Asian Journal of Chemistry Vol. 8, No. 1 (1996), 169–172

NOTE

Some Penta-Coordinated Complexes of Oxovanadium(IV) with 4[N-(3,4,5-Trimethoxy Benzylidene) Amino] Antipyrine

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In the present note, a series of penta-coordinated complexes of VO^{2+} with 4[N-(3,4,5-trimethoxy benzylidene) amino] antipyrine (TMBAAP) with the general composition $VOX_2 \cdot n(TMBAAP)$ ($X = Cl^-, Br^-, I^-, NO_3^-$ or NCS, n = 1; $X = ClO_4^-$, n = 2) have been synthesized and characterized. The IR data reveal the bidentate nature (N,O) of the ligand. The probable coordination number of the central metal ion is found to be five. Thermal stabilities of the complexes have been studied through thermogravimetric analysis.

A keen interest in the study of Schiff bases arose due to their ease of preparation and considerable use of their metal complexes in industries, medicines, pesticides or insecticides etc. Recently Chakraborti *et al.*[1] have reported oxovanadium(IV) complexes of various Schiff bases of 4-amino-antipyrine. As an extension of the work, in the present paper, we report our results on VO^{2+} complexes of 4[N-(3,4,5-trimethoxybenzylidene) amino] antipyrine. The ligational properties of this ligand were first reported by Agarwal *et al.*[2] with UO_2^{2+} and Th^{4+} ions.

The ligand TMBAAP was synthesized in the laboratory by reported method[2]. The metal salts were prepared by known methods[3]. IR 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[4] and vanadium in estimated as V_2O_5.

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. This solution was mixed with a stoichiometric amount of the ligand in hot ethanol. The resulting mixture was refluxed for about $\frac{1}{2}$ 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}.

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The elemental analyses of the complexes suggested the general composition of the complexes in $VOX_2 \cdot nTMBAAP$ ($X = Cl^-$, Br^-, I^-, NO_3^- or NCS^-, $n = 1$; $X = ClO_4^-$, $n = 2$). The complexes are generally soluble in common organic solvents. The molar conductance measured in nitrobenzene suggests the non-electrolytic nature of the halo, pseudohalo and nitrato complexes, while the perchlorate complex is a 1 : 2 electrolyte. The molecular weight data also support a similar behaviour. The magnetic moments of these complexes were found to be in 1.82–1.69 B.M. range. These magnetic moments are close to "spin only" values expected for $3d^1$(VO)(IV) complexes with normal magnetic properties[5, 6].

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

Complex	Found (Calcd.) %			Mol. wt. Found (Calcd.)	Λ_m (ohm^{-1} cm^2 mole^{-1})	μ_{eff} (B.M.)
	V	N	Anion			
$VOCl_2 \cdot TMBAAP$	9.74 (9.82)	7.98 (8.09)	13.50 (13.68)	510 (519)	4.2	1.81
$VOBr_2 \cdot TMBAAP$	8.32 (8.38)	6.82 (6.90)	26.19 (26.31)	599 (608)	4.3	1.79
$VOI_2 \cdot TMBAAP$	7.18 (7.26)	5.90 (5.98)	36.02 (36.18)	692 (702)	5.1	1.69
$VO(NO_3)_2 \cdot TMBAAP$	8.82 (8.91)	12.13 (12.23)	— —	563 (572)	3.9	1.82
$VO(NCS)_2 \cdot TMBAAP$	8.96 (9.04)	12.30 (12.41)	20.45 (20.56)	557 (564)	4.2	1.76
$VO(ClO_4)_2 \cdot 2TMBAAP$	4.90 (4.96)	8.11 (8.17)	19.25 (19.35)	337 (1028)	50.6	1.79

TMBAAP: 4[N-(3,4,5-trimethoxybenzalidene) amino] antipyrine ($C_{21}H_{23}N_3O_4$).

The infrared spectra of all the complexes (Table-2) show a considerable negative shift in carbonyl (pyrazolone) absorption ν(C=O) 50–45 cm^{-1}, indicating a decrease in stretching force-constant of C=O as a consequence of coordination through the oxygen atom of the free base[1, 2]. It is well known[7] that as a result of coordination through the carbonyl oxygen the double bond character between the carbon and the oxygen is reduced. The decrease in the bond character causes a bathochromic effect in the carbonyl stretching frequency. The C=O stretching frequency occurring at 1650 cm^{-1} in free ligand has been shifted to lower wave number in the region 1605–1600 cm^{-1} in all the complexes. Another important band occurs at 1590 cm^{-1} attributed to ν(C=N) mode[1, 2]. In spectra of all the complexes this band is shifted to lower wave number and appears at 1552–1545 cm^{-1} indicating the involvement of N-atom of the azomethine group in coordination[1, 2]. The metal-ligand stretching vibrations ν(V—O)/ν(V—N) modes are observed in 450–360 cm^{-1} region[1, 2]. In all the complexes of oxovanadium(IV) with TMBAAP, the V=O stretching frequency occurs in 982–965 cm^{-1} region suggesting the monomeric nature of these complexes[8, 9]

TABLE-2
KEY IR BANDS (cm^{-1}) of VO^{2+} COMPLEXES OF TMBAAP

Compound	ν(C=O) (pyrazolone)	ν(C=N) (azomethine)	ν(V=O) (oxocation)	ν(V—O)/ν(V—N) (metal-ligand)
TMBAAP	1650 s	1590 s	—	—
$VOCl_2$·TMBAAP	1600 s	1550 s	970 m	450 m, 370 m
$VOBr_2$·TMBAAP	1600 s	1550 s	965 m	440 m, 360 m
VOI_2·TMBAAP	1605 s	1552 s	982 m	455 m, 367 m
$VO(NO_3)_2$·TMBAAP	1602 s	1552 s	975 m	460 m, 365 m
$VO(NCS)_2$·TMBAAP	1600 s	1545 s	970 m	445 m, 362 m
$VO(ClO_4)_2$·2TMBAAP	1605 s	1550 s	970 m	440 m, 360 m

In $VO(ClO_4)_2$·2TMBAAP, the presence of the ν_3 and ν_4 at 1085 and 625 cm^{-1} respectively indicates that the T_d symmetry has not been disturbed in this complex and both the perchlorato groups are present outside the coordination sphere[10, 11]. The thiocyanate complex $VO(NCS)_2$·TMBAAP shows three bands at 2040, 840 and 465 cm^{-1} due to ν(C=N), ν(C—S) and δ(N—C—S) respectively suggesting the N-bonded isothiocyanate groups in this case[12]. In $VO(NO_3)_2$ ·TMBAAP, the absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and occurrence of two strong bands at 1500 cm^{-1} (ν_4) and 1310 cm^{-1} (ν_1) due to the split ν_3 mode in the lower symmetry indicate a coordinated nitrato group[13, 14]. Other bands also occur at 1030 (ν_2), 815 (ν_6) and 740 (ν_3/ν_5) cm^{-1} in this complex. Distinction between monodentate and bidentate nitrate is usually difficult. But by applying Lever's separation method[15], a separation of 15 cm^{-1} in combination bands ($\nu_1 + \nu_4$) concludes the monodenate nitrate coordination.

The VO^{2+} complexes show two bands in 15750–12600 cm^{-1} region. These bands are not well developed. Except nitrato complex, in all other complexes a weak but well developed band at about 22000 cm^{-1} has also been observed. According to Ballhausen and Gray[16] scheme the first and subsequent charge transfer transitions are predicted to occur at higher energies and often band III is not observed but is believed buried beneath the low energy tail of the much more intense charge transfer band. Following the ordering of energy levels (BG scheme), the first band at about 12800 cm^{-1} is assigned to an unresolved band resulting from the $d_{xy} \rightarrow d_{xz} \rightarrow d_{yz}$ ($^2B_2 \rightarrow {}^2E$) transition. The second band at about 15500 cm^{-1} is attributed to $d_{xy} \rightarrow d_{x^2-y^2}$ ($^2B_2 \rightarrow {}^2B_1$) transitions. The band at about 22000 cm^{-1} may either be assigned to the $d_{xy} \rightarrow d_{z^2}$ ($^2B_2 \rightarrow {}^2A_1$) transition or believed to be low energy charge transfer band.

The t.g. curves of present complexes do not show the presence of water molecule either in or out of the coordination sphere. All the pyrolysis curves behave similarly and show that decomposition of the complexes started at 230°C and were completed at *ca.* 440°C. The break in 310°C indicates that at this stage *ca.* 0.5 molecule of the organic ligand has been lost while at *ca.* 440°C, the loss of 62–74% clearly indicates the complete loss of TMBAAP molecule and reduction to VO_2. The oxide V_2O_5 is formed at *ca.* 640°C, following which there is no sensible change in weight. In case of $VO(ClO_4)_2$·2TMBAAP, one molecule of TMBAAP is lost in 230–310°C temperature range while the second molecule of TMBAAP is lost at *ca.* 440°C. Finally at 640°C, V_2O_5 is obtained as final product. In brief these changes can be shown as

$$VOX_2 \cdot TMBAAP \rightarrow VOX_2 \cdot 0.5TMBAAP \rightarrow VOX_2 \rightarrow [VO_2] \rightarrow V_2O_5$$

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

$$VO(ClO_4)_2 \cdot 2TMBAAP \rightarrow VO(ClO_4)_2 \cdot TMBAAP \rightarrow VO(ClO_4)_2 \rightarrow [VO_2] \rightarrow V_2O_5.$$

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

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(*Received*: 29 July 1995; *Accepted*: 13 September 1995) AJC-1011