Indian Journal of Chemistry
Vol. 26A, January 1987, pp. 44-47

Ligational Behaviour of 3-(2-Hydrazinocarbonyl)phenylimino-2-oximobutane Towards Oxovanadium(IV)

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Received 2 *April* 1986; *revised and accepted* 2 *June* 1986

Ligational behaviour of 3-(2-hydrazinocarbonyl)phenylimino-2-oximobutane (LH_2) towards oxovanadium(IV) has been examined. The ligand reacts in either keto or enol form depending on the *p*H of the reaction medium. At *p*H 3.5, the ligand reacts in its keto form to give compound $VO(LH_2)SO_4.H_2O$ (**1**). At *p*H 5.5-6.0, the complex $VO(L).2H_2O$ (**2**) is obtained in which the ligand acts in the enol form. Both **1** and **2** yield mixed ligand complexes of the type $VO(L)(B).H_2O$ and VO(L)(AA) on being reacted with monodentate (B) and bidentate Lewis donors (AA) respectively. All these complexes have been characterised by elemental analyses, spectral, conductance and magnetic susceptibility measurements. Bonding sites of the ligand with the oxometal cation and the most probable disposition of the donor atoms around the VO^{2+} moiety have been suggested. Antitubercular activity, *in vitro* of the complex $VO(LH_2)SO_4.H_2O$ has also been screened.

Ligational behaviour of the acid hydrazones of α-ketooximes towards several first row transition metal ions have been examined[1-4]. However, the coordination complexes of these ligands with oxometal cations have not yet been studied adequately. This has prompted us to undertake the title investigation. The interest in the title ligand also emanates from its strong antituberculosis activity[3]. It has been observed recently that the antituberculosis activity of this ligand is considerably potentiated on its chelation to Cu(II) ions[3]. Since VO^{2+} occupies a position close to Cu(II) in the Irving-Williams series[5], we thought it worthwhile to examine the biological effect of incorporating VO^{2+} ion in place of Cu(II). Again it has been found that the title ligand generally behaves as tridentate and in the case of VO^{2+} ion a 1:1 metal ligand complex can be used as the starting point of synthesizing ternary (mixed-ligand) complexes involving the VO^{2+} moiety.

Materials and Methods

o-Aminobenzoylhydrazine was prepared by standard procedure[6]. The schiff base (LH_2) was prepared by two different methods, one of which is described elsewhere[3,6]. In the alternate method, an ethanolic solution of biacetylmonoxime (0.02 mol) was added slowly to an ethanolic solution of *o*-aminobenzoylhydrazine (0.02 mol) followed by the addition of 2 drops of conc. HCl. The mixture was stirred for 2-3 hr when a light yellow solid was obtained. It was washed with water and recrystallised from ethanol and the crystalline solid dried over fused $CaCl_2$, m.p. 184°.

Preparation of complexes of keto form of the ligand: Preparation of $VO(LH_2)SO_4.H_2O$

An ethanolic solution of $VOSO_4.5H_2O$ (0.002 mol) was added to a well-stirred solution of the ligand (0.002 mol) in ethanol. The mixture was stirred for 1 hr (*p*H 3.5) when a reddish brown compound was precipitated. It was filtered, washed with ethanol and dried over fused $CaCl_2$.

Preparation of $VO(LH_2)(C_2O_4).H_2O$ ($H_2C_2O_4$ = oxalic acid)

An ethanolic solution of $VOC_2O_4.2H_2O$ (0.0025 mol) was added to an ethanolic solution of the ligand (0.002 mol) and the mixture stirred for 30 min. The reddish brown solution (*p*H 3.5) was evaporated to about one-third its volume when a brown compound separated out. It was filtered, washed with ethanol and then with water thoroughly and dried over fused $CaCl_2$.

Preparation of complexes of enol form of the ligand: Preparation of $VO(L).2H_2O$

Vanadyl acetate was prepared *in situ* by adding powdered anhydrous sodium acetate (0.004 mol) to a dry methanolic solution of $VOSO_4.H_2O$ (0.002 mol) and stirring the mixture for a few minutes. The separated Na_2SO_4 was filtered off, and the filtrate added to a methanolic solution of the ligand (0.002 mol). The mixture was stirred for 1.5 hr (*p*H of solution ~5.5), when a scarlet red compound separated out. It was filtered off, washed thoroughly with water and dried over fused $CaCl_2$.

Table 1—Analytical Data, Colour, Magnetic Moment, Conductivity, IR[ν(V=O)] and Electronic Spectral Data of the Complexes

Complex	Colour	Found (Calc.), %					μ_{eff} (B.M.) at 25°C	Λ_M^* (ohm^{-1} cm^2 mol^{-1}) in MeOH	ν(V=O) (cm^{-1})	Electronic spectral band (cm^{-1})
		M	C	H	N	Anion				
LH_2	Light yellow		56.3 (56.4)	5.8 (5.9)	23.7 (23.9)					
$VO(LH_2)SO_4.H_2O$	Reddish brown	12.5 (12.3)	31.6 (31.8)	3.6 (3.8)	13.3 (13.5)	23.4 (23.1)	1.70	42	995(s,br)	25000
$VO(LH_2)C_2O_4.H_2O$	Brown	12.6 (12.5)	38.5 (38.3)	3.3 (3.4)	13.5 (13.7)		1.75	7.3	980(s,br)	19050, 23260
$VO(L).2H_2O$	Scarlet red	15.2 (15.2)	39.3 (39.4)	4.7 (4.8)	16.5 (16.7)		1.69	7	965(s)	21280
$VO(L)(NH_3).H_2O$	Orange red	15.2 (15.2)	39.4 (39.5)	5.1 (5.0)	20.8 (20.9)		1.68	40	940(s)	22520
$VO(L)(Py).H_2O$	Brown	12.8 (12.8)	48.6 (48.5)	4.7 (4.8)	17.5 (17.7)		1.70	25	950(s,br)	18180
$VO(L)(\alpha$-Pic$).H_2O$	-Do-	12.4 (12.4)	49.6 (49.7)	4.9 (5.1)	16.9 (17.0)		1.64	11	950(s)	17860, 24390
$VO(L)(\beta$-Pic$).H_2O$	-Do-	12.6 (12.4)	49.6 (49.7)	5.0 (5.1)	16.8 (17.0)		1.66	15	955-935(s,br)	18020, 19230
$VO(L)(\gamma$-Pic$).H_2O$	-Do-	12.3 (12.4)	49.5 (49.7)	5.0 (5.1)	16.8 (17.0)		1.71	20	950(s,br)	18180
VO(L)(Anilin).H_2O*	Black	12.3 (12.4)	49.8 (49.7)	4.9 (5.1)	16.8 (17.0)		1.78	6	955-935(s,br)	17700, 19050
VO(L)(ISOQ).H_2O*	Brown	11.4 (11.2)	53.7 (53.8)	4.5 (4.7)	15.5 (15.7)		1.77	10	950-935(s,br)	17860, 19230
$VO(L)(MeNH_2).H_2O$	Orange	13.9 (13.9)	39.1 (39.3)	5.0 (5.2)	18.9 (19.1)		1.62	57	940(s)	22420
VO(L)(en)*	Orange	14.1 (14.2)	43.3 (43.4)	5.5 (5.6)	23.3 (23.4)		1.65	19	950(s)	21740
VO(L)(*o*-Phen)*	Light brown	10.6 (10.6)	57.5 (57.6)	4.0 (4.2)	17.4 (17.5)		1.70	17.5	970-950(s,br)	17700, 24630
VO(L)(α,α'-Dipy)*	Light brown	11.2 (11.2)	55.1 (55.4)	4.4 (4.4)	18.3 (18.4)		1.72	19	965(s,br)	17700

*Conductivities and electronic spectra of these complexes were recorded in DMSO. For other complexes methanol was used as the solvent.

Preparation of mixed ligand complexes

The following methods were adopted for the preparation of these complexes.

Method 1: *p*H of an ethanolic solution of the ligand (0.0025 mol) was raised to ~6.0-6.5 by the careful addition of the monodentate (B) or bidentate Lewis base (AA) (B = NH_3, $MeNH_2$ etc. and AA = *o*-phenanthroline, α,α'-dipyridyl and ethylenediamine). In the case of NH_3 adduct, dry NH_3 gas was passed into an ethanolic solution of the ligand. To this solution, a methanolic solution of $VOSO_4.H_2O$ (0.002 mol) was added slowly and the *p*H adjusted to ~6.0-6.5 by the addition of some more base. The mixture was stirred for 1 hr and the resulting precipitate was filtered, washed with ethanol and water thoroughly and then dried over fused $CaCl_2$.

Method 2: $VO(L).2H_2O$ (0.5 g) was warmed on a water-bath with excess of the base B or AA (B = Py, α, β or γ-picoline, aniline, isoquinoline; AA = *o*-phen, en etc) for ~40 min and the solution (*p*H ~6) was kept in a stoppered conical flask for 8-10 hr. It was evaporated to dryness, the solid obtained washed with water and ether and finally dried over fused $CaCl_2$.

Method 3: The compounds obtained by the method-2 can also be obtained in a similar manner by using the ammonia adduct, i.e. $VO(L)(NH_3).H_2O$ as the starting material.

Physical measurements

Magnetic susceptibilities of the compounds were measured by EG & G PAR Vibrating Sample Magnetometer (model 155) using $Hg[Co(SCN)_4]$ as the calibrant. The electronic spectra of the soluble complexes were recorded in MeOH or DMSO on a Pye-Unicam SP8-150 UV-vis spectrophotometer. IR spectra were recorded in KBr on a Perkin-Elmer 783 IR spectrophotometer. Conductances were measured in doubly distilled MeOH or DMSO using a Philips conductivity bridge (PR-9500) fitted with a dip-type cell.

Results and Discussion

Analytical results, together with the colour, magnetic moments, molar conductance values and more important IR and electronic spectral bands are presented in Table 1.

Conductances and magnetic moments

Molar conductance in methanol of $VO(LH_2)SO_4.H_2O$ having the ligand in the keto form indicates its non-electrolytic nature and points to the presence of coordinated sulphate. This complex is paramagnetic with $\mu = 1.7$ B.M. at 25°C which is slightly lower than the spin-only value expected for a d^1-system. Conductance values of the complex having the ligand with enol form i.e. $VO(L).2H_2O$ and all other mixed ligand complexes included in Table 1 indicate their nonelectrolytic nature. Room temperature magnetic moment values for these complexes are also consistent with the spin-only value of a d^1-system.

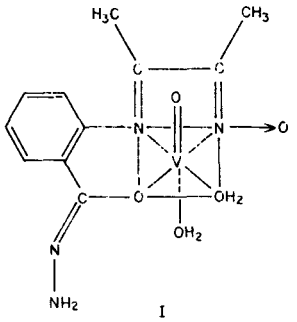
Electronic spectra

The absorption spectrum of $VO(LH_2)SO_4.H_2O$ in methanol exhibits only one high intensity band at ~25000 cm^{-1}. Electronic spectra of most of the other complexes exhibit two bands in the region 25000-17700 cm^{-1}. The bands are of rather high intensity compared to what is usually observed in the case of *d-d* transitions. Of these two, the high energy band may be attributed to the $b_2 \rightarrow a_1$ transition while the lower energy composite band contains both the $b_2 \rightarrow e$ and $b_2 \rightarrow b_1$ transitions[7-9].

IR spectra

Our earlier work revealed that the nuclear substituted amino group of anthranilic acid hydrazide is involved in schiff base formation with biacetylmonoxime and the terminal NH_2 part of the acid hydrazide remains free[3].

The sharp bands at 3400 ($\nu_{as}NH_2$) and 3310 (ν_sNH_2) cm^{-1} in the IR spectrum of the ligand, remains more or less unaltered in the complexes indicating non-participation of the terminal $-NH_2$ group in coordination. The strong free ligand band at 1650 cm^{-1} undergoes shift to lower wavenumber ($\Delta\nu = 20$ cm^{-1}) in the complex $VO(LH_2)SO_4.H_2O$ indicating coordination through oxygen of the amide carbonyl group. Coordination from the azomethine nitrogen to the metal ion is manifested by the lowering of the ν(C = N)(imine) from 1600 to ~1580 cm^{-1} region[10]. A positive shift of free ligand band at 1490 cm^{-1} assignable to ν(C = N)(oxime)[4] by ~10-20 cm^{-1} in the complexes indicates coordination of oxime nitrogen. In all the complexes obtained at higher *p*H in solution, the ligand undergoes enolisation and acts in a tridentate fashion coordinating through the deprotonated enolate oxygen, the imine (>C = N) nitrogen and the oxime (>C = N) nitrogen. The amide-I band which appears at 1650 cm^{-1} in the free ligand is completely absent in the complexes, except $VO(LH_2)SO_4.H_2O$ and $VO(LH_2)C_2O_4.H_2O$ in which amide-I band appears at 1630 and 1620 cm^{-1} respectively. As the ligand contains several bands in the 1000-900 cm^{-1} region, it has not been possible to assign the ν(N − O) band in the ligand or in the complexes. Presence of monocoordinated sulphate in $VO(LH_2)SO_4.H_2O$ is indicated by the splitting of the ν_3 band of free sulphate ion into two bands at 1145 and 1055 cm^{-1} with the ν_1 band located at 995 cm^{-1}. The fairly strong ν(V = O) band is observed at 995 cm^{-1} in



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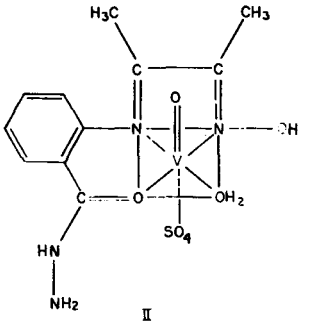

II

$VO(LH_2)SO_4.H_2O$ and at 965 cm^{-1} in $VO(L).2H_2O$. In the mixed ligand complexes the $\nu(V=O)$ band is found to be changed with the change in the nature of the incoming Lewis base (Table 1), an observation also recorded by previous workers[11].

In $VO(L).2H_2O$, the ligand occupies three positions in the equatorial plane while the vanadyl oxygen occupies one axial position because occupation of two equatorial and one axial position by the ligand would introduce much strain in the complex. The other two positions in the coordination octahedron is occupied by the two aquo molecules. Thus the complex $VO(L).2H_2O$ having the enol form of the ligand has the structure (I).

It is well known that in the $VO(H_2O)_5^{2+}$ moiety the axial water molecule is most weakly bound[7] and hence is most easily replaced. Hence, the axial water molecule in $VO(L).2H_2O$ (see structure I) is replaced by a monodentate Lewis base (B) leading to the formation of $VO(L)(B).H_2O$ type complexes. This is corroborated by the fact that the position of $\nu(V=O)$ invariably changes with the change of the ligand (B) (Table 1) which is an indication that (B) replaces the water molecule situated *trans* to the V=O bond. The structure of the complexes with bidentate donors (AA) can also be obtained by replacing the two *cis* water molecules by one bidentate donor.

The structure of the complex, $VO(LH_2)SO_4.H_2O$ having the ligand in the keto form follows from that of the enol form (I) by appropriate modification of the ligand skeleton and replacing the axial water molecule by the sulphate ion as in structure (II). As the oxalate ion can only span two *cis* positions, the probable structure of $VO(LH_2)(C_2O_4).H_2O$ can easily be obtained by replacing SO_4^{2-} and H_2O in the structure of the complex $VO(LH_2)SO_4H_2O$ by the oxalate ion.

Antitubercular activity of $VO(LH_2)SO_4.H_2O$

As bactericidal tests have no practical value in the mycobacteria, bactericidal tests were not performed. Antitubercular activity *in vitro* of $VO(LH_2)SO_4.H_2O$ (moderately soluble in water) was determined following standard procedure[3]. Mycobacteria chosen for this purpose were (i) *Mycobacterium flae* and (ii) *Mycobacterium tuberculosis* $H_{37}R_v$. Minimum inhibitory concentration (MIC) for $VO(LH_2)SO_4.H_2O$ was found to be 4.24 μg/ml while for the ligand (LH_2), it is 5.00 μg/ml (ref. 3). The above results indicate that there is about 16% potentiation of the antitubercular activity of the ligand on chelation to the VO^{2+} cation. The magnitude of the potentiation of such activity on chelation to VO^{2+} was much less than that observed when the same ligand was chelated to the Cu^{2+} ion (MIC = 5.25 μg/ml)[3], in which case nearly 100% potentiation was observed.

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