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Short Communication

Vanadium and niobium complexes with 4-(2-pyridylazo) resorcinol (PAR)

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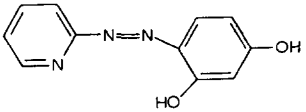
Considerable attention has been given recently to metal complexes of azo compounds[1–3], mainly with regard to the metal–azo bond and its properties. Herein, we report the preparation and properties of vanadium and niobium derivatives of 4-(2-pyridylazo)resorcinol (PAR), an asymmetrical azo compound of the formula



PAR has lately been extensively used as a spectrophotometric agent for a number of transition metal ions[4], but is also of interest with regard to the way of bonding to the metal, which involves the metal–azo bond. The crystal structure analysis of Cu(II) 1-(2-pyridylazo)-2-naphthol (PAN), containing a similar ligand, PAN, has confirmed the previous assumptions that these azo molecules act as tridentate ligands forming, upon coordination, two five-membered chelate rings[5]. Complexes of PAR have not previously been isolated in the solid state.

We have prepared crystalline V(V) and Nb(V) complexes that contain PAR coordinated as a tridentate ligand, as well as compounds containing protonated PAR-onium cation along with oxalato vanadate(IV) and niobate(V) anions, respectively. The compounds and some of their properties are shown in Table I.

Solution studies have shown that the maximum stability of Nb(V)–PAR complex in aqueous oxalato systems[6] occurs between pH 5.0 and 5.5. From such solutions we have extracted the colored Nb(V) species with tetraphenyl-phosphonium and arsonium salts in chloroform. From the chloroform we then separated the crystalline tetraphenyl-onium salts of oxo-oxalato-PAR niobate(V). Tetraphenyl-phosphonium and arsonium salts of dioxo-PAR-vanadate(V) were prepared from aqueous solutions corresponding to the conditions used in the spectrophotometric vanadium determination with PAR. PAR-onium salts of oxo-bis-oxalato vanadate(IV) and oxo-tris-oxalato niobate(V), containing protonated PAR$^+$ cation were separated from the aqueous oxalato solutions in the pH range 0–1. Protonation of azobenzene has been reported recently[1], but for PAR, protonation of the pyridyl nitrogen is expected to occur first. In such acid solutions the stable oxidation state for vanadium is 4+, and the presence of V(IV) in the complex obtained was confirmed by magnetic measurements ($\mu_{eff} = 1.77$ B.M.).

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TABLE I

PROPERTIES OF VANADIUM AND NIOBIUM COMPLEXES WITH 4-(2-PYRIDYLAZO) RESORCINOL

Complex	*Colour*	*M.p. (dec.°C)*	*Molar conductivity ($ohm^{-1}cm^2$)*	*Magnetic moment (B.M.)*
$[(C_6H_5)_4P][VO_2PAR]$	dark violet	230	70–73	diamagnetic
$[(C_6H_5)_4As][VO_2PAR]$	dark violet	210	70–73	diamagnetic
$[(C_6H_5)_4P][NbO(C_2O_4)PAR]$	red	240–245	70–75	diamagnetic
$[(C_6H_5)_4As][NbO(C_2O_4)PAR]$	red	190–195	70–75	diamagnetic
$[PARH_3]_2[VO(C_2O_4)_2]\cdot 2H_2O$	red	160	solvolysis	1.77
$[PARH_3]_3[NbO(C_2O_4)_3]\cdot 3H_2O$	pale red	155	solvolysis	diamagnetic

PAR = $[C_{11}H_7N_3O_2]^{2-}$. The compounds were analysed for C, H, N, P, As and metal. The analyses are in good agreement with the formulae, *e.g.*, $[(C_6H_5)_4P][NbO(C_2O_4)PAR]$requires: C, 59.3; H, 3.6; N, 5.6; P, 4.1; Nb, 12.4%. Found: C, 59.2; H, 3.9; N, 5.7; P, 3.8; Nb, 12.2%.

In the solutions, depending upon pH, PAR can exist in the form of a monobasic anion (present in the commercially available sodium salt) and a dibasic anion, both protons being lost from the hydroxo groups[7,8]. Infrared spectra should show characteristic changes if the donor atoms of PAR-species are engaged in the coordination sphere of the metal. However, the richness of the infrared spectra of the complexes described renders the assignment of some specific group vibrations difficult. On comparing the spectra of different types of compounds however, it is possible to derive some general features characteristic of the PAR^- ion, coordinated PAR^{2-} and the protonated PAR^+ cation. Some i.r. studies of similar azo complexes have correlated the nitrogen coordination of the azo group with characteristic $N=N$ stretchings[9], but no such studies have been reported so far for PAR complexes.

On comparing the i.r. spectra of the compounds containing coordinated PAR^{2-} with the spectrum of the sodium salt of PAR^- ion, characteristic changes are observed, occurring mainly in the 1650–1400 cm^{-1} region, thus comprising CC, CN and NN stretchings. Strong bands appearing in the sodium salt as doublets at 1630, 1600 and 1580, 1560 cm^{-1} are shifted in the complexes to lower frequencies, appearing as a strong band at 1590 cm^{-1} and a medium intensity band at 1540 cm^{-1} for vanadium, and a strong, broad band with a maximum at 1570 cm^{-1} (shoulders at 1550 and 1540 cm^{-1}) for the niobium complex. Shifts are also observed for bands in the region 1300–1200 cm^{-1}, that comprise C–OH and CN modes. This spectral evidence shows that characteristic absorptions for the coordinated PAR ligand are located in the region of absorptions which originate in azo, CN and C–OH vibrational modes, indicating that in the mixed oxalato-PAR-Nb(V) and PAR-V(V) complexes, PAR is acting as a tridentate ligand. This is in agreement with the stereochemistry of V(V) and Nb(V), which then would achieve coordination numbers of five and six, respectively.

The i.r. spectra of hydrated PAR-onium salts are, as expected, very different. A strong, broad absorption occurs between 3500 and 2500 cm^{-1}, indicating the presence of hydrogen bonding, involving the PAR-onium cation and water molecules present. CO stretchings of coordinated oxalato groups (resolved shoulders at 1710 and 1650 cm^{-1}) occur as a part of a strong, broad band (1710–1590 cm^{-1}), comprising also CC, CN and NN stretching modes. A strong absorption between 1400 and 1100 cm^{-1}

shows several maxima, which are much more poorly resolved than in the case of complexes containing coordinated PAR ion. Spectra of PAR-onium V(IV) and Nb(V) derivatives are very similar.

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