

Complexes of VOSO_4 with Multidentate Schiff Base Ligands

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Summary: The present communication deals with the preparation and characterisation of complexes of multidentate schiff base ligands with VOSO_4 . The complexes possess 1:1 stoichiometric ratio (Metal : ligand). In all the complexes the sulphate ion is coordinated in a bidentate manner with C_{2v} symmetry. The complexes possess C_{4v} or D_{4h} symmetry with coordination number five and are highly distorted. There is sufficient degree of overlap between metal and ligand orbitals.

There are a number of reports on the synthesis of Schiff base complexes [1-10] of vanadyl sulphate and their structure elucidation mainly on the basis of i.r. and electronic spectral assignments but all of these reports lack the detailed analysis of electronic and e.s.r. data. Present communication deals with the synthesis of some new Schiff base complexes of VOSO_4 and their structure elucidation using various spectroscopic data specially the calculation of radial parameters, normalised spherical spin hamiltonian parameters and e.s.r. spin hamiltonian parameters.

Experimental

Benzaldehyde, 4-chlorobenzaldehyde, acetyl acetone and salicylaldehyde (B.D.H.), benzidine, p-phenylenediamine, triethylenetetramine, ethylenediamine, anisaldehyde (Riedel, Germany), o-dianisidine, 1,3 propane-diamine, furfuraldehyde, o-phenylenediamine (Koch Light, U.K.) and vanillin (Bush, Broke, Allen, U.K.) were used for the preparation of the ligands.

All the Schiff bases were prepared by condensing two moles of aldehyde or ketone with one mole of diamine in ethanol [26-28]. The solids were recrystallised. The complexes were prepared by stirring the solution of the ligand and vanadyl sulphate in methanol in 1:1 molar ratio.

The complexes were analysed for carbon, hydrogen and nitrogen at the microanalytical section of this department. The molar conductances of the complexes were measured in DMF at 10^{-3} M solution with a Philips conductivity bridge model PR-9500 using a dip type of conductivity cell. The magnetic susceptibilities of the complexes were measured by Gouy method. The thermograms of the complexes were recorded at G.N.D. University, Amritsar, on a manually operated non-recording instrument ambient to 600° at a heating rate of $10^\circ/\text{minute}$. The i.r. spectra of the ligands and the complexes were taken in KBr phase between $4000-200\text{ cm}^{-1}$ on Perkin Elmer I.R. spectrophotometer model 621. The electronic spectra of the complexes

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Table-1: Elemental Analyses and other characterising data

S. No.	Name of Complexes	Colour	m. p., / d, p., in °C	Analyses		Molar Conductance (ohm ⁻¹ cm ² mole ⁻¹)	Magnetic moment μ _{eff} (B.M.)	
				%C	%H			
1.	VO(BAOPD)SO ₄ .H ₂ O	Dirty white	280	63.14 (64.08)	4.61 (4.54)	7.34 (7.47)	44.7	0.98
2.	VO(SAPDA)SO ₄ .H ₂ O	yellow	270	44.30 (44.05)	4.50 (4.31)	6.10 (6.00)	4.3	1.76
3.	VO(SATETA)SO ₄ .H ₂ O	Greenish yellow	250	43.98 (44.86)	4.53 (4.48)	10.12 (10.46)	6.3	1.55
4.	VO(VED)SO ₂ .H ₂ O	Greenish yellow	220	41.30 (42.40)	4.40 (4.30)	5.62 (5.50)	23.8	1.78
5.	VO(VTETA)SO ₄	Light Green	220	44.32 (44.50)	5.40 (5.37)	9.51 (9.40)	9.5	1.20
6.	VO(VED)SO ₄	Light	190	54.21 (53.01)	4.08 (4.12)	4.42 (4.47)	38.8	1.59
7.	VO(VODAD)SO ₄ .H ₂ O	Brown	320	50.86 (51.94)	4.29 (4.32)	4.20 (4.04)	62.7	1.44
8.	VO(VPPDA)SO ₄	Brown	315	47.45 (47.39)	3.92 (3.93)	5.03 (5.00)	38:0	1.80
9.	VO(AAEDA)SO ₄ .H ₂ O	Green	215	45.35 (45.28)	4.92 (4.82)	5.82 (5.86)	5.1	1.07
10.	VO(AAPDA)SO ₄ .H ₂ O	Grey	260	45.59 (46.43)	5.06 (4.99)	5.67 (5.70)	5.9	1.56

continued...

Table-1: Continued.

11. VO(AAPPDA)SO ₄	Light Pink	220	51.70 (50.28)	4.22 (4.19)	5.45 (5.33)	42.8	1.71
12. VO(AABD)SO ₄ .H ₂ O	Yellow	240	53.98 (55.90)	4.36 (4.32)	4.80 (4.65)	47.5	1.75
13. VO(FFABD)SO ₄	Brown	200	51.22 (50.6)	3.84 (3.83)	5.42 (5.36)	42.8	1.59
14. VO(CBAPDA)SO ₄ .H ₂ O	Greyish Green	240	42.01 (40.80)	3.54 (3.60)	5.82 (5.60)	5.9	1.67
15. VO(AANBD)SO ₄	Green	235	48.97 (49.90)	4.40 (4.41)	5.41 (5.29)	15.2	1.56
16. VO(AANPPDA)SO ₄ .H ₂ O	Dirty white	160	43.07 (42.10)	4.91 (4.80)	6.02 (6.10)	36.1	1.49
17. VO(PDABPDA)SO ₄ .H ₂ O	Green	245	48.21 (48.10)	10.76 (10.89)	10.93 (10.83)	28.5	1.72
18. VO(PDABBD)SO ₄ .H ₂ O	Brownish red	270	59.12 (5.10)	5.12 (5.10)	8.45 (8.93)	33.33	1.78
19. VO(PDABOPDA)SO ₄ .H ₂ O	Yellow	280	53.19 (52.26)	5.10 (5.08)	10.25 (10.16)	32.3	1.82
20. VO(PDABPDA)SO ₄ .H ₂ O	red	230	52.13 (50.45)	5.02 (5.08)	10.12 (10.16)	78.9	1.8
21. VO(PDABODA)SO ₄ .H ₂ O	Brown	250	54.98 (55.88)	5.32 (5.23)	8.22 (8.15)	4.47	1.61
22. VO(PDABTETA)SO ₄ .H ₂ O	Light red	270	49.80 (48.80)	6.57 (6.62)	14.32 (14.26)	7.9	1.70

were recorded on Beckman DU-2 spectrophotometer and the e.s.r. spectra of the complexes were recorded at RSIC, IIT Madras.

Results and Discussion

The elemental analyses for C, H and N indicate that all the ligands interact with VOSO_4 in the molar ratio of 1:1 except bis-(benzaldehyde)-*o*-phenylenediamine which interacts in the molar ratio of 2:1 (ligand:metal) (Table-1).

Molar Conductance:

The values of molar conductivities of the complexes in dimethylformamide show that all the complexes are non-electrolytes.

I.R. Spectra:

The i.r. spectra of the complexes of all the Schiff bases show coordination through the azomethine nitrogen of C=N group of the Schiff bases except in cases of the Schiff bases of *p*-dimethyl-amino benzaldehyde. In all these cases there is a negative shift in frequency of $10\text{-}60\text{ cm}^{-1}$ in the complexes as compared to ligand [11]. In the complexes of Schiff bases of *p*-dimethylaminobenzaldehyde, there is the coordination through the two terminal tertiary nitrogens of the *p*-dimethylaminobenzaldehyde part. In these complexes the C=N stretching frequency occurs exactly on the position where it appeared in the coordinating ligand. In these complexes there is marked positive shift of $30\text{-}10\text{ cm}^{-1}$ in the aromatic C-N frequency and marked negative shift in the aliphatic C-N frequency.

The V=O stretching frequency has been observed in some complexes as a new band [12] which appeared in

the region $980\text{-}780\text{ cm}^{-1}$. In corroboration to conductivity data, the i.r. spectra of all the complexes show that SO_4^{2-} is coordinated in bidentate manner (Table 2). Thus invariably in all the complexes, all the four bands appear and some of them also show splittings as shoulders of the band [13].

A few new bands appear in the far i.r. spectra of the complexes in the region $550\text{-}390$ and $380\text{-}315\text{ cm}^{-1}$ which have been assigned to V-N [14] and V-O [15] vibrations respectively (Table 2).

Magnetic moments:

The magnetic moments of all the complexes range between 0.98 and 1.82 B.M. which are low as compared to the value expected for single unpaired electron. A greater lowering may only be caused by either antiferromagnetic exchange coupling or spin-spin coupling [16-20] due to the metal-metal interaction or due to the crystal lattice orientation of spins in opposite directions.

On the basis of the position of spectral bands in the electronic spectra, the complexes may be categorised in two groups. One which has D_{4h} symmetry [21] and the other which has C_{4v} symmetry [22,24].

The complexes with D_{4h} symmetry show three d-d transitions in their electronic spectra in the regions $12000\text{-}13000\text{ cm}^{-1}$, $14000\text{-}18000\text{ cm}^{-1}$ (Table-3B). The values of D_s and D_t when compared with the values obtained for $\text{VOSO}_4 \cdot 4\text{H}_2\text{O}$ show a decrease for D_s and an increase for D_t thus favouring the elongation along the Z axis. The ratio D_t/D_s ranges

Table-2. i.r. and far i.r. spectral data.

	SO ₄				νV=O	νV-N	νV-O
	ν ₁	ν ₂	ν ₃	ν ₄			
1. VO(BAOPD)SO ₄ .H ₂ O	1000	530	1130	620	890	-	-
2. VO(SAPDA)SO ₄ .H ₂ O	1025	425	1130 1120	570	800	410	355
3. VO(SATETA)SO ₄ .H ₂ O	1030	440	1120	600	840	390	350
4. VO(VED)SO ₄ .H ₂ O	980	450	1130	590	840	-	-
5. VO(VTETA)SO ₄	980	515	1140	610	780	-	-
6. VO(VED)SO ₄	1030	515	1130	620	810	435	380
7. VO(VODAD)SO ₄ .H ₂ O	1000	500	1140	610	-	550	-
8. VO(VPPDA)SO ₄	1030	500	1130	610	820	440	360
9. VO(AAEDA)SO ₄ .H ₂ O	975	525	1075	605	-	420	355
10. VO(AAPDA)SO ₄ .H ₂ O	975	440	1105	610	-	-	-
11. VO(AAPPDA)SO ₄	980	310	1140	620	830	450	370
12. VO(AABD)SO ₄ .H ₂ O	1000	530	1170	600	-	-	-
13. VO(FFABD)SO ₄	1010	510	1140	610	980	440	360
14. VO(CBAPDA)SO ₄ .H ₂ O	980	450	1140	610	955	340	315
15. VO(AANBD)SO ₄	1020	505	1125	625	-	430	355
16. VO(AANPPDA)SO ₄ .H ₂ O	1010	-	1110	-	960	-	-
17. VO(PDABPDA)SO ₄ .H ₂ O	1030	530	1120	600	-	410	-
18. VO(PDABBD)SO ₄ .H ₂ O	980	510	1120	590	-	-	-
19. VO(PDABOPDA)SO ₄ .H ₂ O	980	530	1120	610	980	440	-
20. VO(PDAPPDA)SO ₄ .H ₂ O	-	-	1130	600	-	-	-
21. VO(PDABODAD)SO ₄ .H ₂ O	990	440	1130	610	-	440	-
22. VO(PDABTETA)SO ₄ .H ₂ O	970	490	1110	610	780	-	-

Table-3A: Electronic spectral bands and radial parameters

Sl. No.	Name of complex	eg _{2g}	b _{1g} ^a	b _{2g} ^b	a _{1g} ^a	b _{2g} ^b	Charge transfer bands	Dq	Ds	Dt	DQ	DS	DT	DT/DQ
1.	VO(BAOPD)SO ₄ .H ₂ O	12315	17390	23210	33330	1739	-2591	908	33250	18137	12307	.37		
2.	VO(VED)SO ₄ .H ₂ O	12820	16670	22730	23530	1667	-2697	946	30661	18879	12823	.42		
3.	VO(SAPDA)SO ₄ .H ₂ O	12120	16670	21050	41670	1667	-2357	1010	29643	16499	13691	.46		
					32260									
					25000									
4.	VO(AAPPDA)SO ₄ .H ₂ O	12800	16340	22220	30000	1634	-2669	959	29553	18683	12999	.44		
					27030									
					25000									
5.	VO(VODAD)SO ₄ .H ₂ O	12820	16000	21050	29410	1600	-2553	1032	27447	17871	13989	.51		
6.	VO(PAABOPDA)SO ₄ .H ₂ O	-	16530	20000	29450	1653	-	-	-	-	-	-		
7.	VO(PDABBD)SO ₄ .H ₂ O	-	15625	21750	30250	1563	-	-	-	-	-	-		

Table-3B: Electronic spectral bands and radial parameters

S. No.	Name of complex	b_{2g}^e (1)	a_{1g}^e (2)	b_{1g}^e (3)	Charge transfer bands	Dq	Ds	Dt	DQ	DS	DT	DT/DQ
1.	VO(FFABD)SO ₄	12050	14925	25640	33330	1359	3253	-459	44744	-22750	6236	.14
2.	VO(VPPDA)SO ₄	12500	15385	25000	40000 31250	1250	3160	-605	44080	-22120	8201	.19
3.	VO(VTETA)SO ₄	13605	16325	24240	40000 28570	1065	3075	-676	41166	-21525	11879	.29
4.	VO(CBAPDA)SO ₄	13605	15150	24240	36365 29850 25640	1065	3240	-777	41750	-22680	10536	.25
5.	VO(AAPDA)SO ₄ ·H ₂ O	13795	16400	23530	35715 33330	975	2990	-965	42291	-20930	13085	.31
6.	VO(AANPPDA)SO ₄	12500	15150	25000	40000 33300	1300	3192	-585	45133	-22344	8933	.18
7.	VO(PDABODAD)SO ₄ ·H ₂ O	-	18530	21980	33330 29850 27030	-	-	-	-	-	-	-

Table-4: e.s.r. spin hamiltonian parameters of VO^{+2} complexes

S.No.	Name of complexes	$\langle g \rangle$	$\langle A \rangle$	g_{11}	g_1	A_{11}	A_1
1.	$VO(VTETA)SO_4$	1.962	70.0	1.929	1.978	80	60
2.	$VO(VED)SO_4 \cdot H_2O$	1.962	-	1.805	2.045	-	-
3.	$VO(AANBD)SO_4$	2.003	73.3	1.943	2.033	100	60
4.	$VO(SAPDA)SO_4 \cdot H_2O$	1.982	-	-	-	-	-
5.	$VO(SATETA)SO_4 \cdot H_2O$	1.991	-	1.921	2.021	-	-
6.	$VO(PDABODAD)SO_4 \cdot H_2O$	1.976	-	1.863	2.033	-	-
7.	$VO(PDABOPDA)SO_4 \cdot H_2O$	1.971	-	isotropic	-	-	-

between 0.14-0.31 which is an indication of sufficient mixing between the metal σ and ligand σ orbitals [25].

The complexes which seem to have C_{4v} symmetry on the basis of electronic spectra have three transition bands around 12000, 15000-17000 and 20000-23000 cm^{-1} (Table-3A). In all of these complexes the ratio DT/DQ ranges from 0.37-0.51. This higher value indicates either weak bonding in axial and extensive π bonding in equatorial plane or it may also be due to the shifting of metal ion from the plane of the ligands thus making the bonding comparatively weaker.

The e.s.r. spectra of all the complexes were recorded at room temperature as well as at liquid nitrogen temperatures as powdered samples. The spectra were calibrated using DPPH (diphenyl picryl hydrazyl) free radical for which the 'g' value is 2.003. In two complexes the spectra is isotropic due to the misalignment of axes in powdered form.

The e.s.r. spectra of the rest of the complexes are anisotropic and show

well defined hyperfine splitting into eight peaks due to the nuclear spin (Table-4). The shape of the spectra show an axial symmetry of all these complexes with $g_{11} < g_1$ and $A_{11} > A_1$ indicating the D_{4h} or C_{4v} symmetry.

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List of abbreviations

1. BAOPD - Bis(benzaldehyde)o-phenylenediamine
2. SAPDA - Bis(salicylaldehyde)p-phenylenediamine
3. SATETA - Bis(salicyldehyde)triethylenetetramide
4. VED - Bis(vanillin)ethylenediamine
5. VTETA - Bis(vanillin) triethylenetetramine
6. VED - Bis(vanillin)benzidine
7. VODAD - Bis(vanillin)o-dianisidine
8. VPPDA - Bis(vanillin)p-phenylenediamine
9. AAEDA - Bis(anisaldehyde)ethylenediamine
10. AAPDA - Bis(anisaldehyde)p-phenylenediamine
11. AAPPDA - Bis(anisaldehyde)p-phenylenediamine
12. AABD - Bis(anisaldehyde)Benzidine
13. FFABD - Bis(furfuraldehyde)benzidine
14. CBAPDA - Bis(cinnamaldehyde)p-phenylenediamine
15. AANBD - Bis(acetylacetone)benzidine
16. AANPDA - Bis(acetylacetone)p-phenylenediamine
17. PDABPDA - Bis(p-dimethylaminobenzaldehyde)p-phenylenediamine
18. PDABAD - Bis(p-dimethylaminobenzaldehyde)benzidine
19. PDABOPDA - Bis(p-dimethylaminobenzaldehyde)o-phenylenediamine
20. PDABPDA - Bis(p-dimethylaminobenzaldehyde)p-phenylenediamine
21. PDABODA - Bis(p-dimethylaminobenzaldehyde)o-dianisidine
22. PDABTETA - Bis(p-dimethylaminobenzaldehyde)triethylenetetramine