COMPLEXES OF OXOVANADIUM (IV) SULPHATE WITH SOME CYCLOCARBOXYLIC ACID HYDRAZIDES

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ABSTRACT

Complexes of oxovanadium (IV) sulphate with hydrazides of cyclobutane-, cyclopentane- and cycloheptane carboxylic acids, and cyclopentylacetic- and cyclohexylacetic acids have been synthesised. They were characterised by elemental analysis, magnetic, infrared electronic spectral studies. The ligands coordinate via the carboxyl oxygen and the primary amino nitrogen. The sulphate ion is coordinated in all the complexes. A distorted octahedral geometry is proposed for all the complexes.

INTRODUCTION

Metal complexes, hydrazides and their corresponding hydrazone schiff bases have assumed considerable importance in view of the suggestions that mono-amino oxidase enzyme inhibition occurs via metal coordiantion[1]. Hydrazides of some cyclocarboxylic acids may also be used for the treatment of psychotic illness[2], act as pesticides[3], enhance bonding of free sulphur by rubbers during vulcanisation[4], act as antiknock additive[5] in gasoline and play roles in synthetic polymers and dye stuff[6].

The biochemistry of vanadium has attracted interes particularly with respect to its accumulation in certain tunicates and in mushroom Amanita muscaria[7]. Furthermore, the stereochemistry of vanadium (IV) is of interest due to its relationship via the hole formalism to copper (II) and the stability of VO^{2+} cation. Complexes of some cyclocarboxylic acid hydrazides with some transition metal sulphates have been reported in previous work[8]. This paper reports a study of the interaction of VO^{2+} with some cyclocarboxylic acid hydrazides.

EXPERIMENTAL

Reagents and solvents

The cyclocarboxylic acids were obtained commercially from Aldrich Chemicals Co. Ltd and were used without further purification. Other reagents were used as obtained from BDH Chemicals Ltd.

Preparation of the ligands

The cyclocarboxylic acid hydrazides were prepared via their ethyl esters as described in a previous work[8].

Preparation of complexes

[VO(cbch)SO_4]: 0.0114 mole (2.48g) of $VOSO_4.3H_2O$ in 40cm^3 of 60% aq.EtOH was added with stirring to an ethanolic solution (45cm^3) of 0.0114mole (1.30g) of cyclobutane-carboxylic acid hydrazide (cbch). The mixture was concentrated to about half its original volume. Light purple cystals separated were filtered and dried over anhydrous $CaCl_2$ in a desiccator (Yield, 48%).

Other complexes were similarly prepared using quantities of $VOSO_4.3H_2O$ and appropriate ligand as shown below.

Compound	Salt(mole,g)	Ligand(mole,g)
VO(cpch)$SO_4.2H_2O$	0.0124,2.69	0.0123, 1.59
VO(cpah)$SO_4.2H_2O$	0.0083,1.80	0.0083, 1.80
VO(chah)$SO_4.H_2O$	0.0171,2.67	0.0171, 2.67
VO(chpch)$SO_4.3H_2O$	0.0147,3.17	0.0147, 2.30

Instrumental analysis

Elemental analyses were done at the Microanalytical Laboratory, Department of Chemistry, University of Ibadan. Electronic spectra of the complexes were recorded in various solvents, as permitted by solubility, using a Bausch and Lomb Spectronic 20 spectrophotometer. Magnetic susceptibility measurements were taken on a Gouy balance calibrated with Hg[Co(CNS)$_4$]. Infrared spectra of the ligands and complexes were recorded as CCl_4 solution and KBr discs respectively on a Perkin Elmer 457 Grating Infrared Spectrophotometer.

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RESULTS AND DISCUSSION

Oxovanadium (IV) sulphate reacts with the hydrazides according to the equation

$$VOSO_4.3H_2O + RCONHNH_2 \rightarrow VO(RCONHNH_2).nH_2O$$

The analytical data and some physical constants for the complexes are shown in Table 1 while the electronic spectral and magnetic data are in Table 2. The infrared data for the ligands and complexes are shown in Table 2.

Table 1. Analytical data and some physical constant's for complexes

Compound	Formula	Formula weight	Yield (%)	Colour	M.Pt/Dec. Temp. (°C)	Elemental analysis (calc.)		
						C	H	N
$VO(cbch)SO_4$	$C_5H_{10}N_2O_6SV$	277.86	84	purple	238	21.88 (21.59)	3.04 (3.62)	10.25 (10.08)
$VO(cpch)SO_4.2H_2O$	$C_7H_{18}N_2O_8SV$	340.90	54	light brown	230	21.86 (22.03)	4.61 (4.89)	8.32 (8.57)
$VO(cpah)SO_4.2H_2O$	$C_7H_{18}N_2O_8SV$	340.90	63	grey	220	24.20 (24.64)	4.85 (5.28)	8.63 (8.21)
$VO(chah)SO_4.2H_2O$	$C_8H_{18}N_2O_7SV$	337.09	65	light green	220	28.22 (28.48)	5.09 (5.34)	8.08 (8.31)
$VO(chah)SO_4.2H_2O$	$C_8H_{22}N_2O_9SV$	373.27	75	brown	250	25.33 (25.72)	6.19 (5.89)	7.47 (7.50)

Table 2. Electronic spectral and magnetic data

Compound	μ_{eff}(B.M.)	λ_{max} x 10^3 (cm^{-1})	Assignments
$VO(cbch)SO_4$	1.68	12.50	$^2B_2 \rightarrow {}^2E$
		18.18	$^2B_2 \rightarrow {}^2B_1$
		28.57	$^2B_2 \rightarrow {}^2A_1$
$VO(cpch)SO_4.2H_2O$	1.74	11.91	$^2B_2 \rightarrow {}^2E$
		17.24	$^2B_2 \rightarrow {}^2B_1$
		27.03	$^2B_2 \rightarrow {}^2A_1$
$VO(cpah)SO_4.2H_2O$	1.77	13.16	$^2B_2 \rightarrow {}^2E$
		17.86	$^2B_2 \rightarrow {}^2B_1$
		28.57	$^2B_2 \rightarrow {}^2A_1$
$VO(chah)SO_4.2H_2O$	1.83	13.25	$^2B_2 \rightarrow {}^2E$
		18.87	$^2B_2 \rightarrow {}^2B_1$
		29.41	$^2B_2 \rightarrow {}^2A_1$
$VO(chph)SO_4.3H_2O$	1.78	12.50	$^2B_2 \rightarrow {}^2E$
		19.23	$^2B_2 \rightarrow {}^2B_1$
		28.57	$^2B_2 \rightarrow {}^2A_1$

The syntheses and characterisation of the ligands have been described in a previous work[9].

The complexes are amorphous, high melting and insoluble in water; they however dissolve to varying extent in organic solvents. Their insolubility in water and their high melting points indicate some form of polymeric interactions probably of the V=O·····V type.

The room temperature magnetic moments of the complexes is close to the spin-only value for one unpaired electron where orbital contribution is quenched by low symmetry fields[10]. The electronic spectra of the complexes were measured in MeOH except that of $VO(chpch)SO_4.3H_2O$ which was measured in CCl_4. In general, three low intensity bands are observed in the spectrum of each complex. Band III located around 28,000cm^{-1} in the spectra of the complexes is probably charge transfer in origin; its assignment is therefore tentative[10].

The magnetic and electronic data indicate that the complexes are coordinate[10,11]. This is more likely since the solvents are either very weak donors or non-coordinating.

The infrared spectra of the complexes are compared to those of the ligands in Table 3. Non-ligand broad bands located around 3450cm^{-1} in the spectra of some of the complexes have been assigned to the νs(O-H) vibration of water molecules.

The infrared spectra of the ligands in CCl_4 solution differed from those in the solid state due to hydrogen bonding[12-14].

In comparison with the spectra of the ligands in CCl_4, the position of the ν(NH) band in the complexes is lowered by 20 - 70cm^{-1} indicating that coordination occurs via the primary amino N; coordination via the imino N is ruled out on steric grounds[15]. The amide I (i.e. ν(C=O)) band located in the spectra of the ligands around 1700 cm^{-1} is similarly lowered in the spectra of the complexes by about 60 cm^{-1}. This is consistent with coordination via the carboxyl O. The ν(SO_4^{2-}) band of the free sulphate ion usually located as a singlet is split in the spectra of the complexes into a doublet. This is due to the coordination of the sulphato group with an attendant lowering of its symmetry[16]. The ν(V=O) band is located around 990cm^{-1} in the complexes. Low frequency V-O and V-N bands have also been assigned.

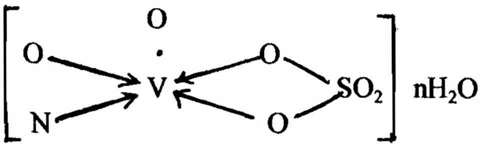
Table 3. Diagnostic IR bands for the ligands and complexes (cm^{-1})

Compound	ν(OH)	ν(NH, NH_2)	ν(C=O)	ν(SO_4^{2-})	ν(V=O)	ν(V-O, V-N)
cbch		3200s	1710s			
VO(cbch)SO_4		3180m	1650s	1120s, 1026w	980	430w, 370w
cpah		3250s	1680s			
VO(cpah)SO_4.$2H_2O$	3450br	3180s	1630s	1100s, 1000m	990m	450w, 380w
chah		3460s	1680s			
VO(chah)SO_4.$2H_2O$	3450br	3200	1630m	1170w, 1100s	980m	500w, 390w
chah		3450s	1675s			
VO(chah)SO_4.$2H_2O$	3340m	3340m	1645m	1120w, 1100m	990m	470w, 350w
chpch		3440s	1680s			
VO(chph)SO_4.$3H_2O$	3450br	320m	1630s	1100m, 1000w	980	450w, 400w

s = sharp, m = medium, br = broad, w = weak

CONCLUSION

Oxovanadium (IV) sulphate reacts with the ligands in a 1:1 mole ratio. The resulting complexes are five coordinate. The ligands coordinate via the carboxyl oxygen and the primary amino nitrogen. The sulphate ions are in the primary coordination sphere of the cation. On the basis of their physicochemical properties, the structure below is proposed for the complexes.



(n = 0, 2 or 3)

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