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Synthesis and Characterization of Oxovanadium(IV) Coordination Compounds Derived from 4[N-(4-Hydroxy-3-Methoxy Benzalidene) Amino] Antipyrine Semicarbazone and 4[N-(3,4,5-Trimethoxybenzalidene) Amino] Antipyrine Semicarbazone†

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The interaction of various VO^{2+} salts in non-aqueous medium with 4[N-(4-hydroxy-3-methoxy benzalidene) amino] antipyrine semicarbazone (HMBAAPS) and 4[N-(3,4,5-trimethoxybenzalidene) amino] antipyrine semicarbazone (TMBAAPS) results in the formation of the complexes of the general composition $VOX_2 \cdot L$ ($X = Cl^-$, Br^-, I^-, NO_3^- or NCS^-) and $VO(ClO_4)_2 \cdot L \cdot H_2O$ (L = HMBAAPS or TMBAAPS). The ligands behave as tridentate (N, N, O) donors in these complexes. All the complexes are penta-coordinated. Thermal stabilities of the complexes have been studied through thermogravimetric analysis.

INTRODUCTION

Although Agarwal *et al.*[1–4] and others[5] have reported Schiff base complexes of oxovanadium (IV). But no report is available in literature of oxovanadium(IV) coordination compounds of semicarbazones having pyrazolone ring. Thus, it is worthwhile to study the ligational behaviour of 4[N-(4-hydroxy-3-methoxy benzalidene) amino] antipyrine semicarbazone (HMBAAPS) and 4[N-(3,4,5-trimethoxybenzalidene) amino] antipyrine semicarbazone (TMBAAPS) towards oxovanadium(IV) salts.

EXPERIMENTAL

Various oxovanadium(IV) salts were prepared as reported in literature[5, 6]. The ligands HMBAAPS and TMBAAPS were synthesized in the laboratory by reported method[7, 8]. All the complexes were synthesized by the following general method. To a hot solution of the respective oxovanadium(IV) salt in ethanol, a sufficient amount of 2,2′-dimethoxypropane (a dehydrating agent) was added.

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This solution was mixed with a 1 : 1 molar ratio with respective ligand in hot ethanol. The resulting mixture was refluxed for *ca.* 1 h and then concentrated to half of its volume. On cooling crystalline products were obtained which were filtered, washed with organic solvents and dried in vacuum desiccator over P_4O_{10}.

Infrared spectra (in KBr pellets) were recorded on a Perkin-Elmer 5998 (4000–200 cm^{-1}) spectrophotometer and all other physico-chemical measurements were done as reported earlier[9] and vanadium was estimated as V_2O_5.

RESULTS AND DISCUSSION

The reaction of VO^{2+} salts with HMBAAPS and TMBAAPS gave complexes of the general composition $VO(L)X_2$ ($X = Cl^-$, Br^-, I^-, NCS^- or NO_3^-) and $VO(L)(ClO_4)_2 \cdot H_2O$ (L = HMBAAPS or TMBAAPS). The analytical data of these complexes are presented in Table-1. All the complexes are quite stable and could be stored for months without any appreciable change. The complexes do not have sharp melting points but decompose on heating beyond 250°C. The molar conductance values in nitrobenzene of these complexes indicate that except perchlorate complexes, all other complexes behave like 1 : 1 electrolytes. But perchlorato complexes behave as 1 : 2 electrolytes. The molecular weight of the complexes as determined cryoscopically in freezing nitrobenzene are in good agreement with the conductance values. The magnetic moments of the present complexes were found to be in 1.62–1.79 BM range. These magnetic moments are close to "spin-only" values expected for $3d^1$ (VO)(IV) complexes with normal magnetic properties[1–3, 10].

Infrared Spectra

The ligands HMBAAPS and TMBAAPS are expected to act as tridentate coordinating through the carbonyl-O, hydrazinic-N and azomethinic-N atoms. The key infrared bands (cm^{-1}) of these complexes are presented in Table-2. The characteristic absorption of the carbonyl group in free semicarbahzones is observed[11] at *ca.* 1700 cm^{-1} (amide-I band). In all the complexes this band is shifted toward lower energy in 1650–1640 cm^{-1} region. The amide-II band in these ligands is observed in 1565–1560 cm^{-1} region. In all the present complexes, this band is also shifted towards lower wave numbers by 25–30 cm^{-1}. This observation suggests coordination through the carbonyl oxygen atom. The strong band at *ca.* 1600 cm^{-1} apparently has a large contribution from the ν(C═N) band of the semicarbazone band of the semicarbazone moiety. This has been observed as a blue shift in the position of the (C═N) band in all the complexes as compared to the free ligand. Another strong band was observed at *ca.* 1620 cm^{-1} due to azomethnic (C═N) absorption. On complexation, this band is shifted towards the lower frequency region which is suggestive of the coordination through the azomethenic N-atom[12]. In far infrared spectral bands in the ligand are practically unchanged in these complexes. But some new bands with medium to weak

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC DATA OF VO^{2+} COMPLEXES OF HMBAAPS AND TMBAAPS

Complex	Yield (%)	% Analysis, found (calcd.)			m.w. found (calcd.)	Ω_m (ohm^{-1} cm^2 $mole^{-1}$)	μ_{eff} (B.M.)
		V	N	Anion			
$VOCl_2$ (HMBAAPS)	80	9.49 (9.58)	15.64 (15.78)	13.20 (13.34)	262 (532)	23.1	1.73
$VOBr_2$ (HMBAAPS)	75	8.12 (8.21)	13.40 (13.52)	25.60 (25.76)	307 (621)	23.3	1.74
VOI_2 (HMBAAPS)	72	7.08 (7.13)	11.62 (11.74)	35.30 (35.52)	357.5 (715)	33.7	1.76
$VO(NO_3)_2$ (HMBAAPS)	82	8.63 (8.71)	19.00 (19.14)	–	289 (585)	29.1	1.79
$VO(NCS)_2$ (HMBAAPS)	76	8.74 (8.83)	19.30 (19.41)	19.90 (20.10)	285 (577)	23.9	1.69
$VO(ClO_4)_2$ (HMBAAPS)·H_2O	70	7.44 (7.52)	12.23 (12.38)	29.10 (29.35)	222 (678)	53.1	1.78
$VOCl_2$ (TMBAAPS)	82	8.78 (8.85)	14.45 (14.58)	12.20 (12.32)	285 (578)	22.9	1.71
$VOBr_2$ (TMBAAPS)	76	7.70 (7.76)	12.51 (12.63)	23.80 (24.06)	330 (665)	23.1	1.69
VOI_2 (TMBAAPS)	70	6.67 (6.72)	10.95 (11.06)	33.27 (33.46)	376 (759)	33.4	1.71
$VO(NO_3)_2$ (TMBAAPS)	80	8.03 (8.10)	17.63 (17.80)	–	311 (629)	24.1	1.69
$VO(NCS)_2$ (TMBAAPS)	77	8.13 (8.21)	17.94 (18.03)	18.50 (18.67)	308 (621)	26.5	1.62
$VO(ClO_4)_2$ (TMBAAPS)·H_2O	72	6.97 (7.06)	11.53 (11.63)	27.34 (27.56)	238 (722)	52.5	1.72

intensities appear in the region 440–375 cm^{-1} in the complexes under study, which are tentatively assigned to ν(V-O)/ν(V-N) modes[1–3].

In all the complexes of oxovanadium (IV) under discussion the (V═O) stretching frequency occurs in the 975–955 cm^{-1} region. These values are in the range observed for monomeric VO^{2+} complexes[1–4].

In $VO(ClO_4)_2 \cdot L \cdot H_2O$ complexes, the presence of coordinated water was suggested by the very broad absorption centered around 3400 cm^{-1} in the infrared spectra. Bands at *ca.* 930 and 770 cm^{-1} may be attributed to rocking and wagging modes of the coordinated water[13].

TABLE-2

KEY IR BANDS (cm^{-1}) OF VO^{2+} COMPLEXES OF HMBAAPS AND TMBAAPS

Complex	ν(C═N) azomethinic	ν(C═N) hydrazinic	ν(C═O)			ν(V═O)	ν(V—N)/ ν(V—O)
			I	II	III		
HMBAAPS	1620 s	1605 s	1702 s	1560 m	1355 m	–	–
$VOCl_2$ (HMBAAPS)	1600 s	1622 s	1645 s	1535 m	1330 m	970 m	455 m, 390 w
$VOBr_2$ (HMBAAPS)	1595 s	1630 s	1650 s	1530 m	1332 m	940 m	458 m, 387 w
VOI_2 (HMBAAPS)	1602 s	1632 s	1652 s	1532 m	1330 m	965 s	460 m, 385 w
$VO(NO_3)_2$ (HMBAAPS)	1598 s	1628 s	1645 s	1530 m	1328 m	955 s	455 m, 382 w
$VO(NCS)_2$ (HMBAAPS)	1595 s	1630 s	1640 s	1535 m	1332 m	950 s	465 m, 390 w
$VO(ClO_4)_2$ (HMBAAPS)·H_2O	1593 s	1635 s	1642 s	1530 m	1325 m	952 m	470 m, 392 w
TMBAAPS	1615 s	1600 s	1700 s	1565 m	1350 m	–	–
$VOCl_2$ (TMBAAPS)	1592 s	1622 s	1645 s	1535 m	1335 m	960 m	460 m, 392 w
$VOBr_2$ (TMBAAPS)	1585 s	1630 s	1650 s	1530 m	1332 m	952 m	462 m, 390 w
VOI_2 (TMBAAPS)	1580 s	1625 s	1652 s	1532 m	1330 m	957 m	465 m, 392 w
$VO(NO_3)_2$ (TMBAAPS)	1590 s	1632 s	1645 s	1528 m	1332 m	965 m	470 m, 390 w
$VO(NCS)_2$ (TMBAAPS)	1592 s	1630 s	1640 s	1530 m	1330 m	962 m	465 m, 385 w
$VO(ClO_4)_2$ (TMBAAPS)·H_2O	1590 s	1625 s	1642 s	1533 m	1335 m	972 m	470 m, 370 w

The presence of numerous bands in the spectra of VO^{2+} complexes complicates the identification of the nature of coordination of nitrate, isothiocyanate and perchlorate groups. However, a close comparison of the spectra makes some inference possible.

In the nitrate complexes, the presence of ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the occurrence of two strong bands at *ca.* 1520 and 1310 cm^{-1} suggest the presence of one coordinated nitrato group[14, 15]. By applying Lever's separation method[16], a separation (*ca.* 20 cm^{-1}) in combination bands ($\nu_1 + \nu_4$) concludes the monodentate nitrate coordination. Other bands appeared at *ca.* 1035 (ν_2), 810 (ν_6) and 725 cm^{-1} (ν_3/ν_5) due to nitrate group. In isothiocyanate complexes the three fundamental absorptions ν(C—N) (ν_1), ν(C=S)(ν_3) and δ(NCS) (ν_2) appeared at *ca.* 2060, 860 and 475 cm^{-1} respectively suggesting that these frequencies are associated with the terminal N-bonded isothiocyanate ions[17, 18]. In both the perchlorate complexes the presence of the ν_3 (1090–1080 cm^{-1}) and ν_4 (625–620 cm^{-1}) bands indicates that the T_d symmetrly of ClO_4^- is maintained in these complexes. This, therefore, suggests the presence of ClO_4^- outside the coordination sphere in these complexes[19, 20].

Electronic Spectra

The assignments of the spectral bands of VO^{2+} complexes have been a subject of controversy[21, 22]. In general, three low intensity absorption bands are observed at room temperature in the spectral region 25000–13000 cm^{-1} (Table-3).

TABLE-3
ELECTRONIC SPECTRAL BANDS (cm^{-1}) OF VO^{2+} COMPLEXES OF HMBAAPS AND TMBAAPS

Complex	Band-I $d_{xy} \rightarrow d_{xz}, d_{yz}$	Band-II $d_{xy} \rightarrow d_{x^2-y^2}$	Band-III $d_{xy} \rightarrow d_{z^2}$
$VOCl_2$ (HMBAAPS)	13300	17250	24900
$VOBr_2$ (HMBAAPS)	13550	17050	25000
VOI_2 (HMBAAPS)	13600	16900	–
$VO(NO_3)_2$ (HMBAAPS)	13500	16850	24800
$VO(NCS)_2$ (HMBAAPS)	13200	17200	25200
$VO(ClO_4)_2$ (HMBAAPS)·H_2O	13550	17300	–
$VOCl_2$ (TMBAAPS)	12500	17200	23000
$VOBr_2$ (TMBAAPS)	13000	16800	24000
VOI_2 (TMBAAPS)	13300	17000	23500
$VO(NO_3)_2$ (TMBAAPS)	13500	17300	24400
$VO(NCS)_2$ (TMBAAPS)	12900	17200	23900
$VO(ClO_4)_2$ (TMBAAPS)·H_2O	13200	17400	–

TABLE-4

THERMOANALYTICAL RESULTS OF VO^{2+} COMPLEXES OF HMBAAPS

Complex	Sample wt. (mg)	Residual wt. (mg)	Mass loss (%)						Residual (%) *ca.* 650°C	
			70–120°C		230–315°C		380–440°C			
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.	Theor.[d]	Exp.
$VOCl_2$ (HMBAAPS)	18.20	3.24	–	–	37.03	36.82	74.06	73.70	17.10	17.82
$VOBr_2$ (HMBAAPS)	20.70	3.09	–	–	31.72	31.32	63.44	63.11	14.65	14.93
$VO(NO_3)_2$ (HMBAAPS)	22.20	3.53	–	–	33.67	33.31	67.35	67.05	15.55	15.92
$VO(ClO_4)_2$ (HMBAAPS)·H_2O	24.60	3.37	2.65	2.80	31.71	31.29	60.76	60.42	13.42	13.73

[a]Calculated for loss of H_2O mole; [b]Calculated for loss of 0.5 mole of organic ligand; [c]Calculated for total loss of organic ligand; [d]Calculated as V_2O_5.

TABLE-5

THERMOANALYTICAL RESULTS OF VO^{2+} COMPLEXES OF TMBAAPS

Complex	Sample wt. (mg)	Residual wt. (mg)	Mass loss (%)				Residual (%) *ca.* 645°C	
			235–330°C		385–450°C			
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$VOCl_2$ (TMBAAPS)	18.20	2.90	38.02	37.69	76.04	75.63	15.79	15.92
$VO(NO_3)_2$ (TMBAAPS)	20.30	3.01	34.81	34.24	69.63	69.04	14.46	14.84
$VO(NCS)_2$ (TMBAAPS)	23.10	3.47	35.26	34.63	70.53	69.98	14.65	15.02

[a]Calculated for loss of 0.5 mole of organic ligand; [b]Calculated for total loss of organic ligand; [c]Calculated as V_2O_5.

Ballhausen and Gray[23] have assigned these bands as band-I to the electronic transition $^2B_2 \rightarrow {}^2E_1$; band-II to $^2B_2 \rightarrow {}^2B_1$; and band-III to $^2B_2 \rightarrow {}^2A_1$. All other higher energy bands are assumed to the charge transfer in origin. Thus, the three optical transitions are predicted by the symmetry C_{4v} of the $[VO(H_2O)_5]^{2+}$. On lowering the symmetry of C_{2v} $[VO(acac)_2]$ the splitting of e* is simply too small to be observed experimentally. Hence any distortion from C_{4v} would not be observable and only three transitions would appear in the electronic spectra[22, 23]. According to Vonquickborne and McGlynn (V-M scheme)[24], the first band which is centred near 13000 cm^{-1} has been assigned to the unresolved band resulting from $d_{xy} \rightarrow d_{yz}$, d_{xz} $(^2B_2 \rightarrow {}^2E_1)$ transition. The second shoulder observed in the 17400–16800 cm^{-1} region is attributed to $d_{xy} \rightarrow d_{x^2-y^2}$ $(^2B_2 \rightarrow {}^2B_1)$ and the third band may either be assigned to the transition $d_{xz} \rightarrow d_{z^2}$ $(^2B_2 \rightarrow {}^2A_1)$ or believed to arise from low energy charge transfer.

In conclusion, due to steric interaction of the larger size of the ligands the lower coordination number five has been assigned to these complexes. The five-coordinated complexes of VO^{2+} may have the usual tetragonal pyramidal structure.

Thermal Studies

The careful analysis of t.g. curves of $VOX_2 \cdot HMBAAPS$ (Table-4) ($X = Cl^-$, Br^- or NO_3^-) suggests that these complexes do not possess water molecule either in or out of the coordination sphere. The pyrolysis curves behave similarly and show that decomposition of the complexes starts at 230°C and was completed at *ca.* 440°C. The break in curves at *ca.* 315°C indicate that at this stage 0.5 mole of organic ligand has been lost while at 440°C the loss of 63–73% clearly indicates the complete loss of HMBAAPS molecule and reduction to VO_2. The oxide V_2O_5 is formed at *ca.* 650°C, following which there is no sensible change in weight observed. In case of $VO(ClO_4)_2(HMBAAPS) \cdot H_2O$ the coordinate water is lost at *ca.* 120°C and finally at *ca.* 650°C, V_2O_5 is obtained as end product. In brief, the thermal decomposition equations are as

$$VOX_2(HMBAAPS) \rightarrow VOX_2 \cdot 0.5(HMBAAPS) \rightarrow VOX_2 \rightarrow V_2O_5$$

$(X = Cl^-, Br^- \text{ or } NO_3^-)$

$$VO(ClO_4)_2\,(HMBAAPS)\,(H_2O) \rightarrow VO(ClO_4)_2(HMBAAPS)$$

$$\rightarrow VO(ClO_4)_2 \cdot 0.5(HMBAAPS) \rightarrow VO(ClO_4)_2 \rightarrow V_2O_5$$

Similarly the thermal decomposition equations of VO^{2+} complexes of TMBAAPS are (Table-5) as follows:

$$VOX_2(TMBAAPS) \rightarrow VOX_2 \cdot 0.5\,(TMBAAPS) \rightarrow VOX_2 \rightarrow V_2O_5$$

$(X = Cl^-, NO_3^- \text{ or } NCS^-)$

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