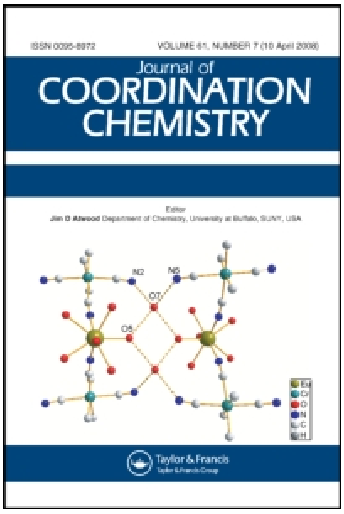

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OXOVANADIUM (IV) AND OXOVANADIUM(V) COMPLEXES OF 8-HYDROXYQUINOLINE-N-OXIDE

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Oxovanadium(IV) and oxovanadium(V) complexes with the stoichiometries $VO(NOQ)_2$ and $VO(NOQ)_2OH$ respectively, containing the N-oxide of 8-hydroxyquinoline (NOQH) as a ligand were synthesized and characterized by elemental analysis, infrared, Raman and electronic spectroscopy. The vibrational spectra are discussed in detail and a full assignment in the spectral range between 1700-200 cm^{-1} is proposed. Some comparisons with related species are made.

Keywords: oxovanadium(IV); oxovanadium(V); 8-hydroxyquinoline-N-oxide; vibrational spectra; electronic spectra

INTRODUCTION

Increasing evidence on the biological relevance of vanadium have been accumulated during the last years,[1-6] especially regarding the essentiality, distribution and toxicity of this element. Its biological and pharmacological activity, constitute areas of growing interest.

As part of our studies devoted to simple inorganic models for the development of the bioinorganic chemistry of vanadium, we have investigated some complexes of 8-hydroxyquinoline ("oxine") [7, 8] and of some of its halogenated derivatives.[9]

In this paper, we present the results obtained with related ligand, the N-oxide of 8-hydroxyquinoline (Figure 1(**a**), NOQH). In this case, and in contrast with

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the previously investigated systems, vanadium coordination occurs exclusively through oxygen atoms of the ligand. The oxygen atom of the N-oxide group is somewhat more polar than other oxygen donors such as alcohols, ethers or amides; in the case of aromatic amine-oxides, the 2pπ electrons of the O atom are conjugated with the ring electrons, a situation which does not occur in the case of the respective aliphatic molecules.[10] Therefore, this electron redistribution over the ring differentiates the NOQH molecule from that of its non-oxygenated parent.

Although NOQH and some of its halogenated derivatives have been used for extraction and analytical determination of different metal cations [11-19] including VO^{2+}, detailed information about the complexes of this oxocation are scarce;[14, 15] studies on similar complexes containing V(V) species have not been published.

EXPERIMENTAL

General procedures, usually employed for the preparation of similar oxine complexes [9, 14-17] were adapted for the synthesis of the two complexes.

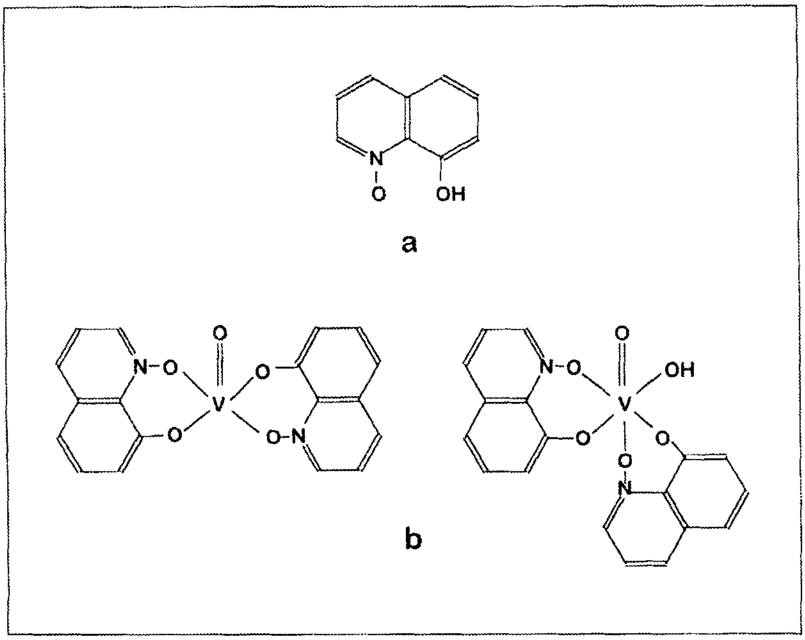

FIGURE 1 Structures of the free ligand (**a**) and of the two investigated complexes (**b**).

$VO(NOQ)_2$

To a solution of 0.35g of the ligand (Aldrich) dissolved in 25 mL of 10% acetic acid, and heated over a water-bath, another warm solution containing 0.25g of $VOSO_4{\cdot}5H_2O$ (Merck) in 10 mL of water, was added dropwise under continuous stirring. The mixture was heated over the water-bath for 15 mins and the precipitated green solid was filtered off, using a G4 glass-fritted funnel. The microcrystalline solid was washed several times with hot water and finally dried in a vacuum desiccator, over H_2SO_4. Anal. Calcd. for $VO(C_9H_6O_2N)_2$(%): C, 55.78; H, 3.10; N, 7.23; V, 13.15. Found: C, 55.66; H, 3.15; N, 7.15; V, 13.22.

$VO(NOQ)_2OH$

A solution containing 1.16g of the ligand dissolved in 100 mL of 5% acetic acid, was slowly added to another solution containing 0.5g of NH_4VO_3 (C.Erba) in 200 mL of the same solvent. The pH of the mixture was adjusted to 4.5 with drops of conc. NH_4OH and then heated at 70°C for one hour with constant stirring. The obtained black powder was digested another hour at the same temperature and put in a freezer. After 24 h, the precipitate was filtered off through a G4 glass-fritted funnel, washed several times with cold water and dried in an oven at 60°C during three days. Anal. Calcd. for $VO(C_9H_6O_2N)_2OH$(%): C, 53.43; H, 3.21; N, 6.93; V, 12.60. Found: C, 53.22; H, 3.27; N, 6.85; V, 12.68.

It was also possible to obtain the vanadium(V) complex by heating the vanadyl(IV) complex at 110°C in an oven, in air for several days. The gradual transformation of the vanadium(IV) to the vanadium(V) species can be conveniently followed by IR spectroscopy.

Attempts to obtain single crystals, suitable for crystallographic studies, failed because both complexes are insoluble in all common solvents.

The infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr pellet-technique. Raman spectra were obtained with a Bruker IFS 66 FTIR instrument provided with a FRA 106 Raman accessory. The samples were excited with the 1064 nm line of a Nd:YAG laser. Electronic absorption spectra of the complexes in different solvents were measured on a Hewlett-Packard 8452A diode-array spectrophotometer, using 10 mm quartz cells.

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectra of both complexes in the spectral range 1800-200 cm^{-1} are shown in Figure 2, the detailed band positions, together with the proposed

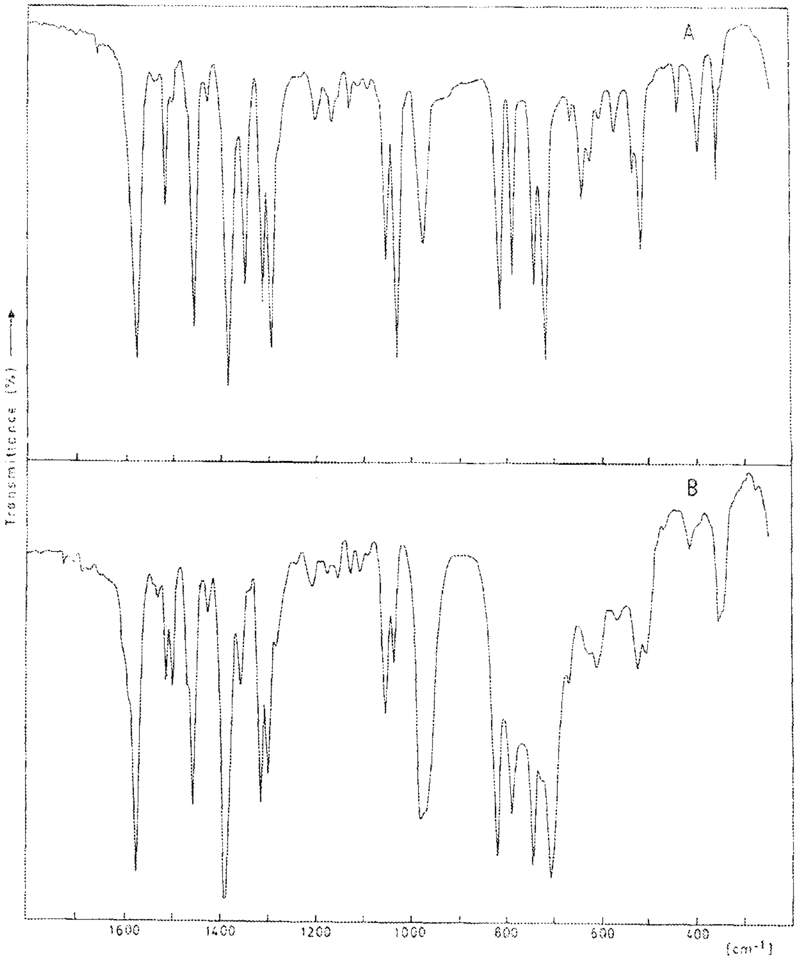

FIGURE 2 Infrared spectra of $VO(NOQ)_2$ (**A**) and $VO(NOQ)_2OH$ (**B**).

assignment, are given in Table I. These assignments are mainly based on comparisons with literature data [15-18] and with results of our own studies of related species.[7-9] Although it was difficult to obtain good-quality Raman spectra, due to fluorescence effects and poor signal to noise ratios, they were useful to confirm and support some of the IR assignments.

The vanadium atom is bonded to two oxygen atoms from each ligand, as shown in Figure 1(**b**), constituting a delocalized π-electron system which involves the rings and the metal atom. The donor character of these oxygen

TABLE I Infrared spectra (cm^{-1}) of the free ligand and the two vanadium complexes of the N-oxide of 8-hydroxyquinoleine

NOQH	*VO(NOQ)$_2$*	*VO(NOQ)$_2$OH*	*Assignment*
		3432 m, br	ν(OH)
		3115 w	3090 sh
			ν(CH)
3065 w	3065 w	3069 w	
3027 w	-	-	ν(OH)
1601 vs	1574 vs	1599 sh, 1586 sh, 1574 vs	ν(C=C)
1584 m	1541 vw	1541 vw	
1568 sh	1534 vw	1530 w	δ(OH) + ν(CO)
1532 s	1514 m	1512 m	
1507 w	1501 w	1499 m	ν(C-NO)
1471 m	1456 vs	1468 sh	
1457 s	1427 w	1457 vs	
1405 s	1387 vs	1428 w	ν(CH) ring
1371 w	1349 s	1391 vs	
		1356 m	
1337 s	1315 s	1316 s	ν(N-O)
1312 m	-	1300 s	
1290 sh	1295 vs	1282 w	
1276 s	1283 sh	1240 w	
1214 vw	1236 vw	1211 w	δ(CH + OH)
1192 vw	1202 m	1205 m	in plane
1179 m	1166 m	1178 w	
1154 m	1155 sh	1154 w	
1122 w	1129 w	1129 w	
1087 vw	1114 vw	1110 w	
1048 vs	1091 vw	1090 vw	δ(CH) out of plane
1038 sh	1054 s	1052 s	
	1030 vs	1034 m	
-	977 s	976 vs	ν(V=O)
-	-	968 sh	δ(V-OH)
930 w	928 w	-	
905sh, 887 m	881 vw	-	δ(CH) out of plane
874 w	-	-	
813 vs	819 vs	δ(NO)	
789 m	788 s	790 s	
			δ(CH) out of plane
749 vs	741 s	744 vs	
744 sh	-	-	δ(OH) out of plane
708 w	718 vs	726 w	ring breathing
-	-	708 vs	ν(V-OH)
666 s	665 w	668 w	
624 w	643 m	629 w	δ(ring) in plane
612 w	624 w	609 m	
-	605 w	568 w	ν_{as}(V-O(C))
570 m	575 m	562 vw	
556 w	-	-	δ(ring) in plane
541 w	538 w	526 m	
523 vw			
-	519 s	509 m	ν_{as} (V-O(N))
500 w	-	496 w	
469 m	-	-	δ(ring) out of plane
426 w	-	-	
-	442 m	418 m	δ(V-O-V)
-	399 m	350 m	ν_s(V-O(C))
-	362 m	345 sh	ν_s(V-O(N))
351 m	350 sh	322 vw	δ(CO)
-	-	278 vw	δ(VO$_2$) (?)

vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

atoms generates a general diminution of the electronic density over the rings, which may be reflected in the vibrational behavior of some chemical bonds. Notwithstanding, most of the characteristic ring modes, involving C and H atoms, are scarcely affected by the coordination; although, as a general trend, small shifts to lower frequencies are observed.

An IR band located at 3027 cm^{-1} in the free ligand can be assigned to the O-H-stretching of the phenolic group because it is absent in the spectra of the complexes. Similar behavior is found for a shoulder observed at 744 cm^{-1} and assigned to the OH-out of plane bending vibration.

In agreement with previous results,[7-9] the very strong IR band found at 1601 cm^{-1} in the free ligand, and displaced to lower frequencies in both complexes, is assigned to the ν(C=C) mode, which also appears as a very strong Raman line in the complexes (1589 cm^{-1} in the V(IV) complex and 1573 cm^{-1} in the V(V) species).

The group of bands found between 1584 and 1352 cm^{-1} in the free ligand and assignable to phenolic deformational modes coupled with the ν(C-O) mode [15] is somewhat simplified in the spectra of complexes. On the other hand, the presence of the N-O group, facilitates the electronic delocalization through the O-N-C-C-O^- bonds with participation of the lone pair of the oxygen atom. As a result, the C-O bond is reinforced, in comparison with the same bond in 8-hydroxyquinoline or in its halogen-substituted derivatives.[9] This explains the appreciably higher frequency of this mode in the present cases.

Especially interesting is the behavior of the ν(N-O), which is located at 1337 cm^{-1} in the free ligand [15] and which, as expected,[10, 19] is shifted to lower frequencies after complex formation. The corresponding δ(NO) mode, located at 816 cm^{-1}, is less affected probably because complexation the N-O group causes a more rigid structure inhibiting bending.

The typical ν(V=O) vibration appears at 977 cm^{-1} in the IR spectrum of the vanadium(IV) complex and at 976 cm^{-1} in the vanadium(V) species. In the Raman spectra these bands are found at 973 and 981 cm^{-1}, respectively. The similar values for this mode can be explained as the result of two opposite effects: the V(IV)=O bond equals the energy of the V(V)=O bond due to the coplanar geometry of the metal/ligand system which favors the electronic delocalization and, consequently, reinforcement of the terminal vanadium-oxygen bond. In the case of $VO(NOQ)_2OH$ the ν(V=O) IR-band presents a doublet also observed in the Raman spectrum, with a lower energy component (968 cm^{-1} in the IR, 950 cm^{-1} in the Raman spectrum). This band can be assigned to a δ(V-OH) mode.[20] The respective ν(V-OH) stretching is seen as a strong IR-band at 708 cm^{-1} and the ν(OH) mode is observed as a somewhat broad band at 3432 cm^{-1}.

The metal-to-ligand vibrations, found below 400 cm^{-1}, lie somewhat higher in the vanadium(IV) complex, showing again the better metal to ligand interaction. In the case of the deformational VO_2 mode, this trend is also observable; although this band is probably of a more complex nature, due to coupling with other low-energy vibrational modes.

In the Raman spectra, this region shows some well defined medium and weak intensity lines located at 605, 523, 409 and 345 cm^{-1} (V(IV) complex) and 538, 515, 403 and 369 cm^{-1} (V(V) complex).

As seen from the spectral data and the proposed assignments, the vibrational spectra of both complexes are clearly compatible with the proposed structural models (Figure 1(**b**)).

Electronic Spectra

The electronic spectra of the ligand and the two complexes were measured in ethanolic solutions between 200 and 800 nm. They are shown in Figure 3 and the exact band positions are presented in Table II. The complexes were almost insoluble and the solutions had a concentration of 10^{-5} M with ϵ-values between 10^3 and 10^4 $M^{-1}cm^{-1}$.

The free ligand presents three absorption maxima, in agreement with literature data,[15] assigned as follows:

$$\pi \Rightarrow \pi^* \text{ (204, 240, 280(sh) nm)}$$

$$n \Rightarrow \pi^* \text{ (346 nm)}$$

The 346 nm band is most affected by coordination, because it is related to the NO group.[15, 21, 22]

The band assignable to ligand-to-metal charge transfer appears partially overlapped with the lower energy intraligand band. In the case of the vanadyl(IV) complex, this band is seen at 320 nm, whereas for the vanadium(V) complex no new bands are seen in this region; the band remains overlapped by the 344 nm band.

Finally, it is interesting that, at least under the experimental conditions, no reactions with the solvent could be established for these complexes. This constitutes another difference with the previously investigated complexes of the halogenated derivatives of 8-hydroxyquinoline for which very complex solution behavior was found.[9]

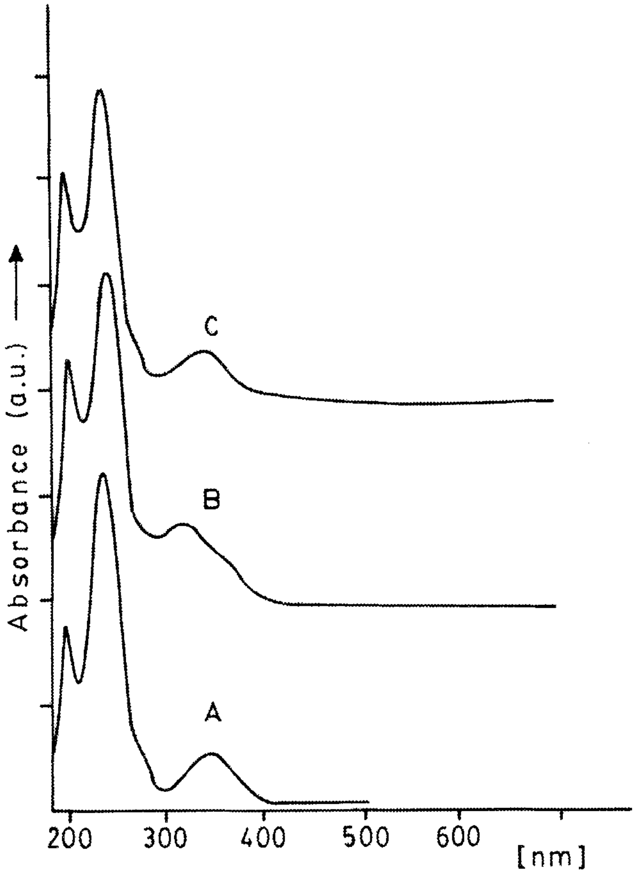

FIGURE 3 Electronic spectra of free NOQH (**A**), $VO(NOQ)_2$ (**B**) and $VO(NOQ)_2OH$ (**C**).

TABLE II Electronic spectra of the ligand and the two complexes in ethanolic solution (absorption maxima in nm)

NOQH	$VO(NOQ)_2$	$VO(NOQ)_2OH$
204	206	206
240	244	242
280 sh	282 sh	
	320	344
346	344 sh	
	368 sh	

sh: shoulder

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