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Note

The 5,6-Benzoquinoline *N*-Oxide Complexes of Oxovanadium(IV)

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5,6-Benzoquinoline *N*-oxide (Benzquo) complexes of oxo-vanadium(IV) with the general composition $VO(Benzquo)_2X_2$ (X = Cl, Br, I, NO_3, NCS, 0.5 C_2O_4) and $VO(Benzquo)_4(ClO_4)_2$ have been prepared and characterized. The chemical analyses, magnetic susceptibility, infrared and electronic spectra of the complexes are reported. The studies show that the complexes are five-coordinated and may have tetragonal pyramidal structures. Thermal properties of the complexes also are reported.

INTRODUCTION

In the present note, we wish to report the synthesis of 5,6-benzoquinoline *N*-oxide (Benzquo) complexes of oxovanadium(IV) which have been characterized by chemical analysis, molar conductivity, molecular weight, magnetic susceptibility, infrared, electronic spectra and thermogravimetric analysis.

EXPERIMENTAL

Oxovanadium(IV) salts were prepared by the reported methods.[1,2] The ligand 5,6-benzoquinoline *N*-oxide was prepared by *N*-oxidation of 5,6-benzoquinoline by the Ochiai method.[3]

All the complexes were prepared as follows: About 2 g of oxovanadium salt in 50 ml of acetone was mixed with Benzquo in acetone in the required molar proportion. Halogeno and oxalato complexes crystallized out immediately while remaining complexes got separated after concentration of the solution by passing dry air. The crystals were filtered off, washed several times with acetone and finally with ether and dried in vacuum.

Analytical Procedure

Vanadium in the complexes was estimated as V_2O_5. The halide contents were determined by Volhard's method and the perchlorate by Kurz's method. The molar conductance of the complexes was measured with a Toshniwal conductivity bridge at room temperature and their molecular weight was determined cryoscopically in freezing $PhNO_2$. The infrared spectra of the complexes were recorded in the 4000—200 cm^{-1} range using a Perkin-Elmer IR spectrophotometer, Model-521. The thermal analyses were made as reported previously.[4]

RESULTS AND DISCUSSION

The analytical results are summarized in Table I. These indicate the molecular formula $VOX_2 \cdot 2Benzquo$ (X = Cl, Br, I, NO_3, NCS or 0.5 C_2O_4) and

$VO(ClO_4)_2 \cdot 4Benzquo$. Except for perchlorato complexes, the conductance values are in the range of 3.2 to 5.2 ohm^{-1} cm^2 mol^{-1} indicating the non-electrolytic nature of the complexes. In the case of perchlorato complex, the conductance value corresponds to 1 : 2 electrolyte. Hence both the perchlorato groups are present outside the coordination sphere. The molecular weight data (cryoscopically in freezing $PhNO_2$) of these complexes are in good agreement with the conductance data.

TABLE I

Analytical and Partial IR data (cm^{-1}) of Oxovanadium(IV) Complexes of 5,6-Benzoquinoline N-*Oxide*

Compound	Analysis % Found (Calc.)			Ω_M ohm^{-1} cm^2 mol^{-1}	Mol. wt. Found (Calc.)	ν(N—O)	ν(V=O)	ν(V—O)
	V	N	Anion					
Benzquo	—	—	—	—	—	1240sh, 1235vs	—	—
$VOCl_2 \cdot 2Benzquo$	9.50 (9.65)	5.18 (5.30)	13.29 (13.44)	3.2	519 (528)	1220s	980s	435m
$VOBr_2 \cdot 2Benzquo$	8.14 (8.26)	4.41 (4.53)	25.79 (25.93)	3.9	609 (617)	1225s	995s	420m
$VOI_2 \cdot 2Benzquo$	7.02 (7.17)	3.18 (3.93)	35.61 (35.72)	4.6	706 (711)	1225s	990s	410m
$VO(NO_3)_2 \cdot 2Benzquo$	8.52 (8.77)	9.52 (9.63)	—	3.6	574 (581)	1215s	975s	425m
$VO(NCS)_2 \cdot 2Benzquo$	8.72 (8.90)	9.62 (9.77)	20.10 (20.24)	5.2	567 (573)	1220s	972s	430m
$VO(ClO_4)_2 \cdot 4Benzquo$	4.69 (4.87)	5.23 (5.35)	18.86 (19.02)	50.9	337 (1046)	1225s	970s	425m
$VOC_2O_4 \cdot 2Benzquo$	9.10 (9.35)	5.04 (5.13)	—	4.7	539 (545)	1220s	980s	420m

The effective magnetic moment for the complexes varies from 1.62 to 1.79 B. M. These values correspond to one unpaired electron per vanadium atom, demonstrating the tetravalency of vanadium in the complexes and also the absence of metal-metal interaction betwen vanadium atoms.[5]

Partial IR data of the complexes are given in Table I. The spectra do not present water bands. The shift of the N—O stretching mode to lower frequencies, in relation to the free ligand, indicate coordination through the oxygen.[6,7] The (NO) bending vibration of the Benzquo is assigned as a strong band at ~840 cm^{-1} and only a slight shift of this vibration is observed on complexation.[6,7] This further supports the oxygen-metal coordination. The positive shift of the C—H out-of-plane vibration of the ligand in all complexes is indicative of the drainage of electron density from the pyridine ring to the metal ion. In 410—435 cm^{-1} region, a new band appears in all complexes which is assignable to ν (V—O). In addition, all the complexes have an absorption band in the 995—970 cm^{-1} region due to V=O stretch. This indicates the high π-bond order of vanadium-oxygen bond of VO^{++} showing that the oxovanadium species is present as a monomeric entity in the solid state.[8]

Both the ν_3 and ν_4 IR bands of perchlorate in $[VO(Benzquo)_4](ClO_4)_2$ occur at 1080 and 625 cm^{-1}, respectively, showing the ionic character of the perchlorate group.[9] In the thiocyanato complex, the $\nu(C{\equiv}N)$, $\nu(C{-}S)$ and $\delta(NCS)$ appear at ~2030 cm^{-1}, ~850 cm^{-1} and ~470 cm^{-1}. These frequencies suggest that all NCS^- ions are coordinated through the nitrogen.[10] In the nitrato complex, the absence of the ν_3 band at ~1360 cm^{-1} clearly indicates the absence of ionic NO_3^-. The bands at ~1450 cm^{-1} (ν_4) and 1305 cm^{-1} (ν_1) are due to the splitting of ν_3 because of the lower symmetry of the coordinated nitrato groups.[11,12] It is usually difficult to distinguish between mono and bidentate nitrato groups on the basis of IR evidence, but on the basis of separation in the combination bands ($\nu_1 + \nu_4$) at 1800—1700 cm^{-1} the monodentate nature of the coordinated nitrato group is concluded.[13] In $VO(Benzquo)_2C_2O_4$, the characteristic bands attributed to the oxalato group occur at 1725, 1662, 1620 (ν_a) and 1310 (ν_s) cm^{-1}. The raising of asymmetric stretching (ν_a) and lowering of symmetric (ν_s) stretching frequencies of carbonyl group compared to the oxalate ion ($\nu_a = 1578$, $\nu_s = 1490$ cm^{-1}) indicate the chelation of the oxalate to vanadium(IV).[14]

The electronic spectra of the complexes in CH_3CN were taken in the visible range. In all the complexes the bands occur in the 12850—12500 cm^{-1} region with a shoulder in the 15700—15300 region. These bands, due to d—d transition spectrum, can be assigned to $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions respectively. The band due to $d_{xy} \rightarrow d_{z^2}$ seems to have been masked by the intense charge transfer bands occurring in the UV region.

Thus, on the basis of the reported data it can be concluded that in all these complexes the coordination number of vanadium(IV) is five and the penta-coordinated oxovanadium(IV) complexes can have tetragonal pyramidal structures.

Thermal Studies

The results of thermal analyses of VO(IV) complexes are summarized in Table II. The t. g. and d. t. curves of these complexes clearly indicate the non-hygroscopic nature of the compounds. The t. g. curves show that all the complexes complete their decomposition process as below:

$$VOX_2 \cdot 2Benzquo \rightarrow VOX_2 \cdot Benzquo \rightarrow VOX_2 \rightarrow [VO_2] \rightarrow V_2O_5$$
$$(X = Cl,\ Br,\ NCS,\ NO_3 \text{ or } 0.5\ C_2O_4).$$

In the first step only one mole of ligand is lost and in the second step both the ligand moles have been lost. Finally, at ~570 °C, V_2O_5 is formed.

TABLE II

Thermoanalytical Results Obtained for the VO^{++} *Complexes of 5,6-Benzoquinoline N-Oxide*

Compound	Sample weight mg	Residual mass mg	Mass loss (%) 210–320 °C		Mass loss (%) 350–390 °C		Residue (%) 570 °C	
			Theor.[a]	Exp.	Theor.[b]	Exp.	Theor.[c]	Exp.
$VOCl_2 \cdot$2Benzquo	25.7	4.60	36.93	38.73	73.86	75.18	17.23	17.91
$VOBr_2 \cdot$2Benzquo	27.9	4.25	31.60	32.92	63.20	65.06	14.74	15.24
$VO(NCS)_2 \cdot$2Benzquo	23.2	3.72	34.03	35.41	68.06	69.45	15.88	16.24
$VO(NO_3)_2 \cdot$2Benzquo	21.2	3.43	33.56	34.78	67.12	68.49	15.66	16.20
$VOC_2O_4 \cdot$2Benzquo	24.2	4.14	35.77	36.93	71.55	73.12	16.69	17.11

[a] — Calculated for loss of 1 mol of ligand.

[b] — Calculated for total loss of ligand.

[c] — Calculated as V_2O_5.

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SAŽETAK

5,6-Benzokinolin-*N*-oksidni kompleksi oksovanadija(IV)

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Pripravljeni su i karakterizirani 5,6-benzokinolin-*N*-oksidni (Benzquo) kompleksi oksovanadija(IV) opće formule: $VO(Benzquo)_2X_2$ (X=Cl, Br, I, NO_3, NCS, 0.5 C_2O_4) i $VO(Benzquo)_4(ClO_4)_2$. Uz elementnu analizu, prikazani su infracrveni i elektronski spektri, magnetska i termička svojstva. Rezultati pokazuju da bi koordinacijski broj vanadija(IV) mogao biti pet, a koordinacijski poliedar tetragonska piramida.