

Studies of Vanadyl(IV) Complexes with Schiff Bases of 2-Aminopyridine

KISHOR ARORA*, R.C. GOYAL†, D.P. SHARMA‡ and M.C. PATHAK†

*Department of Chemistry
Government Auto. K.R.G. College, Gwalior-476 001, India*

A series of oxovanadium(IV) complexes with Schiff bases of 2-aminopyridine, *i.e.*, 2-N-[benzalidene] aminopyridine (BAPY), 2-N-[*p*-dimethyl benzalidene] aminopyridine (PABAPy) and a thiosemicarbazone ligand, *i.e.*, 2-N-[acetylacetone] aminopyridine thiosemicarbazone (AcAyPyT) have been synthesized. On the basis of analytical and spectral studies complexes were found to have general composition VOX_2L_2 ($\text{X} = \text{Cl}^-$, Br^- , $\text{L} = \text{BAPy}$ or PABAPy) and $\text{VOX}_2\cdot\text{AcAcPyT}$ ($\text{X} = \text{Cl}^-$ or Br^-). V-atom is 5 or 6 coordinated depending upon the anion present. NMR and antifungal studies, of representative complexes have been done successfully.

INTRODUCTION

Oxocation complexes are of great interest for most of the workers because of their ample atomic size and high positive formal charge so that they fulfil the optimum conditions for high coordination¹. These metals can be considered as hard acids according to the definition of Pearson². In the recent past a number of workers^{3–7} have reported a series of complex compounds formed by dioxo-uranium(VI), oxozirconium(IV) and oxovanadium(IV) with nitrogen donor-ligands including Schiff bases.

In this present communication we wish to report the investigations on high coordination complexes of oxovanadium(IV) metal with Schiff bases of 2-amino pyridine, *viz.*, 2-N-[benzalidene] amino pyridine (BAPy) (I); 2-N-[*p*-dimethyl amino benzalidene] amino pyridine (PABAPy) (II) and a thiosemicarbazone ligand, *i.e.*, 2-N-[acetylacetone) amino pyridine thiosemicarbazone (AcAcPyT) (III).

These ligands were found to be neutral monodentate (N-coordinating) except (AcAcPyT) which is tridentate ligand (N, N, S) and these ligands lead to the formation of high coordination compounds having the general composition VOX_2L_2 ($\text{X} = \text{Cl}^-$ or Br^- ; $\text{L} = \text{BAPy}$ or PABAPy) and $\text{VOX}_2\text{AcAcPyT}$ ($\text{X} = \text{Cl}^-$ or Br^-). These complexes are generally soluble in common organic solvents and are quite stable.

EXPERIMENTAL

All the reagents were used as supplied by BDH and Merck. Oxovanadium(IV) chloride and bromide were prepared by treating vanadium pentoxide with concentrated hydrochloric acid and hydrobromic acid respectively, in the presence of a few drops of ethanol as reported earlier⁸.

†Govt. P.G. College, Morena-476 001, India.

‡Govt. Girls College, Morena-476 001, India.

Preparation of ligands

(i) A solution of distilled aromatic aldehyde (1 mmole) in absolute alcohol (50 mL) was mixed with corresponding amine, *i.e.*, 2-amino pyridine (1.1 mmole) in the same solvent and the mixture was refluxed for 3–4 h. On cooling a yellow product was separated which was filtered off and recrystallized in the same solvent.

(ii) A solution of acetylacetone (1 mmole) in absolute alcohol (50 mL) was mixed with 2-aminopyridine (1.1 mmole) and thiosemicarbazone (1 mmole) in the same solvent and the reaction mixture was refluxed for 5–6 h. The product was obtained on sufficient cooling the reaction mixture in dark green colour. Excess solvent was removed and product was filtered and washed with solvent and recrystallized in the same solvent and dried *in vacuo* over CaCl_2 .

Preparation of complexes

The respective metal salt solutions were treated with ligand solution (in ethanol) in required molar concentrations (*i.e.*, 1 : 1 or 1 : 2). Resulting solutions were refluxed for 2–3 h at 60–70°C. The complexes were collected, washed with solvent and finally with anhydrous ether and dried *in vacuo* over CaCl_2 .

RESULTS AND DISCUSSION

The reaction of oxovanadium(IV) metal salts with Schiff base ligands and a thiosemicarbazone results in the formation of VOX_2L_2 ($\text{X} = \text{Cl}^-$ or Br^- ; $\text{L} = \text{BAPy}$ or PABAPy) and $\text{VOX}_2\text{AcAcPyT}$ ($\text{X} = \text{Cl}^-$ or Br^-). The elemental analyses of these complexes are given in Table-1. These complexes are quite stable at room temperature (*ca.* 25°C). All are sufficiently soluble in common organic solvents.

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA FOR OXOVANADIUM(IV)
COMPLEXES OF BAPy, PABAPy AND AcAcPyT

Complex	Yield (%)	Colour	m.p. (°C)	Analysis found (calcd.)			m.w. found (calcd.)	Λ_m $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$
				%				
				M	N	Anion		
$\text{VOCl}_2 \cdot 2\text{BAPy}$	72	Brown	188	9.8 (10.1)	12.0 (11.1)	13.2 (14.1)	498 (502)	3.8
$\text{VOBr}_2 \cdot 2\text{BAPy}$	76	Brown	190	7.9 (8.6)	10.8 (9.5)	26.1 (27.0)	586 (591)	3.6
$\text{VOCl}_2 \cdot 2\text{PABAPy}$	74	Brown	188	7.8 (8.6)	15.2 (14.3)	11.1 (12.0)	582 (588)	3.7
$\text{VOBr}_2 \cdot 2\text{PABAPy}$	74	Brown	198	6.8 (7.5)	13.8 (12.4)	21.8 (23.6)	672 (677)	3.6
$\text{VOCl}_2 \cdot \text{AcAcPyT}$	76	Black lustrous	202	12.0 (13.1)	19.2 (18.0)	17.2 (18.3)	381 (387)	3.9
$\text{VOBr}_2 \cdot \text{AcAcPyT}$	76	Black lustrous	198	9.8 (10.7)	15.2 (14.7)	32.1 (33.6)	471 (476)	3.8

Electrical conductance values for these complexes were determined in PhNO_2 medium and it was inferred that all these complexes are essentially

non-electrolyte which is in general agreement with the previous observation⁹. The ratio of molecular weights to be calculated is as 0.98 which shows that these complexes are monomeric in solution.

The IR spectra of these complexes were recorded in the region 4000–200 cm^{-1} using KBr pellets. The ligands are expected to coordinate through azomethine nitrogen. An important band occurs at *ca.* 1600 cm^{-1} attributed to the $\nu(\text{C}=\text{N})$ (azomethine) mode¹⁰. In the spectra of all the complexes this band is shifted to a lower wave number and appears in the range 1550–1540 cm^{-1} , indicating the involvement of the nitrogen atom of the azomethine group in coordination¹⁰. The strong bands observed at 1580–1520 and 1080–1000 cm^{-1} are tentatively assigned^{11–14} to antisymmetric and symmetric $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$ of the pyridine ring and pyridine ring breathing and deformation which remain practically unchanged in frequency and band intensities revealing non-involvement of pyridine nitrogen and metal bond.

The overall IR spectral evidence suggests that the ligands are monodentate (except thiosemicarbazone) coordinating through the azomethine nitrogen to the central metal ion. The far IR spectral bands in the ligands are practically unchanged in the complexes, but some new bands with medium to weak intensities appear in the region 450–400 cm^{-1} in the complexes under study which are tentatively assigned to $\nu(\text{M}-\text{N})$ mode.

For $\nu(\text{C}=\text{S})$, the regions *ca.* 1400 cm^{-1} and *ca.* 730 cm^{-1} have been suggested by Irving *et al.*¹¹, while the region *ca.* 1000 cm^{-1} by Yamaguchi¹³. In the present assignment we agree with Irving's assignments because the IR spectra of the present compounds show sharp absorption bands in the regions 1300–1150 cm^{-1} as well as 870–850 cm^{-1} . The former vibrations are assigned to $\nu(\text{CS})$ stretch and $\nu(\text{CN})$ stretch, $\delta(\text{C}=\text{S})$ bending and $\nu(\text{C}=\text{S})$ stretching respectively, following the observation of Irving *et al.*¹¹ and some other workers^{14,15}. Coordinating of sulfur with the metal ion would result in the displacement of electrons towards the latter, thus resulting in the weakening of (C=S) bond. Hence on complexation $\nu(\text{C}=\text{S})$ stretching vibration should decrease. In the case of 2-N-[acetylaceton]-aminopyridine thiosemicarbazone complexes with VO^{2+} the frequencies in the range 870–850 cm^{-1} are shifted to lower wave numbers and the intensities of the bands also reduced. All these peculiar changes in complexation confidently preclude any unambiguity of metal-sulfur bond. In far IR region, in case of these complexes, new bands of medium to weak intensities appear which are tentatively assigned as $\nu(\text{M}-\text{S})$, $\nu(\text{V}-\text{Cl})$ at *ca.* 380 cm^{-1} and 270 cm^{-1} respectively. In conclusion, thiosemicarbazone ligand may be suggested to act as a tridentate (N, N, S) ligand coordinating through (C=N) nitrogen and (C=S) sulfur atoms. The partial IR data of all these complexes are given in Table-2.

The NMR spectral study of one of the representative complexes was recorded and was compared with that of the ligand. The NMR spectra of BAPy shows important signals at 8.45549 (d); 7.52431 (d); 7.65445 (qt.); 6.71831 (d); 4.56626 (qt.); 4.24862 (s) and that of VOBr_2 (BAPy)₂ shows important signals at 8.03083–8.00630 (d); 7.6870 (s); 7.55571–7.42203 (pt.); 7.34998–7.23338 (pt.); 7.10742–7.07594 (d); 6.67709 (s); 6.16428 (s); 2.60103–2.58287 (qt.); 1.76839 (s); 1.25314 (s).

TABLE-2
PARTIAL IR DATA (cm^{-1}) FOR OXOVANADIUM(IV) COMPLEXES OF BAPy,
PABAPy AND AcAcPyT

Complex	$\nu(\text{C}=\text{N})$ str. azomethine	$\nu(\text{C}=\text{S})$ + $\nu(\text{C}=\text{N})$ + $\nu(\text{C}-\text{N})$	$\nu(\text{C}=\text{S})$	Pyridine ring breathing and deformation modes		$\nu(\text{M}-\text{N})/$ $\nu(\text{M}-\text{S})$
				$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$	
BAPy	1600 (s)	—	—	1570 (m)	1050 (m)	—
$\text{VOCl}_2 \cdot 2\text{BAPy}$	1530 (s)	—	—	1570 (m)	1050 (m)	440 (m)
$\text{VOBr}_2 \cdot 2\text{BAPy}$	1520 (m)	—	—	1575 (m)	1055 (m)	445 (m)
PABAPy	1590 (s)	—	—	1580 (m)	1075 (m)	—
$\text{VOCl}_2 \cdot 2\text{PABAPy}$	1525 (s)	—	—	1580 (m)	1070 (w)	435 (w)
$\text{VOBr}_2 \cdot 2\text{PABAPy}$	1520 (m)	—	—	1586 (m)	1075 (w)	430 (w)
AcAcPyT	1600 (s)	1305 (s)	820 (s) 760 (s)	1580 (m)	1070 (m)	—
$\text{VOCl}_2 \cdot \text{AcAcPyT}$	1540 (s)	1310 (m)	775 (m) 705 (m)	1580 (m)	1075 (w)	450 (m)/ 350 (w)
$\text{VOBr}_2 \cdot \text{AcAcPyT}$	1550 (s)	1310 (m)	770 (w) 710 (w)	1575 (m)	1070 (w)	455 (m)/ 320 (w)

Configuration of complexes

Vanadium is 5-coordinated in the complexes $\text{VOX}_2 \cdot n\text{L}$ ($\text{X} = \text{Cl}^-$, Br^- ; $n = 2$, $\text{L} = \text{BAPy}$ or PABAPy) and 6 coordinated in the complexes $\text{VOX}_2 \cdot n\text{L}$ ($n = 1$; $\text{L} = \text{AcAcPyT}$) as on the basis of electrical conductance and molecular weight determination it is clear that these complexes are monomeric in nature and on the basis of IR spectral studies it reveals that halo anions are covalently singly bonded to vanadium ion. Thus, vanadium is *penta* and *hexa* coordinated in these complexes.

Antifungal activities

Antifungal activities of some of the representative complexes of oxovanadium metal ion with these ligands were done successfully. The radial growth and paper disc methods were used to evaluate antifungal activities¹⁶.

These activities were checked on *Peronospora* sp. and *Albugo* sp., two fungi which were grown in PDA culture on living host tissue, i.e., *Brassica campestris*. Inoculation was made from infected inflorescence of *Brassica* sp. in petriplates containing PDA medium 10 mm paper disc dipped in solutions of complexes in DMF in varied concentrations¹⁷.

The plates containing unamended PDA were maintained as control. The inoculated plates were incubated at $25 \pm 1^\circ\text{C}$ for 5 days. The radial growths of the fungal colonies were measured on 6th day and data was statistically analysed. Table-3 shows the effect of concentrations of different complexes on the mean radial growth (in cm). of fungus. The control petriplate which does not contain any disc of complex solution shows a radial growth of 4.0–4.5 cm for fungal colonies. These values are in general agreement with previous observations^{16–18}

TABLE-3
EFFECT OF VARIED CONCENTRATION OF DIFFERENT COMPLEXES ON
THE MEAN RADIAL GROWTH (in cm) OF FUNGAL COLONIES

Compound	<i>Peronaspoa</i> sp.			<i>Albugo</i> sp.		
	30 mg/ 10 mL	20 mg/ 10 mL	10 mg/ 10 mL	30 mg/ 10 mL	20 mg/ 10 mL	10 mg/ 10 mL
VOBr ₂ -2BAPy	0.5	1.5	1.9	0.6	1.4	1.8
VOBr ₂ -2PABAPy	0.5	1.3	1.5	0.7	1.6	1.8

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REFERENCES

1. J.V. Silverton and J.L. Hord, *Inorg. Chem.*, **2**, 235 (1963).
2. R.G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
3. R.K. Agarwal, K. Arora and P. Dutt, *Polyhedron*, **13**, 957 (1994).
4. R.K. Agarwal and K. Arora, *Synth. React. Inorg. Met.-Org. Chem.*, **23**, 653, 1671 (1993).
5. _____, *Polish J. Chem.*, **67**, 25 (1993).
6. R.K. Agarwal, K. Arora and P. Dutt, *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 301 (1994).
7. K. Arora, *Asian J. Chem.*, **7**, 424 (1995).
8. G. Guruprasad and C.C. Patel, *Indian J. Chem.*, **12**, 840 (1974).
9. R.K. Agarwal, K. Arora and P. Dutt, *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 301 (1994).
10. P.S. Radha Krishnan and P. Indersenan, *J. Indian Chem. Soc.*, **67**, 243 (1990).
11. K. Swaminathan and N.H. Irving, *J. Inorg. Nucl. Chem.*, **26**, 1291 (1964).
12. Y. Kumar, P.D. Sethi and C.L. Jain, *J. Indian Chem. Soc.*, **67**, 796 (1990).
13. A. Yamaguchi, R.B. Paul, B. Muzuchina, T.J. Lane and C. Curren., *J. Am. Chem. Soc.*, **80**, 527 (1958).
14. D. Banerjee and I.P. Singh, *Indian J. Chem.*, **6**, 34 (1968).
15. V.B. Rana, *J. Inorg. Nucl. Chem.*, **37**, 1826 (1975).
16. P.C. Vyas and Navneet Kaur, *Asian J. Chem.*, **9**, 208 (1997).
17. Anshu Dandia, Mitali Saha, Asha Shivpuri and Varinder Sehgal, *Asian J. Chem.*, **9**, 804 (1997).
18. J. Ambwani, *Asian J. Chem.*, **9**, 692 (1997).

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