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MAGNETO, SPECTRAL AND THERMAL INVESTIGATIONS OF SOME OXOVANADIUM(IV) CHELATES OF 2-ETHOXYCARBONYLAMINO PYRIDINE *N*-OXIDE

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ABSTRACT

Some oxovanadium(IV) chelates of 2-ethoxycarbonylamino pyridine *N*-oxide (ECAPO) with general compositions $VOX_2 \cdot ECAPO$ (X = Cl, Br, I, NO_3, NCS or $0.5C_2O_4$) and $VO(ClO_4)_2 \cdot 2ECAPO$ have been isolated and characterized through chemical analyses, conductance, molar weight, magnetic susceptibility, infrared and electronic spectra. Magnetic susceptibilities measured at room temperature (30°C) of the chelates indicate the absence of metal–metal interaction between vanadium atoms. Except the perchlorato complex, all other complexes behave like non-electrolytes in nitrobenzene. In the case of the perchlorate complex, the molar conductance value suggests the 1 : 2 electrolytic nature of the complex. Ir data indicate that ECAPO is bonded to the vanadium atom through oxygens of the carbonyl group and *N*-oxygen forming a seven-membered ring. It is suggested that penta-coordinates oxovanadium(IV) compounds can have a tetragonal pyramidal structure. Thermal properties of the chelates are also discussed.

INTRODUCTION

Numerous metal complexes of pyridine *N*-oxides have been reported in recent years [1–4]. 2-Ethoxycarbonylamino pyridine *N*-oxide (ECAPO) has three potential donor sites in tertiary amine *N*-oxygen, imino nitrogen and carbonyl oxygen. Zirconyl [5], thorium [6], zinc [7], cadmium [7], uranyl [8], copper [9], nickel [9] and cobalt [9] complexes of this ligand have already been reported. Due to the different ligating behaviour of this ligand, it was considered of interest to study the coordination behaviour of ECAPO with oxovanadium(IV) and the thermal properties of the complexes formed.

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EXPERIMENTAL

The ligand was prepared from 2-amino pyridine by the method of Katritzky [10]. $VOCl_2$ and $VOBr_2$ were prepared by treating V_2O_5 with conc. HCl and HBr, respectively, in the presence of a few drops of ethanol. $VO(ClO_4)_2$ and VOC_2O_4 were prepared by previously reported methods [11,12]. VOI_2 solution was prepared by treating an alcoholic solution of $VOCl_2$ with KI. $VO(NCS)_2$ solution was prepared by treating an aqueous solution of $VO(ClO_4)_2$ with KNCS. The clear blue filtrate, obtained after removal of the solid, was concentrated by passing dry air through it, when syrupy green solution was obtained. $VO(NO_3)_2$ was prepared by treating $VOCl_2$ with $AgNO_3$.

Preparation of the complexes

All the complexes were synthesised by the following general method. To a hot solution of the respective metal salt in acetone a sufficient amount of 2,2′-dimethoxy propane (a dehydrating agent) was added. This solution was mixed with a stoichiometric amount of the ligand in methanol. The mixture was refluxed for about half an hour and then concentrated to half its volume. On cooling, crystalline products were obtained which were filtered, washed with organic solvents and dried in a vacuum desiccator over P_4O_{10}.

RESULTS AND DISCUSSION

The complexes are soluble in common organic solvents. The electrical conductance measured in nitrobenzene are consistent with the non-electrolytic nature of nitrato, oxalato, halo and pseudohalo complexes, while the perchlorate complex is a 1 : 2 electrolyte. The elemental analyses also indicate 1 : 1 and 1 : 2 (perchlorate) stoichiometry for these complexes. Accordingly, these complexes may be formulated as $VO(ECAPO)X_2$ (where X = Cl, Br, I, NO_3, $0.5C_2O_4$ or NCS) and $VO(ECAPO)_2(ClO_4)_2$, respectively (Table 1). These formulations are further supported by the results of infrared and electronic spectral studies of these complexes.

The magnetic moments of these complexes were measured at 300 K; the values lie in the range 1.72–1.82 B.M. (Table 1). These values are well within the range observed for the VO(IV) complexes and correspond to one unpaired spin per vanadium atom, demonstrating the tetravalency of vanadium in the complexes [13]. It also indicates the absence of any metal–metal interaction.

Nature of bonding from infrared data

The vibrational assignments in the IR spectra of ECAPO and its VO^{2+} complexes are made from a comparative study of the assignments of

TABLE 1

Analytical, conductivity, molecular weight and magnetic data for VO^{2+} chelates of ECAPO

Compound	Analysis found (calc.) (%)			Λ_m ($ohm^{-1}\,cm^2\,mol^{-1}$)	Average mol. wt. in $PhNO_2$	Formula weight	μ_{eff} (B.M.)
	V	N	Anion				
$VOCl_2 \cdot ECAPO$	15.72(15.93)	8.59 (8.75)	22.01(22.18)	3.2	314	320	1.72
$VOBr_2 \cdot ECAPO$	12.31(12.46)	6.69 (6.84)	38.63(39.11)	4.6	403	409	1.76
$VOI_2 \cdot ECAPO$	10.02(10.13)	5.41 (5.56)	49.31(50.49)	5.3	498	503	1.79
$VOC_2O_4 \cdot ECAPO$	15.01(15.13)	8.16 (8.30)	–	4.9	332	337	1.82
$VO(ClO_4) \cdot 2ECAPO$	7.93 (8.09)	8.62 (8.88)	30.87(31.58)	51.9	210	630	1.74
$VO(NO_3)_2 \cdot ECAPO$	13.49(13.67)	14.81(15.01)	–	4.3	365	373	1.74
$VO(NCS)_2 \cdot ECAPO$	13.73(13.97)	15.19(15.34)	31.18(31.78)	5.2	357	365	1.78

2-ethoxycarbonyl amino pyridine *N*-oxide [14,15] and the earlier work on ECAPO [5–9]. The N–H stretching occurs at 3200 and 3120 cm^{-1} in the free ligand, and remains unaffected after complexation. The C=O stretching band of the urethane moiety occurring at 1730 cm^{-1} is shifted to lower wavenumber after complexation, suggesting that coordination occurs through the carbonyl oxygen atom. In addition to this, the shift of the N–O stretching mode to lower frequencies in relation to the free ligand (Table 2) indicates coordination through the oxygen. The N–O bending vibration at 840 cm^{-1} is either unaffected or slightly shifted on complexation. The overall IR spectral evidence suggests that ECAPO acts as a bidentate ligand and coordinates through the *N*-oxygen and carbonyl oxygen atoms forming a seven-membered chelate ring. In the far IR region the band at 420–400 cm^{-1} has been assigned as V–O (metal–ligand) stretching.

In all the complexes of oxovanadium(IV) under discussion, the V=O stretching frequency occurs in the 980–965 cm^{-1} region. These values are in the range observed for monomeric VO^{2+} complexes [13].

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

In the nitrate complex, the absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and the occurrence of two strong bands at 1495 and 1300 cm^{-1} due to the split ν_3 mode in the lower symmetry indicate a coordinated nitrato group [16,17]. Distinction between monodentate and bidentate nitrate

TABLE 2

Partial IR absorption frequencies (cm^{-1}) of ECAPO and its chelates with VO^{2+}

Compound	ν(N–H)	ν(C=O)	ν(N–O)	δ(N–O)	ν(M–O)
ECAPO	3200s 3120m	1730s	1220s	840m	–
$VOCl_2 \cdot$ECAPO	3200s,br 3120m	1715s	1190s	840m	405m
$VOBr_2 \cdot$ECAPO	3200s,br 3125m	1715s	1200s	837m	410m
$VOI_2 \cdot$ECAPO	3200s 3120m	1715s	1180s	835m	415m
$VOC_2O_4 \cdot$ECAPO	3190s 3120m	1720s	1185s	830m	408m
$VO(ClO_4)_2 \cdot$2ECAPO	3205m 3120m	1720s	1175s	830m	420m
$VO(NO_3)_2 \cdot$ECAPO	3200m 3120m	1720s	1180m	845m	410m
$VO(NCS)_2 \cdot$ECAPO	3200m 3120m	1720s	1175s,br	835m	415m

is usually difficult. However, by applying Lever's separation method, a separation (ca. 20 cm^{-1}) in combination bands ($\nu_1 + \nu_4$) (1760 and 1740 cm^{-1}) concludes the monodentate nitrate coordination [18]. Other bands appeared at 1030 (ν_2), 805 (ν_6) and 730 cm^{-1} (ν_3/ν_5) due to nitrate groups.

In the perchlorate complex the ν_3 and ν_4 bands of the perchlorate group appear at 1085 and 620 cm^{-1}, respectively. This indicates that the T_d symmetry has not been disturbed in the complex and all the perchlorate ions are present outside the coordination field [19]. In the oxalate complex the bands appeared at 1725 (ν_7), 1662 (ν_1) and 1360 (ν_2) cm^{-1} indicating the bidentate nature of the covalently bonded oxalate group [20]. The thiocyanate complex shows three bands at 2050, 860 and 470 cm^{-1} assignable to ν(CN), ν(CS) and δ(NCS) vibrations, respectively, in the case of *N*-coordinated thiocyanate groups [21].

Electronic spectra

In all the ECAPO complexes of VO^{2+}, the electronic spectra show only two maxima in the range 14500–17500 cm^{-1} due to $b_2 \rightarrow c$ transition at the lower wavenumber and $b_2 \rightarrow b_1$ in the higher wavenumber absorption. The third transition, $b_2 \rightarrow a_1$, expected at higher energies, is not observed in these complexes, probably due to its overlap by the broad charge transfer band around 29000 cm^{-1} [22,23].

In conclusion, in all the complexes the coordination number of V(IV) is five and may have the usual tetragonal pyramidal structure.

Thermal studies

Recently we described the thermal properties of complexes of oxocations, e.g., oxozirconium(IV) [24,25] and dioxouranium(VI) [8,26] with oxygen

TABLE 3

Thermoanalytical results obtained for the ECAPO chelates of VO^{2+}

Compound	Sample weight (mg)	Residual mass (mg)	Mass loss (%)				Residue % at 590°C	
			165–230°C		250–340°C		Theor. [c]	Exp.
			Theor. [a]	Exp.	Theor. [b]	Exp.		
$VOCl_2 \cdot$ECAPO	29.5	8.0	28.43	29.62	56.87	58.12	28.43	27.11
$VOBr_2 \cdot$ECAPO	27.8	5.81	22.24	23.46	44.49	46.02	22.24	20.92
$VO(NCS)_2 \cdot$ECAPO	30.2	7.13	24.93	26.27	49.86	51.48	24.93	23.62
$VO(NO_3)_2 \cdot$ECAPO	25.9	6.00	24.39	25.92	48.79	50.21	24.39	23.19
$VOC_2O_4 \cdot$ECAPO	26.9	6.94	27.00	28.19	54.00	55.32	27.00	25.82

[a] Calculated for loss of 0.5 mole of ligand.

[b] Calculated for total loss of ligand.

[c] Calculated as V_2O_5.

donor ligands. Comparatively little is known about the thermal behaviour of the oxovanadium(IV) complexes [27]. In the present work, we wish to report our thermal results of ECAPO complexes of VO(IV) ions. Thermoanalytical results are summarised in Table 3.

The TG curves of the present complexes do not show the presence of water molecules either in or out of the coordination sphere. All the pyrolysis curves behave similarly and show that decomposition of the complexes started at 165°C and were completed at ca. 340°C. The break in curves at ca. 230°C indicates that at this stage ca. 0.5 mol of the ligand has been lost. While at 340°C the loss of 46–58% clearly indicates the complete loss of the ECAPO molecule and reduction to oxide, VO_2. The oxide V_2O_5 is formed at ca. 590°C, following which there is no sensible change in weight. In brief, these changes can be shown as

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

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