To Synthesis And Characterization Of Some Novel HEPTA Coordinated Mixed Ligand Cyanonitrosyl Complexes Of Vanadium With $\{VNO\}_4$ d^4 - Configuration

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Abstract: **A new series of hepta-coordinated mixed-ligand cyanonitrosyl complexes of vanadium (which have $\{VNO\}_4$ electron configuration[1]), have been formed d by the interaction of potassium hexa-cyanonitrosyl vanadiate(I) Isolate monohydrates with some heterocyclic organic bases like 2, 3-, 2, 4-, 2, 6- and 3, 5- lutidines, 2, 3, 6- and 2, 4, 6- collidines and nicotine in aqueous methanol has been done in solid state. The products, which have been characterized by elemental analyses, molar conductances, magnetic measurements, and infrared spectral studies, have the general formula $K_2[VNO(CN)_4\ (L)_2)$ for which a pentagonal bipyramidal structure have been suggested. All complexes of vanadium have the low spin d^4 -configuration.**

1-INTRODUCTION

A perusal of the literature of nitrosyl complexes of vanadium reveals few reports on such complexes[2-6]. Although there has been considerable interest in the study of cyanonitrosyl complexes of vanadium with $\{VNO\}_4$ electron configuration[2,3], there are no reports on mixed-ligand cyanonitrosyl complexes of vanadium of $\{VNO\}_4$ electron configuration with heterocyclic organic bases. furthermore, the educational importance of the $\{VNO\}_4$ complexes of vanadium provides an additional incentive for research. We report here the first synthesis of mixed-ligand cyanonitrosyl complexes of vanadium of the above electron configuration with heterocyclic organic bases like 2, 3-, 2, 4-, 2, 6- and 3,5- lutidines, 2, 3, 6- Lets report and 2, 4, 6- collidines and nicotine.

2-EXPERIMENTAL

Materials

Lutidines and collidines (Aldrich Chemical Co., U. S. A.) nicotine (B. D. H., England), potassium hydroxide and potassium cyanide (Ranbaxy, India), ammonium metavanadate and hydroxyl- ammonium chloride (S. D. Fine chem. Pvt. Ltd., India) were used as supplied. Potassium hexacyanonitrosyl vanadiate(I) monohydrate was prepared according to the procedure of Muller et. al. The purity of the compound was checked by elemental analysis and infrared spectroscopy.

Synthesis of the complexes

To a filtered aqueous solution of the potassium hexacyanonitrosyl vanadiate(I) monohydrate (0.45/0.001M, 35 ml), a methanolic solution of the corresponding ligand (0.002M, 15ml) was added with constant stirring at 50-60°c. The flask containing the stirred solution was evacuated and kept under nitrogen atmosphere for about two hours, whereupon the resultant solution became orange. The content of the flask was dried in vacuo and washed several times with absolute alcohol. Finally, the yellow mass was washed with ether and dried in vacuo to a constant weight. The analytical data are given in Table 1.

Analyses

The metal content in each compound was determined as follows: A weighed amount of the compound was decomposed by alkali fusion. After leaching with water the filtrate was acidified with nitric acid. The vanadium was estimated as V205 gravimetrically by precipitating out vanadiate from the solution using mercurous nitrate and igniting the compound to constant weight.

Physical methods

All the measurements were made at room temperature (30°C). The infrared spectra were recorded in Nujol on a Beckman-IR-20 spectrophotometer. The molar conductances were messured using a Philips conductivity apparatus. Magnetic susceptibilities were measured by a Gouy balance using $Hg[Co(NCS)_4]$ as the magnetic susceptibility standard.

RESULTS AND DISCUSSION

The mixed-ligand complexes $K_2[VNO(CN)_4(L)_2]$ (see Table 1 for ligand names) were prepared according to the following reaction.

$$K_4[VNO(CN)_6].H_2O + H_2O + 2L \xrightarrow{MeOH} K_2[VNO(CN)_4(L)_2] + 2KCN + H_2O$$

All the compounds are yellow coloured solids. They are hygroscopic and form yellow aqueous solutions. They decompose in aqueous solution quickly, Particularly on warning with the deposition of a red-brown mass. Molar conductance values in 10^{-3} freshly prepared aqueous solution indicate that they are uni,bi-valent electrolyte. As they are hygroscopic and quickly decomposible, their molecular weight determination by Rast's method could not be carried out.

Table 1. Analytical Data and Some Physical Properties of the Complexes

Compound	%v (found) (calc.)	%C (found) (calc.)	%H (found) (calc.)	%N (found) (calc.)	M $(\Omega^{-2}$ cm^{2}/ mole)	% yield	Deco. temp.^{0}C
$K_2[VNO(CN)_4(2,3\text{-Lut})_2]$	10.58	45.36	3.64	20.48	250	50	120
	(10.69)	(45.28)	(3.77)	(20.54)			
$K_2[VNO(CN)_4(2,4\text{-Lut})_2]$	10.72	45.34	3.60	20.47	254	50	125
	(10.69)	(45.28)	(3.77)	(20.54)			
$K_2[VNO(CN)_4(2,6\text{-Lut})_2]$	10.60	45.12	3.59	20.63	252	52	122
	(10.69)	(45.28)	(3.77)	(20.54)			
$K_2[VNO(CN)_4(3,5\text{-Lut})_2]$	10.78	45.30	3.58	20.60	256	50	124
	(10.69)	(45.28)	(3.77)	(20.54)			
$K_2[VNO(CN)\{4\}(2,3,6\text{-Coll})_2]$	10.04	47.50	4.26	19.30	255	56	130
	(10.10)	(47.62)	(4.35)	(19.40)			
$K_2[VNO(CN)_4(2,3,6\text{-Coll})_2]$	10.02	47.78	4.30	19.51	258	54	132
	(10.10)	(47.62)	(4.35)	(19.40)			
$K_2[VNO(CN)_4(NiCo)_2]$	9.20	45.68	5.01	22.78	256	56	135
	(9.25)	(45.73)	(5.08)	(22.86)			

The important infrared spectral bands of the synthesized complexes along with the parent compound are presented in Table 2.

A comparison between the parent compound[3] $K_4[VNO(CN)_6].H_2O$ and the synthesized complexes $K_2[VNO(CN)_4(L)_2]$ suggests that the appearance of a very strong band in the region 1530-1545 cm^{-1} for the investigated complexes is due to the coordinated nitric oxide stretching frequencies. A strong band in the region 2120-2130 cm-^{1} for all the complexes is assigned to V(CN) by comparison.

Coordination of organic bases to vanadium is indicated by shifts in the ligand bands in the spectra of the comp lexes from their positions in the spectra of the free ligands. Moreover, the pyridine ring breathing mode occuring at approximately 1000 cm^{-1} in all the heterocyclic bases used es ligands undergo significant positive shifts in the complexes. These features indicate that coordination of these bases involves only the pyridine ring nitrogen atoms.[7,8]

The diamagnetic nature of all the complexes are consistent with a low spin d^4 configuration of vanadium(I).

The analytical data and all the above results correspond to the formulation of these complexes as $K_2[VNO(CN)_4(L)_2]$ (L=2,3-, 2, 4-, 2,6-, 3,5- Lut, 2,3,6-, 2,4,6-Coll or Nico).

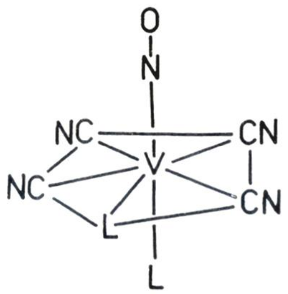

Fig 1. Trigonal Bipyramidal Structure of $K_2[VNO(CN)_4(L)_2]$

Table 2. Important Infrared Spectral Bands and Assignment

Compound	v(NO)$^+$ (cm^{-1})	v(CN) (cm^{-1})	Symmetric ring breathing vibration
$K_2[VNO(CN)_6].H_2O$	1508(vs)	2100(s)	-
$K_2[VNO(CN)_4(2,3\text{-Lut})_2]$	1540(vs)	2125(s)	1025
$K_2[VNO(CN)_4(2,4\text{-Lut})_2$	1535(vs)	2120(vs)	1030
$K_2[VNO(CN)_4(2,6\text{-Lut})_2]$	1540(vs)	2125(s)	1025
$K_2[VNO(CN)_4(3,5\text{-Lut})_2]$	1545(vs)	2130(s)	1020
$K_2[VNO(CN)_4(2,3,6\text{-Coll})_2]$	1535(vs)	2125(s)	1030
$K_2[VNO(CN)_4(2,3,6\text{-Coll})_2]$	1530(vs)	2125(s)	1035
$K_2[VNO(CN)_4(NiCo)_2]$	1540(vs)	2130(s)	1025

CONCLUSION

As the hepta-coordinated parent compound $K_4[VNO(CN)_6]$. H_2O is structurally characterized as pentagonal bipyramidal having a linear V-N-O group, it is reasonable to assume that the synthesized complexes may retain the linearity of the V-N-O group as well as pentagonal bipyramidal geometry .

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