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OXOVANADIUM(IV) COMPLEXES OF CYCLOPROPYLCARBO- AND CYCLOHEXYLACETOHYDROXAMIC ACIDS

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ABSTRACT

A spectroscopic investigation of the reactions of VO^{2+} with cyclopropylcarbohydroxamic acid (CPAH) and cyclohexylacetohydroxamic acid (CHAH) in aqueous solution reveals the sole formation of 1:2 complexes at equilibrium. The stability constants (log β_2 at 25°C and $I = 0.1$ mol dm^{-3}) are 21.45 and 17.60 for $[VO(CPA)_2]$ and $[VO(CHA)_2]$, respectively. Spectral and magnetic studies of the isolated complexes indicate five-coordination via the oxygen atoms of the hydroxamate group.

INTRODUCTION

The biochemistry of vanadium has attracted increasing interest, particularly with respect to its accumulation in certain tunicates[1-4] and in the mushroom Amanita muscaria[5-7]. Hydroxamates are important functionalities of two major groups of siderophores[8]; they are also present in amavadine, a natural product containing V(IV)[9] and have been used extensively as reagents in the quantitative determination of vanadium[10-12]. Hydroxamic acids provide an array of different types of interactions with vanadium and vanadates. While there are reports on the interaction of some monohydroxamic acids with oxovanadium(IV) ion[13], nothing is reported on the interaction of the cation with hydroxamates derived from cyclocarboxylic acids, RCONHOH (R= cyclo-C_3H_5, cyclo-$C_6H_{11}CH_2$). Furthermore, speciation and equilibrium studies have not been done on these systems. In this work, therefore, the interaction of the title hydroxamic acids with the oxovanadium(IV) cation is studied with a view to determining the composition and stability of the species present in aqueous solutions at equilibrium and the physico-chemical properties of the isolated complexes.

RESULTS AND DISCUSSION

Equilibrium Studies

The presence of only one absorbing species in solution was established by graphical matrix-rank analysis of the absorbance data[14,15]. The spectral data from the equilibrium studies were processed by the computer program SQUAD[16]. The program calculates the composition, stability constants (log ßi) and the molar absorptivities (ϵi) of the complexes by minimising the sum S,

$$S = \Sigma (A_{obs} - A_{calc})^2$$

where A_{obs} denotes the measured absorbance and A_{calc} is that calculated by the program from the equation shown below,

$$A_{calc} = 1\Sigma\ \beta i[M][L]^i \epsilon i$$

assuming the formation of mononuclear complexes only. Dissociation constants (pKa's) of the ligands were taken from a previous work[15] (9.80 and 9.85 for CPAH and CHAH, respectively, at 25°C and I = 0.1 mol dm^{-3}). The results of the calculations indicate the formation of $[VO(CPA)_2]$ and $[VO(CHA)_2]$ with $\log\beta_2 = 21.45 \pm 0.08$ and 17.60 ± 0.08, respectively, where $\beta_2 = [ML_2]/[M][L]^2$. Several equilibrium models were tried but it was only with the ML_2 model that convergence was achieved. The standard deviations in the absorbance data are 4.25 x 10^{-3} and 2.21 x 10^{-3} for [$VO(CPA)_2$] and [$VO(CHA)_2$], respectively; these, together with the standard deviations in the calculated constants indicate the goodness of fit of data[16,17]. Analysis of the calculated spectra of the complexes show that [$VO(CPA)_2$] shows an absorption maximum at 750 nm ($\epsilon=96$) while [($VO(CHA)_2$] shows the absorption maximum at 733 nm ($\epsilon=20$) In each of the systems, the spectra were identical; this observation, together with the absence of any isosbestic points, is consistent with the presence of only one absorbing species[18] .

Isolated solid complexes

The analytical data and some physical constants for the complexes formed according to the equation shown below

$VOSO_4$ + 2RCONHOH → $VO(ONHCOR)_2$ +H_2SO_4

are shown in Table I. The visible spectra of the complexes in ethanol are similar, showing a single broad band centred around 760 nm which has been assigned to the $^2B_2 \rightarrow {}^2E(1)$ transition[19] . The bands due to the transitions from the $^2B_2$ level to the $^2B_1$ and $^2A_1$ levels were probably obscured by high-energy charge transfer bands in the ultraviolet region. The position of the single band and a room temperature magnetic moment close to the spin-only value support five-coordination around the oxovanadium(IV) ion[19].

The infrared spectra of the ligands have been reported in a previous work[15]. In Table III, the diagnostic infrared bands in the complexes are compared with their positions in the free ligands. The $\upsilon(C=O)$ vibrations located at 1623 cm^{-1} and 1630 cm^{-1} in the spectra of CPAH and CHAH are lowered to 1600 cm^{-1} and 1610 cm^{-1} in [$VO(CPA)_2$] and [$VO(CHA)_2$], respectively. This indicates ligation via the carbonyl oxygen; this is further supported by an increase in the $\upsilon(C\text{-}N)$ band from around 1330 cm^{-1} in the ligands to around 1370 cm^{-1} in the complexes[20]. The $\upsilon(V=O)$ band is located around 990 cm^{-1} in the complexes.

Table I. Analytical Data and Some Physical Constants of the Complexes

Compound	Formula	Formula Weight	Colour	Dec.pt. °C	**Found (Cald) %**			μ_{eff}(B.M.)
					C	**H**	**N**	
[VO(CPA)$_2$]	$C_8H_{12}N_2O_5V$	267.14	light purple	174	36.02 (35.97)	4.77 (4.53)	10.12 (10.49)	1.81
[VO(CHA)$_2$]	$C_{16}H_{28}N_2O_5V$	379.35	"	168	50.83 (50.66)	7.82 (7.44)	7.62 7.38	1.85

Table II. Composition of Solutions for Stability Constant Determination

VO^{2+}/CPAH			VO^{2+}/CHAH		
[$VOSO_4$]	[CPAH]	pH	[$VOSO_4$]	[CHAH]	pH
1. $2.5x10^{-3}$	$2.5x10^{-3}$	2.17	0.015	0.015	2.00
2. "	"	3.42	"	"	2.49
3. "	"	4.81	"	"	2.60
4. "	"	5.06	"	"	3.10
5. "	"	8.56	"	"	2.22
6. "	"	11.93	$7.5x10^{-3}$	"	1.55
7. $1.25x10^{-3}$	"	2.89	"	"	1.58
8. "	"	4.04	"	"	2.33
9. "	"	7.42	"	"	2.53
10. "	"	8.73	"	"	2.77
11. "	"	10.31	$5.0x10^{-3}$	"	2.89
12. $8.33x10^{-4}$	"	1.87	"	"	1.70
13. "	"	3.58	"	"	2.77
14. "	"	3.77	"	"	3.80
15. "	"	11.96	"	"	3.58

Table III. Diagnostic IR Bands (cm^{-1}) for the Ligands and Complexes.

Compound	ν(NH)	ν(C=O)	ν(C-N)	ν(V=O)
CPAH	3191	1623	1330	
[$VO(CPA)_2$]	3190	1600	1365	990
CHAH	3191	1630	1334	
[$VO(CHA)_2$]	3191	1610	1370	990

CONCLUSION

A knowledge of the complex equilibria of VO^{2+} and monohydroxamic acids in aqueous media is relevant in understanding the possible interaction of this cation with naturally occurring hydroxamates and related ligands. It is hoped that this work on speciation and stability constants will help in elucidating the not yet clearly defined role of vanadium in biological systems, these simple systems serving as models.

On the basis of their physico-chemical properties, the square-pyramidal stucture shown in Fig. 1 is proposed for the complexes.

EXPERIMENTAL

Reagents and Instruments

$VOSO_4.3H_2O$ (99.9%), *ethyl cycloproanecarboxylate and ethyl cyclohexylacetate* were obtained from Aldrich Chemical Co. Ltd. Analar $NaNO_3$ was used for the preparation of the background electrolyte. Water was doubly distilled, degassed using purified N_2 and stored in glass stoppered flasks. KOH and HNO_3 used for adjusting the pH were stored in glass ampoules and were standardized with potassium hydrogen phthalate and tris-(hydroxymethyl)methylamine, respectively. All other reagents were of the purest grade. pH Measurements were made using a Ciba-Corning Check-mate 90 or a Radiometer Copenhagen Research pH meter calibrated with standard buffer tablets (pH 2 and 12). Electronic spectra were recorded on a Kontron Uvicon 930 UV-VIS spectrophotometer. IR spectra of the ligands and complexes were recorded as Nujol mulls in the range 4000-500 cm^{-1} on a Nicolet DX510 FTIR spectrophotometer and as pressed KBr discs in the 4000-200 cm^{-1} range on a Perkin-Elmer 577 grating IR spectrophotometer. Room temperature magnetic susceptibility measurements were made on a Johnson Matthey balance calibrated with $Hg[Co(SCN)_4]$.

Preparation of the Ligands

Cyclopropanecarbohydroxamic acid was prepared as described in the literature[21] while the preparation of cyclohexylacetohydroxamic acid has been described in a previous work[15].

Preparation of the Complexes

$[VO(CPA)_2]$. To 40 mL of an aqueous solution of 1.085 g (0.005 mole) of $VOSO_4.3H_2O$ was added with stirring a solution of 1.012 g (0.010 mole) of CPAH in 30 mL of ethanol.

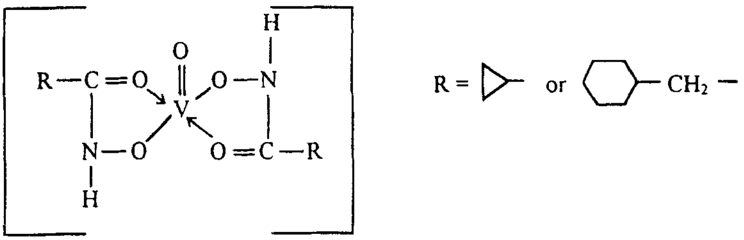

Fig. 1. Proposed Stucture of the Complexes

To this mixture a 10% solution of $NaHCO_3$ was added until a light purple precipitate appeared. The precipitate was removed by filtration, washed with small aliquots of Et_2O and dried over silica gel in a vacuum desiccator. (Yield = 0.708 g; 53%).

[VO(CHA)$_2$]. This compound was prepared similarly using 1.572 g (0.010 mole) of CHAH. (Yield =1.100 g; 60%).

Equilibrium Studies

Cells of 1 cm path length were used to generate the spectral data for the calculation of equilibrium constants. In all cases spectral measurements were made using a spectrophotometer fitted with a thermostated water bath after the solutions had been left for 2 h in a Decon FS100b ultrasonic bath. Fifteen solutions containing 1:1-1:3 metal : ligand ratios and the pH varying from 1.87-11.96 were used for the VO^{2+}/CPAH system while fifteen solutions containing 1:1-1:3 metal: ligand ratio and pH varying from 1.55-3.50 were used for the VO^{2+}/CHAH system. A solution of 0.1 M $NaNO_3$ (I = 0.1 mol dm^{-3}) was used as background electrolyte and in the preparation of a 0.015 M $VOSO_4.3H_2O$ stock solution. The background electrolyte was used for all dilutions. The composition of the solutions used are shown in Table II. In each system, the spectra were measured in the 560-850 nm range and the data digitized at 10 nm intervals. In the VO^{2+}/CHAH system, precipitation, probably accompanied by formation of polymeric species, occured above pH 4, hence solutions above this pH were discarded.

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