15	Endothermic	$VO(C_{10}H_9O_2)_2$
	235–590	76.64	76.67	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ piperidine	82–142	17.94	17.89	Endothermic	$VO(C_{10}H_9O_2)_2$
	210–580	76.64	76.68	Exothermic	V_2O_5
$VO(bza)_2 \cdot$ pyrrolidine	102–170	15.44	15.48	Endothermic	$VO(C_{10}H_9O_2)_2$
	225–570	76.64	76.61	Exothermic	V_2O_5

TABLE 5

IR and kinetic data for $VO(bza)_2$ and $VO(dbm)_2$ adducts

Compound	ν(V=O) (cm^{-1})	ν(V–N) (cm^{-1})	Temperature (°C) [a]			ΔH (kcal mol^{-1})	E_A (kcal mol^{-1})	pK_b [b]
			T_i	T_p	T_f			
$VO(dbm)_2$	996	–	–	–	–	–	–	–
$VO(dbm)_2$·morpholine	947	340–350	106	164.5	179	17.1	24.30	5.67
$VO(dbm)_2$·cyclohexylamine	942	335	102	149.6	162	16.8	22.90	3.34
$VO(dbm)_2$·ethylamine	945	330–340	112	161.5	177	17.5	23.87	3.19
$VO(dbm)_2$·piperidine	940	340	98	143.7	157	17.9	23.56	2.87
$VO(dbm)_2$·pyrrolidine	945	335	105	159.0	167	16.9	22.46	2.73
$VO(bza)_2$	1000	–	–	–	–	–	–	–
$VO(bza)_2$·morpholine	955	330	104	156.0	174	15.8	19.58	5.67
$VO(bza)_2$·piperazine	950	340	94	142.7	158	16.8	23.40	4.17
$VO(bza)_2$·piperidine	945	340	82	128.8	142	19.4	28.29	2.87
$VO(bza)_2$·pyrrolidine	925	320	102	161.5	170	16.7	21.17	2.73

[a] T_i and T_f refer to the temperatures at the beginning and end of a reaction respectively; T_p refers to the peak maxima in the thermograms. [b] pK_b values of coordinated organic bases.

DSC data and from the linear region the activation energy was determined using the equation

$$-\log K = -\log(\mathrm{d}H/\mathrm{d}t)(1/A) = +\frac{E_A}{2.303RT} - \log c$$

where K is the rate constant and A is the total area of the DSC peak.

RESULTS AND DISCUSSION

The analytical data (Table 1) show that the stoichiometry of the complexes is 2 : 1 (ligand : metal) and that of the adducts is 1 : 1 (base : complex); the general formulae are VOL_2 (L = dbm and bza) and VOL_2B (B = morpholine, cyclohexylamine, piperidine, pyrrolidine, ethylamine and piperazine) respectively.

All the complexes studied have magnetic moments in the range 1.68–1.72 BM (Table 1) at room temperature (295 K). These values are for one unpaired spin and therefore show the existence of monomeric species of vanadium(IV) (ion d^1).

The IR spectra of the compounds show the coordination of the dbm or bza ligands in the enol form. All compounds show an intense band at 1528–1540 cm^{-1} [13,14], which can be assigned to the combined vibrational stretching mode of the C=C and C=O bonds. This band can also be described as a combination of the vibrational stretching modes of the C–O–V and C–C bonds; the former corresponds to the ligand coordinated to the metal and the latter to the chelate ring formed. A very strong band in the 1320–1400 cm^{-1} region is attributed to the C–O–V vibrational mode, which confirms the formation of a vanadium chelate [15].

IR spectra exhibit a very strong band at 925–1000 cm^{-1}, which is attributed to the stretching vibration of the terminal V=O bond. If the IR spectra of the complexes VOL_2 are compared with the IR spectra of the adducts VOL_2B, it can be seen that in the adducts the ν(V=O) band is displaced to lower frequencies (925–950 cm^{-1}) compared with the complexes (996–1000 cm^{-1}).

The decrease in strength of the V=O bond (and hence ν(V=O)) can be attributed to the electronic donation of the organic base to the vanadium (N → V), which increases the electron density on the metal d orbitals; consequently, the $p\pi \rightarrow d\pi$ donation from the oxygen atom to vanadium is expected to be reduced to an extent which depends on the donor ability of the base.

The pK_b value reflects the basicity of the ligand towards the proton. It may be assumed that the pK_b value of the ligand provides a measure of the ability of the ligand to form σ bonds with metal ions. In general (see Table 2) the greater the basicity the lower the frequency of the V=O vibration.

The IR spectra of the adducts exhibit a band at 320–340 cm^{-1}, which is assigned to the stretching vibration of the N → V bond.

The IR spectra of all the compounds obtained show two bands at 560–590 cm^{-1} and 360–385 cm^{-1} which are assigned to the antisymmetrical and symmetrical stretching vibrations of $V-O_{lig}$. Both bands are displaced to greater frequencies in the adducts than in the complexes, which indicates that in the adducts the ligand–metal bond is strengthened because of the electronic donation from the base to the vanadium atom.

The electronic spectra of the compounds obtained are in accordance with the Ballhausen-Gray [16] scheme for a square pyramidal structure for the complex and a distorted octahedral structure for the adducts.

The electronic spectra of the compounds obtained exhibit three bands in the visible zone at 14400–14800, 16000–17000 and 20400–23300 cm^{-1} (Table 3). The first band can be attributed to a $^2B_2 \rightarrow {}^2E$ (I) transition. It is displaced to lower frequencies in the adducts, which indicates that the $^2B_2 \rightarrow {}^2E$ (I) transition is very sensitive to the electronic donation O → V (see Table 3).

The second band can be assigned to a $^2B_2 \rightarrow {}^2B_1$ transition. This band indicates the strength of bonding between the vanadium and the ligands. Therefore the band is displaced to higher frequencies in the adducts, because the introduction of the base in the six-coordination position and the *trans* effect strengthen the β-diketonate–vanadium σ bond, as is observed in the IR spectra.

In the UV region two intense bands are observed between 29400 and 38900 cm^{-1}, which can be attributed to intraligand transitions.

The DTA curves of all the compounds show an initial endothermic peak between 82 and 179 °C; the mass loss accompanying this endothermic transition corresponds, on the TG curve, to the loss of one molecule of base coordinated to vanadium (Table 4). A series of exothermic processes is produced between 210 and 590 °C for $VO(bza)_2$ and between 200 and 565 °C for $VO(dbm)_2$ corresponding to the decomposition of the complexes. In all cases the residue is V_2O_5.

For each adduct, the loss of one mole of base occurs over a specific range of temperature; after this, once the process of decomposition has stopped, the residues can be identified by IR spectroscopy as either $VO(bza)_2$ or $VO(dbm)_2$. This supports the rupture of the N → V bonding and the loss of one molecule of base as seen on the TG curve.

In order to establish the degree of thermal stability the initial temperature of the loss of base was used. For $VO(bza)_2$ adducts the values of T_i decrease in the order: morpholine > pyrrolidine > piperazine > piperidine. For $VO(dbm)_2$ adducts the values of T_i decrease in the order: ethylamine > morpholine > pyrrolidine > cyclohexylamine > piperidine.

The initial temperature of the endothermic process bears no relation to the basicity of the ligand (pK_b values).

The DSC study of the initial endothermic process enabled us to determine the activation energy using the procedure of Thomas and Clarke [11,12] (Table 5).

If the E_A values calculated for the $VO(bza)_2$ adducts are compared with the values obtained for the ν(V=O) and ν(N → V) frequencies (IR spectroscopy) and the pK_b values, a relationship is observed. The pyrrolidine adduct is an exception and presents a lower value of E_A than would be expected from its basic character and its ν(V=O) and ν(N → V) vibration values.

The activation energies obtained for the $VO(dbm)_2$ adducts are similar for all the compounds (Table 5). This seems to indicate that in these adducts the strength of the N–V bonding is similar, which concurs with the values obtained from IR spectroscopy for the frequencies ν(V–N) and ν(V=O). This similarity may be due to the steric hindrance of the two phenyl groups of the dbm ligand. These groups also produce mesomeric effects in the chelate ring which, in the preparation and stability of the adducts, predominate over the overall basic character of the coordinated base used.

The values obtained for the enthalpy of the initial endothermic process do not show a clear relationship with the basicity of the pyridines as reflected in the strength of the metal–base bonding. Another factor affects these enthalpies [17,18] and we were unable to evaluate this with the numerical formula used.

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