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SYNTHESIS AND CHARACTERIZATION OF OXOVANADIUM (IV) DITHIOCARBAMATES WITH PYRIDINE

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SYNTHESIS AND CHARACTERIZATION OF OXOVANADIUM (IV) DITHIOCARBAMATES WITH PYRIDINE We report the synthesis and study of a new series of oxovanadium (IV) dithiocarbamate adducts and derivatives with pyridine and cyclohexyl, di-iso-butyl, di-n-propyl, anilin, morpholin, piperidin and di-iso-propyl amines. The complexes have been characterized by analytical, magnetochemical, IR, visible-UV spectral and thermal studies, and are assigned the formulas $[VO(L)_2]$.py, where L=cyclohexyl, di-iso-butyl, di-n-propyl, anilin dithiocarbamate and $[VO(OH)(L)(py)_2]OH.H_2O$ (L=morpholin, piperidin and di-iso-propyl dithiocarbamate).

The effect of the adduct formation on the $p_{V=0}$ bound is discussed in terms of the IR (V=O, V-S and V-N stretching frequencies) and electronic spectra (d-d transitions).

Keywords: vanadium(IV); dithiocarbamates; pyridine.

INTRODUCTION

In former investigations, we have synthesized and characterized five-coordinated oxovanadium(IV) complexes. Oxovanadium (IV) complexes with dithiocarbamates show a square pyramidal structure[1], which can react with Lewis bases to form mainly stable adducts, in which the base occupies the sixth coordination position in an octahedral complex[2], as in the oxovanadium (IV) xanthates[3] and dithiocarboxylates[4,5]. So, the adduct formula is $[VO(L)_2]$.B (L=bidentate ligand, B=base).

In this paper, we report the synthesis and characterization of a new series of oxovanadium(IV) dithiocarbamates complexes with pyridine, which also form complexes of the general formula $[VO(L)_2]$.py, noted as adducts, and alternating complexes of the general formula $[VO(OH)(L)(py)_2]OH.H_2O$, that are soluble in water and noted as derivatives.

We have studied the variations in the IR and electronic spectra caused by the addition of the organic base.

The study of these complexes by IR and electronic spectroscopy, magnetic susceptibilities, thermal methods and analytical data, shows that the adducts stoichiometry is 1:1 (base:complex) and in the derivatives 2:1 (base: metal) with lost of a ligand. From IR and electronic spectral data, we assign a six-coordinated distorted octahedral structure for the adducts $[VO(L)_2]$.py, and possible six-coordinated structure for the derivatives $[VO(OH)(L)(py)_2]OH.H_2O$ from the metallic center. We have also observed a relationship between the V=O, V-S stretching modes and the $^2B_2 \rightarrow ^2B_1$, $^2B_2 \rightarrow ^2E(I)$ transition frequencies.

EXPERIMENTAL PART

MATERIALS AND METHODS

Starting materials

$VOSO_4.5H_2O$ and Pyridine were Merck commercial products and used as supplied. Cyclohexyl, di-iso-butyl, di-n-propyl, anilin, morpholin, piperidin and di-iso-propyl amines were Merck or Aldrich commercial products. The solvents used were Merck (analytical grade). Solutions for absorption spectra were prepared using pyridine. All these reagents were supplied by Micron Analítica S.A. (Madrid, Spain).

Analytical procedures

C, H and S elemental analyses were made on a Perkin-Elmer model 240B (Boston, Massachusetts, USA) analyzer and N elemental analysis using a Leco model SC32 analyzer (Leco Corporation, St Joseph, USA). Vanadium was determined by atomic absorption spectrophotometry after decomposition of the adduct by heating in a 1:1 concentrated HNO_3:H_2SO_4 mixture or dissolving the derivative in water. The melting points were determined on a melting point apparatus by using open capillary tubes and the conductivity measurements were made on a Metrohm Herisau E365B conductometer at room temperature.

Methods

Magnetic susceptibilities were measured by the Gouy method at room temperature on a Mettler H-51A.R. balance (Mettler Toledo, Greifensee Switzerland) using a Newport electromagnet, made from Oxford Instrument (Oxfordshire, UK). Molar susceptibilities were corrected for the diamagnetism of the constituent molecules.[6, 7]

The IR spectra were recorded as KBr pellets on a Perkin Elmer recording spectrophotometer model 283.

The visible/near U.V. spectra of the complexes were determined in the range of 300–900 nm on a Beckman DK 2A (Beckman Coulter, Inc, Fullerton, USA) recording spectrophotometer using solution of the complexes in pyridine (derivatives in water).

Thermograms were recorded on a Mettler HE20 thermobalance with Mettler DSC20 module and DSC were determined on a Mettler TA3000 system in static air with a heating rate of 10 ºC per minute.

Preparations

Oxovanadium(IV) dithiocarbamates complexes $VO(RNCS_2)_2$ were prepared by the same general method described in another paper.[1]

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$\{[C_6H_{11}HNCS_2]_2VO\}.py$: 1.5 g ($3.03.10^{-3}$ mol) of the complex previously obtained (oxovanadium(IV) cyclohexyl dithiocarbamate) was dissolved in pyridine (50mL) by continuous stirring for 3 hours at room temperature. After cooling for 24 hours, the adduct was separated by filtration in vacuo, washed repeatedly with cool water and dried over P_4O_{10} in a nitrogen atmosphere. Yield: 50%.

Similar procedure was used for the other complexes with di-iso-butyl, di-n-propyl, anilin, morpholin, piperidin and di-iso-propyl dithiocarbamate as ligands. The yields were 50-70 %. (see Table 1).

RESULTS AND DISCUSSION

The adducts $[VO(L)_2].py$ and the $[VO(OH)(L)(py)_2]OH.H_2O$ derivatives were prepared by the direct reaction between the $VO(RNCS_2)_2$ complex and pyridine at room temperature. The source of the water and consequently the OH^- could be the solvent pyridine. Cyclohexyl, di-iso-butyl, di-n-propyl and anilin dithiocarbamate ligands are adducts, and morpholin, piperidin and di-iso-propyl dithiocarbamates are derivatives. The adducts are soluble in pyridine and DMSO, but less soluble in dichloromethane, benzene or hexane. The derivatives are soluble in water, methanol or ethanol, and insoluble in organic solvents.

The complexes obtained in this study gave analytical results which are concordant with the formulas assigned, as summarised in Table 1.

The molar conductivity values calculated from the conductivities measured on millimolar solutions of the derivatives complexes $[VO(OH)(L)(py)_2]OH.H_2O$, in water, support the electrolytic nature of the complexes.

All these complexes are paramagnetic, with values of the magnetic moments between 1.6 to 1.75 BM (see Table 1). These results show the existence of monomeric species of oxovanadium (IV).

The most relevant bands in the infrared spectra of the complexes are presented in Table 2. The IR spectra of the adducts $[VO(L)_2].py$, exhibit a very strong band at 990–975 cm^{-1} and the derivatives,

Table 1. Physical and Analytical Data of $[VO(L)_2].py$ and $[VO(OH)(L)(py)_2]OH.H_2O$ complexes

Compound	M.P. (ºC)[a]		C	H	S	N	V	%Yield	Molar[b] conductance	μ (BM)
$[VO(C_6H_{11}HNCS_2)_2].py$	245	%Calcd	46.2	5.7	26.0	8.5	10.2	50		1.65
		%Found	47.9	6.0	26.1	8.7	10.8			
$[VO(i\text{-}C_4H_9)_2NCS_2)_2].py$	232	%Calcd	49.8	7.4	23.1	7.6	9.0	65		1.60
		%Found	50.0	7.2	23.9	8.1	9.8			
$[VO(C_3H_7)_2NCS_2)_2].py$	235	%Calcd	45.8	6.6	25.7	8.4	10.1	70		1.68
		%Found	46.1	7.2	25.8	8.9	10.6			
$[VO(C_6H_5NCS_2)_2].py$	235	%Calcd	47.5	3.1	26.7	8.8	10.4	52		1.75
		%Found	47.9	3.3	26.8	9.2	10.8			
$[VO(OH)(i\text{-}C_3H_7NCS_2)(py)_2]OH.H_2O$	234	%Calcd	45.0	6.2	14.1	9.3	11.1	60	300	1.70
		%Found	46.8	7.6	14.8	8.2	11.7			
$[VO(OH)(C_5H_{10}NCS_2)(py)_2]OH.H_2O$	230	%Calcd	43.9	5.5	14.6	9.6	11.5	70	280	1.72
		%Found	44.2	6.1	15.1	9.7	12.1			
$[VO(OH)(C_4H_8ONCS_2)(py)_2]OH.H_2O$	240	%Calcd	41.0	5.0	14.6	9.6	11.4	60	305	1.71
		%Found	41.2	5.2	15.1	9.8	11.1			

[a]decomposed without melting. [b]in H_2O (ohm^{-1} cm^2 mol^{-1} at 25 ºC).

Table 2. Infrared spectral data (cm^{-1}) of $[VO(L)_2].py$, $[VO(OH)(L)(py)_2]OH.H_2O$ and $[VO(L)_2]$ complexes

Compound	ν(NH⁺)	ν(CN)	ν(CS)	ν(VOH)	ν(VO)	ν(VS)		ν(VN)
$[VO(C_6H_{11}HNCS_2)_2].py$		1510	1110-1150		975	420[1]	400[2]	340
$[VO(C_6H_{11}NHCS_2)_2]^3$		1500	1140		980	390	350	
$[VO(i\text{-}C_4H_9)_2NCS_2)_2].py$		1490	1110-1150		990	400	350	330
$[VO(i\text{-}C_4H_9)_2NCS_2)_2]^3$		1490	1100		1000	380		
$[VO(C_3H_7)_2NCS_2)_2].py$		1520	1130-1180		980	410	380	330
$[VO(C_3H_7)_2NCS_2)_2]$		1505	1110		985	380	360	
$[VO(C_6H_5NCS_2)_2].py$		1500	1100-1180		985	420	400	330
$[VO(C_6H_5NCS_2)_2]$		1500	1150		990	370	340	
$[VO(OH)(i\text{-}C_3H_7NCS_2)(py)_2]OH.H_2O$	2480	1460	1110	740	970	430	390	330
$[VO(i\text{-}C_3H_7NCS_2)_2]^3$		1490	1110		980	370		
$[VO(OH)(C_5H_{10}NCS_2)(py)_2]OH.H_2O$	2500	1460	1110	740	975	400	380	330
$[VO(C_5H_{10}NCS_2)_2]^3$		1500	1110		980	380	350	
$[VO(OH)(C_4H_8ONCS_2)(py)_2]OH.H_2O$	2480	1420	1110	750	975	440	410	325
$[VO(C_4H_8ONCS_2)_2]^3$		1495	1100		985	375	355	

[1]antisymmetric. [2]symmetric. [3]ref 1

$[VO(OH)(L)(py)_2]OH.H_2O$ at 975- 970 cm^{-1}, which is attributed to the stretching vibration of the terminal V=O bond. If we compare the $VO(RNCS_2)_2$ complex with the adduct or derivative, we observed that these show the V=O band displaced to lower frequencies (990–970 cm^{-1}) than the complex (1000-980 cm^{-1}). Similar results are obtained in other complexes of oxovanadium(IV) with dithiocarbamates[8], dithiocarboxylates[9], 8-quinolinate[10], benzoylacetonate[11] or dibenzoylmethanate[12] as ligands. This displacement can be attributed to the electronic donation of the base to the vanadium (N→V), which increases the electron density on the metal d-orbitals, and consequently the $p_\pi \rightarrow d_\pi$ donation from the oxygen atom to vanadium is expected to be reduced.

The IR spectra of the adducts and derivatives exhibit a medium band at 340–325 cm^{-1} which are assigned to the stretching vibration of the $V\text{-}N_{(base)}$ bond.[2, 10-12] This band is not present in the complex $VO(RNCS_2)_2$.

The IR spectra of all the complexes studied in this work show two bands at 440–370 cm^{-1} and 410–340 cm^{-1}, which are assigned to the antisymmetrical and symmetrical vibrations respectively, of the stretching $V\text{-}S_{ligand}$. Both bands are displaced to greater frequencies than in the complex $VO(RNCS_2)_2$, according to the displacement to lower frequencies observed in the stretching vibration V=O bond.

One C-S stretching frequency (n(CSS), 1180–1100 cm^{-1}) is observed in the IR spectra of all the complexes. The presence of the an only C-S band can be due to the greatest contribution of the resonant form ($RN^+CS_2^-$) in the adducts and derivatives.

The IR spectra of the derivatives $[VO(OH)(L)(py)_2]OH.H_2O$ exhibit a band at 2480-2500 cm^{-1}, which is assigned to the stretching vibration of the NH^+ bond, and a band at 750-740 cm^{-1}, which can be assign to the vibration of the V-OH bond. These bands are not present in the adducts $[VO(RNCS_2)_2].py$ nor in the $VO(RNCS_2)_2$ complexes.

Finally**,** one stretching frequency at 1520–1420 cm^{-1} is observed

Table 3. Electronic Absorption Spectra (cm^{-1}) in pyridine

Compound	$^2B_2 \rightarrow ^2E(I)$	$^2B_2 \rightarrow ^2B_1$	$^2B_2 \rightarrow ^2A_1$
$[VO(C_6H_{11}HNCS_2)_2].py$	14000	20230	24500
$[VO(C_6H_{11}NHCS_2)_2]^1$	16666	15290	20661
$[VO(i\text{-}C_4H_9)_2NCS_2)_2].py$	14000	20400	23696
$[VO(i\text{-}C_4H_9)_2NCS_2)_2]^1$	17806	15243	20833
$[VO(C_3H_7)_2NCS_2)_2].py$	14000	20400	Not detected
$[VO(C_3H_7)_2NCS_2)_2]$	16666	15151	20408
$[VO(C_6H_5NCS_2)_2].py$	14000	20400	23696
$[VO(C_6H_5NCS_2)_2]$	16666	15384	21276
$[VO(OH)(i\text{-}C_3H_7NCS_2)(py)_2]OH.H_2O$	Not detected	20400	23696
$[VO(i\text{-}C_3H_7NCS_2)_2]^1$	16949	15197	20241
$[VO(OH)(C_5H_{10}NCS_2)(py)_2]OH.H_2O$	14000	20400	Not detected
$[VO(C_5H_{10}NCS_2)_2]^1$	16949	15243	20618
$[VO(OH)(C_4H_8ONCS_2)(py)_2]OH.H_2O$	Not detected	20400	23696
$[VO(C_4H_8ONCS_2)_2]^1$	Not detected	15384	19230

[1]ref 1

Table 4. Thermal data of $[VO(L)_2].py$ and $[VO(OH)(L)(py)_2]OH.H_2O$ (heating rate of 10ºC in static air)

Compound	Δm/m	Temperature (ºC) 25-150	Temperature (ºC) 150-220	Temperature (ºC) 220-380	Temperature (ºC) 380-430	Temperature (ºC) 430-500
$[VO(C_6H_{11}HNCS_2)_2].py$	%Calcd					81.5
	%Found					79.9
$[VO(i\text{-}C_4H_9)_2NCS_2)_2].py$	%Calcd					83.5
	%Found					81.1
$[VO(C_3H_7)_2NCS_2)_2].py$	%Calcd					81.7
	%Found					80.5
$[VO(C_6H_5NCS_2)_2].py$	%Calcd					81.0
	%Found					81.4
$[VO(OH)(i\text{-}C_3H_7NCS_2)(py)_2]OH.H_2O$	%Calcd	4.0	11.5	28.9	46.3	79.9
	%Found	3.9	10.8	29.4	45.5	78.7
$[VO(OH)(C_5H_{10}NCS_2)(py)_2]OH.H_2O$	%Calcd	4.1	11.9	29.9	48.0	79.1
	%Found	3.8	10.9	29.5	47.7	79.8
$[VO(OH)(C_4H_8ONCS_2)(py)_2]OH.H_2O$	%Calcd	4.1	11.8	29.8	47.8	79.2
	%Found	3.9	11.4	29.8	48.2	80.1
Thermal reaction (description)		Endotherm- loss of 1 water molecule	Endotherm- loss of 2 OH molecules	Endotherm- loss of 1 pyridine molecule	Endotherm- loss of 1 pyridine molecule	Exotherm- formation of V_2O_5

in the IR spectra of all the complexes, and can be assign to the stretching vibration of the C-N bond.

The electronic spectra of the adducts and derivatives, exhibit three bands (Table 3). The first band at 14000 cm^{-1}, can be attributed to a d-d transition $^2B_2 \rightarrow ^2E(I)$ and it is displaced to lower frequencies than in the complex $VO(RNCS_2)_2$, according to the displacement to lower frequencies of the νV=O in the IR spectra, which is indicative that this d-d transition is very sensitive to the electronic O→V donation**.** The second band at 20230–20400 cm^{-1} can be assigned to a $^2B_2 \rightarrow ^2B_1$ transition. This band is displaced to higher frequencies in the adducts and derivatives, due to the introduction of the base into the sixth-coordination position, and is according to the displacement of the ν(V-S) in the IR spectra. This d-d transition is sensitive to the V–S bonding force variation. The third band about 24000 cm^{-1} is attributed to a $^2B_2 \rightarrow ^2A_1$ transition.

However, the coordination of a sixth ligand as pyridine to the complex $VO(RNCS_2)_2$ apparently displaces the sulphur atoms towards the oxygen atom with concomitant reduction of the O-V-S angles, with destabilization of the b_1^* level relative to the e_p^* and renders the Balhausen-Gray[13] scheme applicable to the adducts and derivatives. In the $VO(RNCS_2)_2$ complexes, the three d-d transitions are assigned to $^2B_2 \rightarrow ^2B_1$, $^2B_2 \rightarrow ^2E(I)$ and $^2B_2 \rightarrow ^2A_1$ transitions respectively, according to the inverse energetic levels scheme proposed by Selbin[14] for a square pyramidal structure.

The data on thermal decomposition of the adducts and derivatives complexes are given in Table 4. The thermograms of the derivatives complexes showed a first decomposition (endothermic) corresponding to loss of water molecule, a second decomposition (endothermic) corresponding to loss of 2 OH^- species, a thrid and fourth decomposition (endothermic) corresponding to loss of pyridine molecules and a formation of corresponding metal oxide (V_2O_5) at 430-500 ºC. On heating, the adducts showed a decomposition (exothermic) with metal oxide formation.

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