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Studies on Oxovanadium(IV) Complexes with 4-[(N-Acetyl) Amino]-Antipyrine†

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Oxovanadium(IV) complexes of 4-[(N-acetyl) amino]antipyrine (AAAP) having the composition $[VO(AAAP)X_2]$ ($X=Cl$, Br, I, NO_3, NCS or $0.5C_2O_4$) and $[VO(AAP)_2](ClO_4)_2$ have been synthesised and characterised. The probable C.N. of V(IV) is found to be five.

The coordination chemistry of various oxocations is of interest because of the existence of a strong multiple metal-oxygen covalent bond persisting in various chemical environments. Selbin[1,2] has summarised various oxovanadium(IV) complexes in his review articles. But less is known about the oxovanadium(IV) complexes of pyrazolone ligands[3-5]. In the present communication we report the oxovanadium(IV) complexes with 4-[(N-acetyl)amino]-antipyrine (AAAP).

The ligand AAAP was prepared from 4-aminoantipyrine by acetylation and extracted the material with ether.[6]

The metal complexes were prepared by mixing the corresponding oxovanadium(IV) salt in methanol and 2,2′-dimethoxypropane (a dehydrating agent) and the ligand in the same solvent. The reaction mixture was refluxed for 1 h. In each case the solid product obtained was filtered and washed with methanol and ether. All the complexes were dried in vacuum desiccator over anhyd. $CaCl_2$.

Vanadium in all the complexes was determined by igniting them in air and determining the metal as V_2O_5. Halide was determined by Volhard's method. Perchlorate was determined by the method of Kurz *et al.*[7] Magnetic measurements were made on a Gouy balance at room temperature using $CuSO_4.5H_2O$ as calibrant. All other physico-chemical studies of the complexes were made as reported earlier.[5]

According to elemental analysis and molecular weight determination (Table 1) these complexes may be formulated as $VO(AAAP)X_2$ ($X = Cl$, Br, I, NO_3, NCS or $0.5C_2O_4$) and $VO(AAAP)_2(ClO_4)_2$. The molar conductance values of the complexes (in nitrobenzene) indicate that halo, thiocyanato, nitrato and oxalato complexes are non-electrolytes, while the perchlorato complex dissociates in nitrobenzene and behaves as 1 : 2 electrolyte and hence in this case both the anion ligands are not coordi-

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TABLE 1

ELEMENTAL ANALYSIS AND SOME IMPORTANT IR FREQUENCIES OF OXOVANADIUM(IV) CHELATES OF AAAP

Compound	Analysis % Found/ (Calcd) V	N	Anion	Mol. wt. Found (Calcd.)	ν_{max}(cm^{-1}) ν(C=O)	Amide band I	II	VI	ν(V-O)
$C_{13}H_{15}N_3O_2$	—	—	—	—	1670s 1640s	1700s	1580s	555m	—
$VO(C_{13}H_{15}N_3O_2)Cl_2$	13.18 (13.31)	10.72 (10.96)	18.21 (18.53)	379 (383)	1590s	1672m	1560s	570m	450m
$VO(C_{13}H_{15}N_3O_2)Br_2$	10.69 (10.80)	8.69 (8.69)	33.36 (33.89)	468 (472)	1580s	1675s	1555s	582m	430m
$VO(C_{13}H_{15}N_3O_2)I_2$	8.88 (9.01)	7.26 (7.42)	44.29 (44.87)	561 (566)	1585s	1665m	1562s	575m	400m
$VO(C_{13}H_{15}N_3O_2)(NCS)_2$	11.77 (11.91)	16.18 (16.35)	26.83 (27.10)	422 (428)	1570s	1660m	1560m	572m	425m
$VO(C_{13}H_{15}N_3O_2)(NO_3)_2$	11.55 (11.69)	15.87 (16.05)	—	431 (436)	1575s	1670s	1560s	575m	420m
$VO(C_{13}H_{15}N_3O_2)C_2O_4$	12.63 (12.75)	10.36 (10.50)	—	393 (400)	1582s	1672m	1558m	570m	430m
$VO(C_{13}H_{15}N_3O_2)_2(ClO_4)_2$	6.67 (6.74)	10.93 (11.11)	25.91 (26.32)	250 (756)	1585s	1675m	1560m	575m	435m

nated. The molecular weight determination also behaves in a similar way.

The room temperature (32°C) magnetic moments of the solid compounds lie in the range 1.67–1.83 B.M. These values corresponding to one unpaired spin per vanadium atom, demonstrating the presence of vanadium(IV) in these complexes and the absence of metal-metal interactions between vanadium atoms[1,2].

The electronic spectra of the chelates closely resemble data published for comparable compounds[1,2]. In most cases three ligand field bands were observed in 13200–12600; 15950–15200 and 22750–21700 regions. In some cases the third band was obscured by charge transfer band. The first shoulder is assigned to an unresolved band resulting from the $d_{xy} \rightarrow d_{xz}$, d_{yz} ($^2B_2 \rightarrow {}^2E$) transition, the second band is attributed to the $d_{xy} \rightarrow d_{x^2-y^2}$ ($^2B_2 \rightarrow {}^2B_1$) transition and the third band may either be assigned to the $d_{xy} \rightarrow d_{z^2}$($^2B_2 \rightarrow {}^2A_1$) transition or to low energy charge transfer[1,2].

The two main IR frequencies in AAAP, viz. N-acetyl (R-NH-COCH$_3$) and pyrazolone (C=O) are expected to be influenced on complex formation. In R-NH-$COCH_3$ the carbonyl absorption, responsible for the amide I band, is likely to be lowered. The amide I band in AAAP appearing at 1700 cm^{-1} is shifted to lower wave number after forming complexes. An absorption at *ca* 1580 cm^{-1}, known as amide-II band, is a mixed vibration of out-of-plane combination of OCN and NH deformation modes. A negative shift of the band of the complexes also supports coordination through the oxygen atom. As a result of coordination from the oxygen atom of the carbonyl group, the C-N stretching frequency attains a partial double bond character and as expected shifts to higher frequency region. Amide VI band occurs at *ca* 550 cm^{-1} shifted to higher wave number. The decrease in frequency of band I and the increase in frequency of band VI confirm that the amide group is O-bonded. Further, the NH stretching absorption in free ligand occurs at 3200 and 3120 cm^{-1}, which remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom.

The most important mode of vibration in the spectra of AAAP is the one associated with the pyrazolone C=O stretching which occurs at *ca* 1670 and 1640 cm^{-1}. This absorption undergoes a significant negative shift on chelation. The decrease in C=O stretching is attributed to coordination of the oxygen atom of the base to the metal ion[8]. The overall IR spectral evidence suggests that AAAP acts as a bidentate ligand and coordinates through amide oxygen and carbonyl oxygen atoms forming a seven-membered chelate ring. The band observed in the 450–400 cm^{-1} region is assigned to the metal-ligand (V-O) vibrations.

The oxocation band (V=O) in all the chelates has been assigned in 990–960 cm^{-1} region. These values are in the range observed for monomeric VO^{++} species in oxovanadium(IV) complexes[1,2].

In thiocyanato chelate the bands occurring at *ca* 2065, 830 and 465 cm^{-1} are due to ν(CN), ν(CS) and δ(NCS) respectively suggesting N-bonded isothiocyanate[9]. The IR spectra of $VO(AAAP)(NO_3)_2$, the absence of ionic band (D_{3h}) at *ca* 1360 cm^{-1} and presence of ν_1 and ν_4 bands at *ca* 1300 and 1500 cm^{-1} respectively suggest the covalent nature of nitrate groups[10]. The view is in support of conductance measurement. Since the two bands appear at 1760 and 1745 cm^{-1} assigned to ($\nu_1 + \nu_4$) combination vibrations and the small difference (*ca* 15 cm^{-1}) between them reveals that the nitrato groups are attached to the VO^{++} as monodentate ligands[11]. In the oxalato chelate the bands appeared at *ca* 1720(ν_7), 1660(ν_1) and 1360(ν_2) cm^{-1} indicating the bidentate nature of the covalently bonded oxalate group[12]. The strong ν_3 and ν_4 bands in the spectra of perchlorate chelate occur unsplit at *ca* 1080 and 625 cm^{-1}, respectively indicating the ionic nature of the perchlorato groups[4,7].

DTA profiles have three peaks in the temperature region 250–290°C, 340–360°C and 510–550°C. Perchlorate complex decomposes exothermally while the rest of the complexes decompose endothermally. The peak I is due to the decomposition of the complex to VO_2, the peak II is due to the oxidation of VO_2 to V_2O_5 and the final peak III is due to the oxidation of carbon of the decomposed ligand. On the basis of decomposition temperature the thermal stability of these complexes is in the order

Perchlorate $<$ Bromide $\sim$ Thiocyanate $<$ Chloride $<$ Nitrate.

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