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Studies on Some Ternary Complexes & Heterobinuclear Complexes of Oxovanadium(IV)

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Some binary and ternary complexes of oxovanadium(IV) with salicylaldimine, 2-hydroxyacetophenoneimine and 2-hydroxy-1-naphthaldimine have been prepared and characterized by elemental analyses, magnetic susceptibility measurements and spectral studies. The amine exchange reactions of coordinated schiff bases in these complexes have been also carried out which give symmetrical and unsymmetrical tetradentate schiff base complexes. Metal exchange reaction of these oxovanadium(IV) complexes with $CuCl_2.2H_2O$ gives the corresponding Cu(II) complexes. Reaction of tetradentate schiff base complexes of Cu(II) so obtained with $VOCl_2$ gives heterobinuclear complexes containing Cu(II) and oxovanadium(IV).

Study of symmetrical and unsymmetrical tetradentate schiff base complexes has attracted considerable attention recently[1-6]. In continuation of our earlier work on tetradentate symmetrical and unsymmetrical schiff base complexes[7,8], we report here the synthesis and characterization of some tetradentate schiff base (TSB) complexes of oxovanadium(IV). These complexes have been obtained by the reaction of diamines with binary and ternary oxovanadium(IV) complexes of schiff bases derived from salicylaldehyde, 2-hydroxyacetophenone, and 2-hydroxy-1-napthaldehyde. Further, heterobinuclear complexes containing Cu(II) and oxovanadium(IV), similar to the homobinuclear complexes studied earlier[9-11], have been also synthesized.

Materials and Methods

All the chemicals and the solvents used were of AR grade.

Preparation of complexes of the type VOL_2

Liquor ammonia (1 ml) was added to 0.2 mol of salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxy-1-naphthaldehyde dissolved in 50 ml of ethanol. The solution was refluxed and the excess of liquor ammonia was removed. To the resulting schiff base was added 0.1 mol of vanadyl sulphate in 200 ml water. On digesting the resultant solution on a water bath for 30 min, a greenish solid separated out. It was filtered, washed thoroughly with 50% ethanol, dried well *in vacuo* and analysed.

Preparation of ternary complexes of the type VOLL′

Liquor ammonia (1 ml) was added to a mixture of 0.1 mol salicylaldehyde + 0.1 mol 2-hydroxyacetophenone, 0.1 mol salicylaldehyde + 0.1 mol 2-hydroxy-1-naphthaldehyde, or 0.1 mol 2-hydroxyacetophenone + 0.1 mol 2-hydroxy-1-naphthaldehyde in 50 ml ethanol. The solution was refluxed to remove excess ammonia. To this resulting mixture of the schiff bases was added 0.1 mol of vanadyl sulphate in 200 ml of water. On digesting the resultant solution on a water bath for 30 min, a greenish solid separated out. It was filtered, washed thoroughly with 50% ethanol, dried well *in vacuo* and analysed.

Synthesis of symmetrical and unsymmetrical tetradentate schiff base (TSB) complexes by amine exchange reactions

The preformed schiff base complex of oxovanadium(IV) (0.1 mol) in 300 ml of ethanol-water mixture (1:1, v/v) was refluxed with ethylenediamine (0.1 mol) in 50 ml of ethanol for 6 hr with intermittent stirring. The solid thus obtained was filtered, washed thoroughly with 50% ethanol and dried well *in vacuo* and analysed.

Metal exchange reaction of [VO(TSB)]

To a solution of [VO(TSB)] (0.0035 mol dissolved in 100 ml chloroform) was added with constant stirring, a solution of $CuCl_2.2H_2O$ (0.003 mol dissolved in 100 ml acetone). The mixture was refluxed for 5 hr with constant stirring. The resulting solid was filtered, washed well with chloroform - acetone mixture (2:1, v/v) and dried *in vacuo*.

Preparation of heterobinuclear complexes starting from [Cu(TSB)]

To a solution of [Cu(TSB)] (0.0035 mol in 100 ml chloroform) was added $VOCl_2.5H_2O$ solution (0.003

Table 1—Analytical, Magnetic Susceptibility and Electronic Spectral Data of Oxovanadium(IV) Complexes

Complex	Found (Calc), %				λ_{max} (nm)	$\mu_{eff.}$ (B.M.)
	V	N	C	H		
Bis(salicylideneaminato)oxovanadium(IV)	.16.91 (17.50)	9.60 (9.12)	50.84 (54.72)	3.90 (4.39)	510	1.96
Bis(α-methylsalicylideneaminato)oxovanadium(IV)	15.42 (15.22)	8.08 (7.76)	55.31 (57.31)	4.75 (4.71)	530	1.72
Bis(2-hydroxy-1-naphthylmethyleneaminato)oxovanadium(IV)	12.64 (12.84)	7.00 (6.87)	61.32 (64.86)	4.15 (3.94)	610	1.98
N,N′-ethylene bis(salicylideneaminato)oxovanadium(IV)	15.43 (15.31)	8.11 (8.41)	57.20 (57.65)	4.37 (4.20)	590	1.73
N,N′-ethylene bis (α-methylsalicylideneaminato) oxovanadium(IV)	14.21 (14.13)	7.32 (7.76)	59.40 (59.83)	5.20 (4.98)	578	1.93
N,N′-ethylene bis(2-hydroxy-1-naphthylmethyleneaminato) oxovanadium(IV)	11.50 (11.78)	6.47 (6.47)	66.07 (66.51)	4.22 (4.15)	620	1.62
(Salicylideneaminato) (α-methylsalicylideneaminato) oxovanadium(IV)	15.20 (15.88)	8.81 (8.72)	52.17 (56.07)	4.31 (4.36)	520	1.84
N,N′-ethylene(salicylideneaminato) (α-methylsalicylideneaminato)oxovanadium(IV)	14.74 (14.89)	9.26 (8.06)	58.31 (58.78)	4.91 (4.60)	580	1.80
(Salicylideneaminato) (2-hydroxyl-l-naphthylmethyleneaminato)oxovanadium(IV)	14.17 (14.36)	7.21 (7.89)	59.53 (60.84)	4.23 (3.38)	570	1.73
N,N′-ethylene(salicylideneaminato) (2-hydroxy-1-naphthylmethyleneaminato)oxovanadium(IV)	13.57 (13.32)	7.73 (7.31)	58.23 (62.66)	4.00 (4.17)	610	1.73
(α-methylsalicylideneaminato) (2-hydroxy-1-naphthylmethyleneaminato)oxovanadium(IV)	13.19 (13.82)	7.57 (7.58)	64.33 (61.78)	4.40 (3.70)	570	2.09
N,N′-ethylene(α-methylsalicylideneaminato-2-hydroxy-1-naphthylmethyleneaminato)oxovanadium(IV)	12.08 (12.84	7.32 (7.05)	59.29 (63.47)	4.56 (4.53)	610	1.97
$[Cu(TSB^1)VOCl_2]$	Cl					
	14.05 (14.74)	5.81 (6.11)	41.91 (42.36)	3.77 (3.32)	—	2.27 for both Cu(II) and VO(II) centres
$[Cu(TSB^2)VOCl_2]$	15.27 (15.18)	6.22 (5.98)	38.42 (41.06)	3.50 (2.99)	—	2.72 for both Cu(II) and VO(II) centres
$[Cu(TSB^1)]$	Cu					
	18.12 (18.49)	8.03 (8.15)	59.17 (59.38)	4.66 (4.65)	550	1.92
$[Cu(TSB^2)]$	18.98 (19.28)	8.59 (8.59)	58.72 (58.26)	4.12 (4.24)	564	1.80

TSB^1 = N,N′-ethylene(salicylideneamine, α-methylsalicylideneamine)

TSB^2 = N,N′-ethylene bis(salicylideneamine)

mol in 100 ml acetone) with constant stirring. The mixture was refluxed for 5 hr with constant stirring. The resulting solid was filtered, washed thoroughly with chloroform-acetone mixture (2:1, v/v) and dried well *in vacuo*. The C, H, N and Cl analyses of the resulting solid agreed with its proposed formation as heterobinuclear complex (Table 1). Due to non-availability of suitable techniques, separate analysis of Cu(II) and oxovanadium(IV) was not possible; only mixed oxide (%) was determined and it agreed with the expected values.

Electronic spectra of the complexes were recorded on a UV-VIS CZ spectrophotometer. Infrared spectra of the complexes were recorded in KBr on a Perkin Elmer IR spectrophotometer model No.567. Reflectance spectra of the solid complexes were recorded on a Carl-Zeiss VSU-2p instrument. Magnetic susceptibility measurements on solid complexes were carried out at room temperature (300 K) by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrating agent ($\chi_g = 16.4 \times 10^{-6}$ cgsu).

Results and Discussion

The compounds prepared in this study are sufficiently stable at room temperature under atmospheric conditions. All the schiff base complexes obtained are insoluble in water and are found to be non-conducting in their methanolic solutions. Their analytical data agree with the proposed formulae (Table 1).

The reaction of bidentate schiff bases with oxovanadium(IV) results in the formation of bis-binary and ternary complexes of the type VOL_2 and VOLL′(I).

The reaction of the above mentioned complexes(I) with ethylenediamine results in amine-exchange[12] and formation of symmetrical and unsymmetrical tetradentate schiff base(TSB) complexes of type(II). It is observed that this exchange is accompanied by change in geometry of the complexes. The *trans* form of the complex(I) is converted to *cis* form(II).

All the binary complexes exhibit magnetic moment values in the range 1.9 B.M.-1.6 B.M. as expected for the presence of one unpaired electron.

The complexes of oxovanadium(IV) have square-pyramidal structure with coordinating atoms of the schiff base in the square plane and the oxygen atom in the axial position. The *d* orbitals of vanadium get split giving rise to four electronic transitions, $d_{xy} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{yz}$, $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{z^2}$. There may be reversal in the order of energies of $d_{x^2-y^2}$ and d_{xz} levels. In the present complexes, the four absorption bands are observed in the ranges 15,000 - 20,000, 20,000 - 27,000, 27,000 - 30,000 and 30,000 - 35,000 cm^{-1}, respectively[13-15].

The IR spectra of the complexes show ν V=O frequency at 985 ± 5 cm^{-1} as expected[14]. The νOH frequency, which is known to occur at 3,400 cm^{-1} in the free ligand, is absent in the spectra of the complexes indicating deprotonation of phenolic OH during the complex formation. The −C=O stretching of aldehydic or ketonic group occurring at 1625 cm^{-1} disappears and a new band appears in the region 1610-1570 cm^{-1} due to the formation of −C=N bond. A sharp band appears at 3300 cm^{-1} corresponding to N-H stretching in bidentate schiff base complexes of the type VOLL′. This band is, however, absent in the tetradentate schiff base complexes[8] of oxovanadium(IV), indicating complete exchange of NH by ethylenediamine.

Reaction of [VO(TSB)] with Cu(II)

The preformed tetradentate schiff base complexes of the type [VO(TSB)], when treated with $CuCl_2.2H_2O$, give the complexes [Cu(TSB)]. This indicates that oxovanadium(IV) is replaced by Cu(II) ion and consequently the stability of Cu(II) tetradentate schiff base complexes is greater than that of oxovanadium(IV) tetradentate schiff base complexes. The magnetic susceptibility measurements of the resulting Cu(II) complexes show them to be paramagnetic ($\mu_{eff.}$ = 1.9 B.M.) corresponding to one unpaired electron.

The complexes show the characteristic electronic spectra, magnetic moment values, and IR spectra of [Cu(TSB)].

Reaction of $VOCl_2.5H_2O$ with [Cu(TSB)]

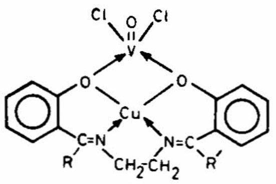
Reaction of $VOCl_2.5H_2O$ with [Cu(TSB)] resulted in the formation of heterobinuclear complexes of the type(III)

[Cu(TSB)] has an additional lone pair of electron at each of the coordinated phenolic O^- and hence, it acts as a ligand and gets coordinated with $VOCl_2$.

Room temperature magnetic moments show a significant lowering from the expected value of one unpaired electron each on Cu(II) and oxovanadium(IV) ions. This is evidently due to antiferromagnetic interaction between two paramagnetic centres. Since the distance between the two metal centres is rather large, direct metal - metal interaction is due to antiferromagnetic super-exchange interaction through the phenolic O^-.

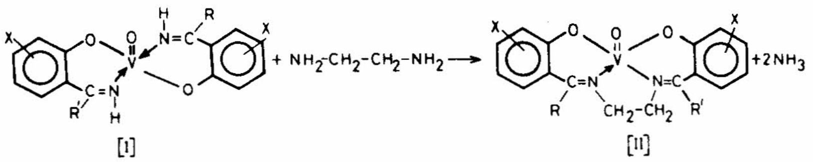
In the IR spectra of the binuclear complexes νC=O appears at 1545 cm^{-1}, showing a shift of 15-20 cm^{-1} from the value of νC=O in [Cu(TSB)] (1530 cm^{-1}). This indicates that the bridging is through phenolic O^-. The binuclear complex shows a band at 985 cm^{-1} ± 5, corresponding to V=O stretching.

The reflectance spectra of the binuclear complexes show bands at 16260 cm^{-1} and 9090 cm^{-1} corresponding to the *d-d* transitions in Cu(II) and oxovanadium(IV). The Cu(II) band in the binuclear complex shows a shift from its value in mononuclear



(III)

R=H, CH_3
R′=H, CH_3



[I]

[II]

R=H, CH_3
R′=H, CH_3
X=H or 5,6-Phenyl

complex [Cu(TSB)]. This lowering in the ligand field band of [Cu(TSB)] may be due to change in the planarity of TSB and also due to reduction in strength of Cu-O bond on the formation of second bond with oxovanadium(IV)[9].

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