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Anionic Complexes of Oxovanadium(IV), Part-III

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Anionic complexes of oxovanadium(IV) of the type $[(CH_3)_4N]_2[VO(NCS)_4L]$, where L = pyridine (py), γ-picoline (γ-pic), imidazole (Imz), quinoline (Q), isoquinoline (IQ), 2-amino 4-methyl pyridine (2-Am 4-MePy), urea, pyridine N-oxide (PyNO), triphenyl phosphine oxide (TPPO), thiourea (Tu), phenyl thiourea (ph-Tu), 1-naphthyl thiourea (1Naph-Tu) and diphenyl thiourea (Ph_2Tu) have been isolated and characterised on the basis of their elemental analyses, conductance, room temperature magnetic moment, infrared and electronic spectral data.

INTRODUCTION

In continuation of our earlier studies on mixed ligand complexes of oxovanadium(IV),[1–6] we now report here preparation and characterisation of some anionic complexes of oxovanadium(IV) containing a neutral monodentate nitrogen, oxygen or sulphur donor ligands.

EXPERIMENTAL

All the chemicals used were of A.R. grade. The ethanolic solutions of $[(CH_3)_4N]_2[VO(NCS)_4H_2O]$ with ligands (L) pyridine, γ-picoline, imidazole, quinoline, isoquinoline, 2-amino 4-methyl pyridine, urea, pyridine-N-oxide, triphenyl phosphine oxide, thiourea, 1-naphthyl thiourea, phenyl thiourea, diphenyl thiourea were mixed separately in 1 : 1 molar ratio, stirred on magnetic stirrer for 10 minutes and refluxed for 1 h. The resulting complexes were filtered, washed with small volume of ethanol, ether and dried under reduced pressure over fused $CaCl_2$.

Vanadium and sulphur were estimated by standard methods[7]. Carbon, hydrogen and nitrogen were estimated microanalytically. Molecular weights of the complexes were determined by Rast's method using biphenyl as solvent. Molar conductances of complexes were measured using a Systronic-303 direct reading conductivity meter. Magnetic moments at room temperature were determined using solid specimens by Gouy method. Dimagnetic corrections were made using Pascal's constant. Infrared spectra (KBr) of the complexes were recorded on a Perkin-Elmer 317 spectrophotometer in the range 4000–400 cm^{-1} and electronic spectra on Unicam SP-500 spectrophotometer.

The relevant characterisation data are presented in Table-1.

TABLE-1
ANALYTICAL DATA OF OXOVANADIUM(IV) COMPLEXES

Complexes	% Analysis, Found (Calcd.)			
	V	C	H	N
$[(CH_3)_4N]_2[VO(NCS)_4(Py)]$	9.28 (9.68)	37.92 (31.81)	4.63 (5.51)	16.92 (18.62)
$[(CH_3)_4N]_2[VO(NCS)_4(\gamma\text{-pic})]$	8.89 (9.40)	38.27 (39.98)	4.68 (5.73)	17.97 (18.12)
$[(CH_3)_4N]_2[VO(NCS)_4(Imz)]$	9.72 (9.87)	32.88 (34.94)	4.78 (5.43)	19.90 (21.72)
$[(CH_3)_4N]_2[VO(NCS)_4(Q)]$	8.68 (8.83)	42.77 (43.73)	4.93 (5.37)	15.78 (16.99)
$[(CH_3)_4N]_2[VO(NCS)_4(Iq)]$	7.92 (8.83)	41.87 (43.73)	4.95 (5.37)	16.72 (16.99)
$[(CH_3)_4N]_2[VO(NCS)_4(2Am\text{-}4MePy]$	8.87 (9.16)	38.02 (38.91)	4.82 (5.76)	18.96 (20.16)
$[(CH_3)_4N]_2[VO(NCS)_4(Urea)]$	9.92 (10.03)	28.88 (30.75)	5.26 (5.51)	20.87 (22.06)
$[(CH_3)_4N]_2[VO(NCS)_4(PyNO)]$	8.48 (9.39)	35.83 (37.63)	4.92 (5.34)	17.25 (18.06)
$[(CH_3)_4N]_2[VO(NCS)_4(TPPO)]$	5.87 (7.01)	48.03 (49.63)	4.89 (5.37)	10.92 (11.58)
$[(CH_3)_4N]_2[VO(NCS)_4(Tu)]$	8.68 (9.72)	29.62 (29.81)	5.23 (5.34)	20.29 (21.38)
$[(CH_3)_4N]_2[VO(NCS)_4(PhTu)]$	8.00 (8.49)	37.82 (38.06)	4.92 (5.33)	17.97 (18.68)
$[(CH_3)_4N]_2[VO(NCS)_4(1NaphTu)]$	6.84 (7.84)	41.27 (42.52)	4.29 (5.23)	16.88 (17.24)
$[(CH_3)_4N]_2[VO(NCS)_4(Ph_2Tu)]$	6.92 (7.54)	43.45 (44.44)	4.29 (5.32)	14.92 (16.58)

RESULTS AND DISCUSSION

The analytical data are in conformity with the stoichiometry of the complexes. The monomeric nature of the compounds is evident from their molecular weight measurements. The molar conductance values of (Λ_m = 35–40 mhos) of the complexes in *ca.* 10^{-3} M DMSO solutions suggest them to be 1:1 electrolytes. The room temperature magnetic susceptibilitie values (μ_{eff} = 1.70–1.72 BM) are

close to the spin-only values for one unpaired electron and indicate the paramagnetic nature of the complexes[8].

The infrared spectral bands of the complexes are observed at 1160 cm^{-1} and 960 cm^{-1} due to tetramethyl ammonium ion. The complexes exhibit bands at *ca.* 2060 cm^{-1}, *ca.* 820 cm^{-1} and *ca.* 480 cm^{-1} due to ν(C—N), ν(C—S) and δ(NCS) respectively, suggesting the presence of N-bonded thiocyanate ion[9]. Bands of ν(C=C) + ν(C=N)[10] bands at *ca.* 1622 cm^{-1} and at *ca.* 1554 cm^{-1} due to the pyridine, γ-picoline, quinoline, isoquinoline and 2-amino 4-methyl pyridine suggest the coordination of the ligands through nitrogen atoms. The bonding of pyridine-N-oxide to the metal ion usually discussed from the viewpoint of ν(N—O), δ(N—O) and ν(C—H) of the ligand in free state and on complexation. These ligands exhibit bands at 1265 cm^{-1} and 840 cm^{-1} due to ν(N—O), δ(N—O) respectively while ν(N—O) undergoes a small negative shift on complexation[11]. The presence of bands at 3000 cm^{-1} and 1440 cm^{-1} due to ν(N—H) and δ(N—H) respectively indicates the bonding of imidazole through the tertiary nitrogen atom[12]. The bands at 685 cm^{-1}, 3290 cm^{-1} and 1620 cm^{-1} are due to ν(C—S), νNH_2 and δNH_2 respectively indicating the bonding of diphenyl thiourea and 1-naphthylthiourea[13]. A negative shift of 20–25 cm^{-1} in ν(C=O) indicates that the urea is coordinated through oxygen atom to the metal ion[14] (free ligands at 1660 cm^{-1}). A band at 1170 cm^{-1} due to ν(P—O) in triphenyl phosphine oxide complex (*ca.* 1195 cm^{-1} in free ligand) indicates the coordination of the ligand through oxygen atom to the metal ion. A negative shift of 20–25 cm^{-1} in ν(C=S) in the thiourea and substituted thiourea complex indicate the coordination through sulphur atom to the metal ion[15] (*ca.* 685 cm^{-1} in free ligand). The band at *ca.* 980 cm^{-1} in all the complexes is attributed to (V=O)[16].

Two bands were observed in the electronic spectra of the complexes around 12000 and 16000 cm^{-1} due to $d_{xy} \rightarrow d_{yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transition respectively suggesting octahedral geometry[17,18].

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