SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 6, N° 7, 1998

Synthesis and Characterization of New Oxovanadium(IV) Coordination Compounds with Pyrazol-5-one Azo Derivatives

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ABSTRACT

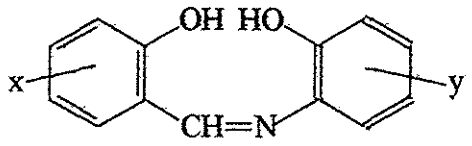
A new series of oxovanadium(IV) chelates containing bi-and tridentate pyrazol-5-one azo derivatives ligands of the type (1) $[VO(L)_2]$ *and (2)* $[VO(L)(H_2O)]$ *have been prepared and characterized by elementary analysis, IR, electronic spectra, conductance measurements and molecular weights. The ligands coordinate through (O-N) donor system as monobasic and bidentate (HL) for the first type and through (O-N-O) donor system as dibasic and tridentate* (H_2L) *for the second type of complexes. The molecular weghts, the presence of the (V=O) stretching band around 950* cm^{-1} *and the visible spectra suggest a monomeric penta-coordinated structure for these complexes.*

Keywords: oxovanadium(IV) coordination compounds, pyrazol-5-one, azo dye, UV, IR spectroscopie

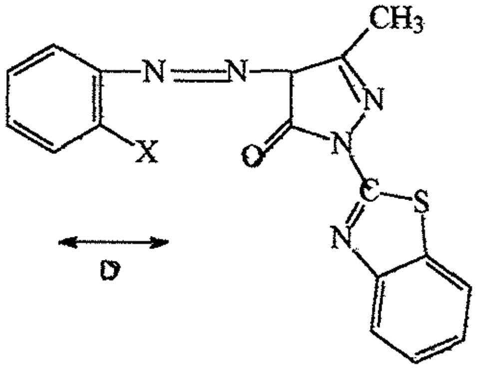
DOI: 10.48141/SBJCHEM.v6.n7.1998.90_1998_2.pdf

INTRODUCTION

In recent years there has been considerable interest in the synthesis, magnetic and structural properties of oxovanadium(IV) complexes of bi- and tridentate Schiff bases[1,2,3]. Zelenstov[4] and Ginsberg[5] have suggested a dimeric structure for the complexes of oxovanadium(IV) with Schiff bases of the general formula:



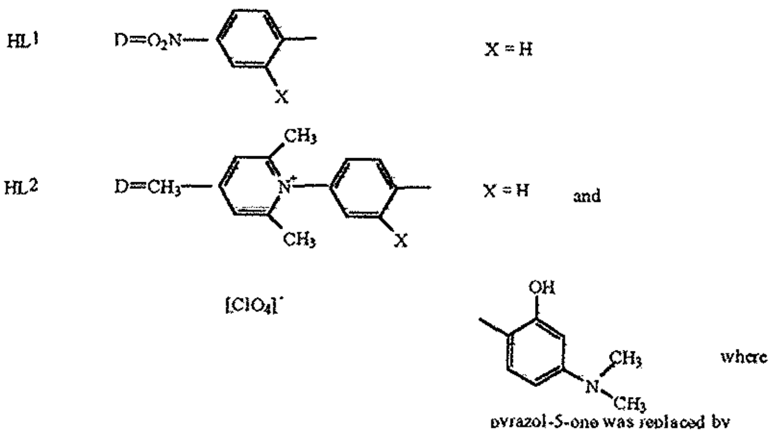
These results have suggested an investigation of the posibility of obtaining dimeric compounds of oxovanadium(IV) with bi- and tridentate 1-(2'-benzthyazolyl)-3-methyl-4-substituted-pyrazol-5-one azo derivatives of general formula:



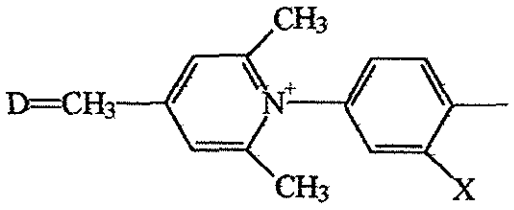
X = OH, COOH, H.
D = diazo component

The pyrazol-5-ore azo derivatives are very important pigments[6]. In the present paper we report the results of the study of the behavior of these new ligands with the vanadyl(IV) ion. It has been found that according to the nature of the substituents D and X two different types of complexes are obtained.

(*i*) complexes with the general formula $[VO(L)_2]$, in which the vanadium is linched to two azo derivatives obtained as the anionic part L of the following HL ligands.



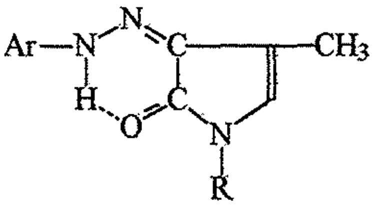
HL^3 D=



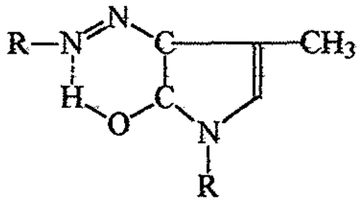
X = H

$[BF_4]^-$

In solution, there is an equilibrium between the hydrazoketo and azoenol forms of pyrazol-5-one azo derivatives[7]



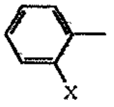
Hydrazoketo form



Azoenol form

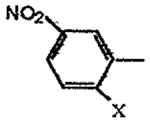
and therefore, these ligands act bidentately and have monobasic properties.
(*ii*) complexes with general formula $[VO(L)(H_2O)]$, in which the vanadium is linked to only one azoderivative and to one water molecule. The L corresponds to the anionic part of the following H_2L ligands

H_2L^4 D=



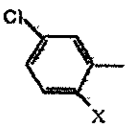
X - COOH

H_2L^5 D=



X = OH and

H_2L^6 D=



X = OH and

Six compounds of these two series have been prepared and characterized. Their molecular weights, IR, UV-VIS spectra and conductance have been measured and the results were analyzed in order to obtain information on the structure and the stereochemistry of the compounds in solid state.

EXPERIMENTAL PROCEDURE

All compounds and solvents were pure BDH grade chemicals. The ligands used were prepared according to the method previously described[8,9].

Physical Measurements

The electronic spectra of all compounds were obtained by the diffuse-reflectance technique, dispersing the sample in MgO, with a Specord M400 Carl Zeiss Jena Spectrophotometer.

The IR spectra were determined with a Perkin-Elmer FT-IR spectrophotometer in the range of 4000-200 cm^{-1}, in KBr pellets.

Molecular weights were determinated in chloroform at 37°C with a Mechrolab Model 301A vapor pressure osmometer. Concentrations of the solutions were in the range of 10^{-3}-10^{-4} M.

Elementary analysis were determined with a Carlo Erba EA 1108 apparatus. Vanadium was determined by the gravimetric method. Conductance measurements were obtained with a Radelkis conductometer type OK-102/1.

Preparation of the compounds

Complexes of type (1) $[VO(L)_2]$ were synthesized by dissolving (0.004 mol) HL in 50 ml of hot ethanol/acetone mixture (1/1 v/v) and then adding (0.002 mol) of vanadyl sulphate (dissolved in 10 ml H_2O/ethanol 50%). The pH of the reaction medium was adjusted with (0.004 mol) $CH_3COONa.3H_2O$ from 4-4.5 to 8-8.5 followed by stirring the reaction mixture, under reflux on a water bath for about 1.5 hours. The solid complexes were separated by filtration, washed with ether and dried at room temperature.

The complexes were purified by recrystallization, (η = 60%). The general reaction was

$$VOSO_4.2H_2O + 2HL + 2\ CH_3COONa.3H_2O \rightarrow [VO(L)_2] + Na_2SO_4 + 2CH_3COOH + 8H_2O$$

Complexes of type (2) $[VO(L)H_2O]$ were prepared by dissolving (0.004 mol) of the H_2L in 50 ml of hot ethanol and adding an aqueous solution of $VOSO_4.2H_2O$ (0.004 mol). The pH of the reaction was adjusted with (0.004 mol) $CH_3COONa.3H_2O$. The mixture of reaction was heated under reflux on a oil bath at 112°C for 0.5 hr. The solid complexes were filtered off, washed with ether and then dried at room temperature. The complexes were purified by recrystallization, (η = 65%). The general reaction was:

$$VOSO_4.2H_2O + H_2L + 2\ CH_3COONa.3H_2O \rightarrow [VO(L)(H_2O)] + Na_2SO_4 + 2CH_3COOH + 7H_2O$$

RESULTS AND DISCUSSION

The solution conductance values in DMF for the solid complexes (Table 1) are in good agreement with the data obtained by previous authors[10] and suggest a non electrolyte behavior of the complexes of both type (1) and type (2). The elementary

Table 1. Analytical data, conductance measurements for Complexes of Oxovanadium (IV)

Complex	Formula	Microanalysis Results				λ^c $\Omega^{-1}cm^2mol^{-1}$	Mol wt	M.p. ^oC	Powder colour
		% C^a	% H^a	% N^a	% V^a				
$[VO(L^1)_2]$	$VO(C_{34}H_{22}N_{12}O_6S_2)$	49.45 (50.01)	2.66 (3.00)	20.36 (20.40)	6.17 (6.20)	35.4	824.94	350^b	green
$[VO(L^2)_2]$	$VO(C_{44}H_{48}N_8O_2)\ [ClO_4]_2$	53.55 (53.76)	4.86 (5.01)	11.35 (11.44)	5.16 (5.24)	58.6	985.94	357^b	brown
$[VO(L^3)_2]$	$VO(C_{50}H_{44}N_{12}O_2S_2)\ [BF_4]_2$	52.23 (52.30)	3.83 (4.00)	14.62 (14.70)	4.43 (4.50)	59	1148.56	431^b	red - brown
$[VO(L^4)(H_2O)]$	$VO(C_{18}H_{11}N_5O_3S)\ (H_2O)$	46.75 (46.80)	2.81 (2.95)	15.15 (15.30)	11.02 (11.00)	44.2	461.94	275	yelow - green
$[VO(L^5)(H_2O)]$	$VO(C_{17}H_{10}N_6O_4)\ (H_2O)$	45.64 (45.70)	2.68 (2.71)	18.79 (18.80)	11.39 (11.40)	45.3	446.94	271	brown - red
$[VO(L^6)(H_2O)]$	$VO(C_{17}H_{10}N_5O_2SCl)\ (H_2O)$	43.54 (43.55)	2.56 (2.70)	14.94 (15.00)	10.87 (10.95)	44.37	468.44	>300	brown - dark

a Calculated (Experimental) ; b Decomposition temperature ; c 10^{-4} M solution in DMF

Table 2. Assigments of IR Spectral Bands (cm^{-1}) for Complexes of Oxovanadium (IV)

Frequencies	Complexes					
	VO(L^1)$_2$	VO(L^2)$_2$	VO(L^3)$_2$	VO(L^4)(H$_2$O)	VO(L^5)(H$_2$O)	VO(L^6)(H$_2$O)
ν(C=O) pyrazolone	1690 * -	-	1690 * -	~1690 * -	~1690 * -	~1690 * -
ν(C=O) enolic	1280	-	1280	1280	1280	1280
ν(C-O-M)	1540	-	1540	~1545	~1540	~1545
ν(N=N) + ν(C-N-N-C)	1475-1570* +880-900* 1565+910	1560+920	1560+900	1577* 1565+920	1577* 1560+910	1575* 1560+900
δ(OH) phenolic	-	1385* -	-	-	1380* -	1380* -
ν(OH) phenolic	-	3460* -	-	-	3450* -	3450* -
ν(C-O) phenolic	-	1150* 1285	-	-	1140* 1285	1140* 1285
ν(OH...N)	-	1650* -	-	-	1656* -	1656* -
ν(COOH)	-	-	-	2570* -	-	-
ν(OCO)	-	-	-	1425	-	-
ν(C-O-H) of aromaticCOOH	-	-	-	810* -	-	-
δ(OH)+ ν(CO) of aromaticCOOH	-	-	-	1410* -	-	-
ν(CH), δ(CH)	3030*+720* 3030+730	3100+605	3000+720	~3100+730	~3111~720	~3000~730
ν(MN)	410	410	410	405	410	410
ν(MO)	505	500	505	500	500	505
ν(VO)	950	950	950	940	950	952
ν(HO) of H$_2$O coordinated	-	-	-	3095	3090	3095

* Bands in the free ligands

analysis (Table 1) indicates a ratio VO/HL = ½ for the type (1) complexes and a ratio VO/H$_2$L = 1/1 for the type (2) complexes. The molecular weights for all complexes correspond to a monomeric structure.

The infrared group frequencies of diagnostic importance are shown in Table 2. Complexes of type (1) [VO(L)$_2$] $_{sp}$exhibit a new band corresponding to ν($C_{sp}{}^2$-O) enolic at 1280 cm^{-1} while the band corresponding to ν(C=O) pyrazolone dissapears. The band ν(N=N) at around 1475-1570 cm^{-1} in the free ligands is shifted to around 1560 cm^{-1} in the complexes. In the complexes the bands ν(OH) phenolic at around 3460 cm^{-1} and ν(OH...N) at around 1650 cm^{-1} in the free ligand dissapear, while the band ν(C-O) phenolic is shifted from 1150 cm^{-1} in the free ligand to 1285 cm^{-1} in the complex.

Table 3. The Reflectance Electronic Spectral Data for Oxovanadium (IV) Complexes (cm^{-1}) and the Assigments of their Bands

Complexes	v_1 (cm^{-1})	v_2 (cm^{-1})	v_3 (cm^{-1})	Change transfer bands
[VO $(L^1)_2$]	12 750 $b_2 \rightarrow e_\pi^*$ d(xy) d(xz,yz)	17 100 $b_2 \rightarrow b_1^*$ d(xy) $d(x^2-y^2)$	-	~20 000 ($a_1 \rightarrow b_2$) ~28 000 ($e_\pi \rightarrow b_2$)
[VO $(L^2)_2$]	13 000 $b_2 \rightarrow e_\pi^*$	17 000 $b_2 \rightarrow b_1^*$	-	~20 000 ($a_1 \rightarrow b_2$) ~29 000 ($e_\pi \rightarrow b_2$)
[VO $(L^3)_2$]	13 200 $b_2 \rightarrow e_\pi^*$	18 200 $b_2 \rightarrow b_1^*$	-	~21 500 ($a_1 \rightarrow b_2$) ~27 800 ($e_\pi \rightarrow b_2$)
[VO (L^4) (H_2O)]	-	15 873 $b_2 \rightarrow b_1^*$	18 181 $b_2 \rightarrow a_1^*$ d(xy) $d(z^2)$	~30 303 ($a_1 \rightarrow e_\pi^*$) ~23 809 ($a_1 \rightarrow b_2$) ~27 397 ($e_\pi \rightarrow b_2$)
[VO (L^5) (H_2O)]	-	16 100 $b_2 \rightarrow b_1^*$	19 100 $b_2 \rightarrow a_1^*$	~31 100 ($a_1 \rightarrow e_\pi^*$) ~24 500 ($a_1 \rightarrow b_2$) ~29 800 ($e_\pi \rightarrow b_2$)
[VO (L^6) (H_2O)]	-	16 129 $b_2 \rightarrow b_1^*$	18 867 $b_2 \rightarrow a_1^*$	~33 333 ($a_1 \rightarrow e_\pi^*$) ~24 500 ($a_1 \rightarrow b_2$) ~28 800 ($e_\pi \rightarrow b_2$)

The complexes of type (2) [VO(L)H_2O] exhibit new bands due to ν(OCO) coordinated at 1425 cm^{-1}, and a large band corresponding to the coordinated water molecule appears at 3095 cm^{-1}. In all complexes new bands appear around 505 cm^{-1} and around 410 cm^{-1} corresponding to ν(V-O) and respectively to ν(V-N)[11,12].

Furthermore the presence of the V=O stretching band around 950 cm^{-1} all complexes indicates a monomeric VO unit[13].

The IR spectral data suggest:

(*i*) a coordination through (ON) donor system of the HL ligands after deprotonation of the enolic group.

(*ii*) two HL acting bidentately around a vanadyl unit.

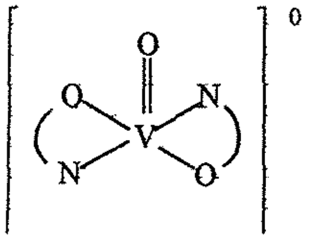
(*iii*) a coordination through (ONO) donor system of the H_2L ligands which act tridentately and dibasic after undergoing the deprotonation of (COOH) group in (H_2L^4) ligand, and (OH) group in (H_2L^5) and (H_2L^6), and the enolic group proceeded from pyrazolone ν(C=O) frequence.

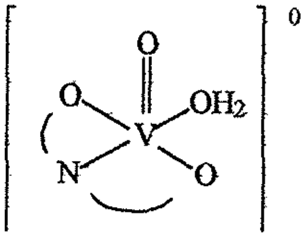
Electronic reflectance spectral data are provided in (Table 3). The complexes [VO$(L)_2$] exhibit only two bands as shoulders around 13000 cm^{-1} and 17000 cm^{-1}. These bands were assigned to ($b_2 \rightarrow e^*_\pi$) respectively to ($b_2 \rightarrow b^*_1$) transitios [14]. and respectively to ($b_2 \rightarrow a^*_1$) transitions[14].The third band is covered by a charge transfer transition.

The complexes [VO(L)H_2O] exhibit a band beetwin (15873-16129)$cm^{-1}$and a low intensity shoulder beetwin (18181-18867)cm^{-1} assigned to ($b_2 \rightarrow b^*_1$) and respectively to($b_2 \rightarrow a^*_1$) transitions.[14] Charge transfer bands are also observed at (30303-33333) cm^{-1} and (23809-27397) cm^{-1}.

F.A.Cotton[15] noted that the differences in the energy of the third band ν_3 are caused by the nature of the electron-attracting groups around the equatorial atoms. A strong electron-attracting effect causes a shift of the band ν_3 to a lower wave length. In our paper the value ν_3 =19100 cm^{-1}corresponds to (NO_2) group and the value ν_3 =18867 cm^{-1} corresponds to (Cl) atom. These bands are in good agreement with Cotton's observation.

Based on the above results the following structures are proposed for mononuclear oxovanadium (IV) complexes: structure(I) for [VO$(L)_2$] complexes and structure (II) for [VO(L)H_2O] complexes.





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