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Oxovanadium(IV) Complexes of Halogenated Oxines

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Summary. Six VO^{2+} complexes of 8-hydroxyquinoline (oxine) and of some of its mono- and dihalogenated derivatives have been prepared. The complex of 5-chloro-oxine is very unstable and oxidizes rapidly, generating a V(V) complex of stoichiometry $VO(QCl)_2OH$ which could also be prepared in pure form. The infrared spectra of all complexes have been recorded and are discussed in detail. The complexes containing halogenated ligands appear as polymeric species, interacting through $V{=}O\cdots V{=}O$ bridges. The magnetic moments, investigated at room temperature, indicate completely quenched orbital contributions. The analysis of the electronic spectra reveals very complex solution behaviour including, oxidation phenomena, ligand loss, and interaction with the solvent.

Keywords. Vanadyl(IV); Oxine; Halogenated oxines; IR; Magnetic susceptibilities; Electronic spectra; Solution behaviour.

Oxovanadium(IV)-Komplexe von halogenierten Oxinen

Zusammenfassung. Sechs VO^{2+}-Komplexe von 8-Hydroxyquinolin (Oxin) und einige seiner mono- und dihalogenierten Derivate wurden dargestellt. Der Komplex des 5-Chloroxins erwies sich als besonders instabil und oxidiert sehr schnell unter Bildung eines V(V)-Komplexes der Stöchiometrie $VO(QCl)_2OH$, welcher auch in reiner Form dargestellt werden konnte. Die Infrarotspektren aller Komplexe wurden aufgenommen und werden eingehend diskutiert. Die Komplexe mit halogenierten Liganden erscheinen als polymere Spezies, welche über $V{=}O\cdots V{=}O$-Brücken wechselwirken. Die bei Raumtemperatur gemessenen magnetischen Momente zeigen die totale Abwesenheit von Orbitalbeiträgen. Die Analyse der Elektronenspektren weist auf ein besonders kompliziertes Lösungsverhalten hin, welches Oxidationsphänomene, Ligandenabspaltung und Wechselwirkung mit den Lösungsmitteln einschließt.

Introduction

Increasing evidence on the biological relevance of vanadium has been accumulated during the last years [1–4], and its essentiality, distribution, and toxicity as well as its biological and pharmacologic activity are areas of great interest. Nevertheless, the role of vanadium in higher organisms is still unclear. Up to now, the best evidence for a biological role of this element comes from bacteria (vanadium containing nitrogenase in *Azotobacter* species [5, 6]) and from plants (vanadium dependent haloperoxidases in algae and lichens [7]). On the other hand, and although the accumulation of vanadium in tunicates and in the toadstool *Amanita muscaria* has been well established, the possible functions of the systems containing the metal (hemovanadine and amavadin, respectively) remain obscure [8].

As part of our studies about simple inorganic models of interest for the development of the bioinorganic chemistry of vanadium [9–16], we have started investigations on VO^{2+} complexes with 8-hydroxyquinoline (oxine) and some of its halogenated derivatives which appear to be suitable models due to the preference of oxovanadium(IV) for oxygen and nitrogen donors in biological systems.

Oxine, which forms particularly stable complexes with many metal cations [17–19], has been used as a ligand in previous studies belonging to this general project, involving V(III) [10] and VO_2^+ [12] as central cations.

In the present paper, we analyze the infrared and electronic spectra as well as the magnetic behaviour of the VO^{2+} complexes of 8-hydroxyquinoline and its following halogenated derivatives: 5-chloro, 5,7-dichloro, 5,7-dibromo-, 5,7-diiodo-, and 5-chloro-7-iodo-8-hydroxyquinoline. The structures of the ligands are depicted schematically in Fig. 1, including a general diagram of the metal-ligand interactions supported by experimental evidences discussed in the following sections. Some of these compounds have been described earlier [20, 21], but their spectroscopic and magnetic behavior has not been investigated in detail. The complexes derived from 5-chloro-8-hydroxyquinoline and 5-chloro-7-iodo-8-hydroxyquinoline as well as the vanadium(V) complex of the first of these ligands (whose probable structure is also given in Fig. 1) are reported here for the first time.

Some unexpected results, related to the oxidation behavior of the central cation, apparently depending on the nature of the ligands, are also discussed.

Results and Discussion

Synthesis of the complexes

Oxo*bis*(8-hydroxyquinolinate)vanadium(IV) (VOQ_2) was obtained according to the procedure described by Doadrio and Martínez [20]. In contact with air, the obtained greenish precipitate oxidizes immediately, turning its colour to black.

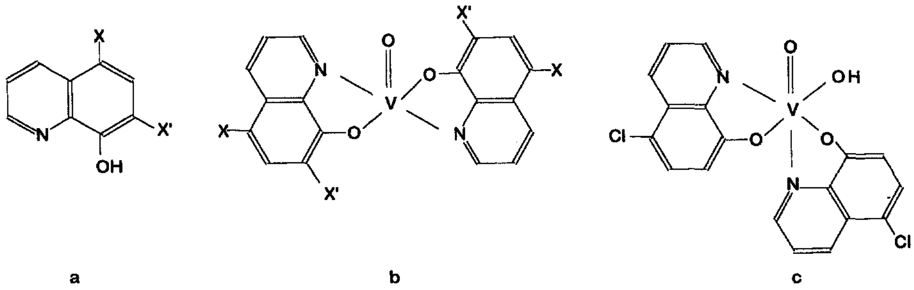


Fig. 1. a: Schematic structure of the ligands (oxine $X = X' = H$); **b**: diagram of the VO^{2+} ligand interactions; **c**: probable structure of the V(V) complexes of 5-chloro-8-hydroxyquinoline

The other five complexes were prepared following general procedures described in *Gmelin*'s handbook [22] which are described in detail in the experimental part of this paper. The low solubility of some of these ligands in usual solvents generates a major problem in the syntheses.

A very peculiar behaviour was observed in the case of 5-chloro-8-hydroxyquinoline. In our first attempts to obtain oxo*bis*(5-chloro-8-hydroxyquinolinate)vanadium(IV) ($VO(QCl)_2$) using similar procedures to those employed with the other ligands, no precipitation of the complex was observed. Concentration of the solution to half its volume or cooling the total volume to −20°C for two days afforded a dark-brownish precipitate. This colour, as well as the IR spectra of these products, suggest a partial oxidation of the metal to vanadium(V). To clarify this aspect, the synthesis was also performed following the procedure used in the preparation of VOQ_2 [20]. In this case, an orange solid was obtained. Its air stability was markedly higher than that of VOQ_2, and only after heating this solid in air at 70–100°C oxidation, accompanied with gradual colour changes, could be observed. The final dark product was similar to that obtained after short heating of the precipitates resulting from the first synthetic procedure, confirming the partially oxidated nature of these species.

Finally, in order to clarify completely the behaviour of this system, oxo-hydroxo*bis*(5-chloro-8-hydroxyquinolinate)vanadium(V) was also prepared and investigated.

Infrared spectra

Vanadyl(IV) complexes

The IR spectra of the ligands and the complexes were measured in the range between 4000 and 200 cm^{-1}. The assignment of the bands was performed on the basis of a comparative analysis of the results with respect to literature data of related systems. The positions of the most relevant and characteristic bands are shown in Table 1.

The broad bands at 3060–3200 cm^{-1} in the ligand spectra can be assigned to Ar-OH vibrations, as they are not present in the complexes where the deprotonated O-atom is coordinated to vanadium. This is also in agreement with data reported by *Marchon et al.* for oxine [23].

The assignment of the CN and CC stretching modes is based on our previous work [12] and investigations by *Henry et al.* [24]. Comparing the position of these bands for the different ligands, it is obvious that ring substitution results in a shift to lower frequencies. This behaviour can probably be explained by the lowering in the electronic density caused by electronegative groups.

ν(C=N) always occurs at higher frequencies in the ligands than in the respective complexes. In this case, the decrease of the electronic density of the ring may be correlated with the donor character of the nitrogen atom in the N–V bond. There is also another correlation, observable when comparing the position of the ν (C=N) band in the free ligands and in the corresponding complexes. In these cases, the higher shift corresponds to higher electronegativity. Evidently, the presence of electronegative groups in the ring affects the donor capacity of the N-atom.

Table 1. Assignment of relevant IR bands of the investigated complexes

	Wavenumber (cm^{-1})											
	QH	VOQ_2	QClH	VO(QCl)$_2$	QClIH	VO(QClI)$_2$	QCl$_2$H	VO(QCl$_2$)$_2$	QBr$_2$H	VO(QBr$_2$)$_2$	QI$_2$H	VO(QI$_2$)$_2$
ν(Ar–OH)	3176	–	3211	–	3132	–	3090	–	3065	–	3061	–
ν(C=N)	1627	1602	1622	1596	1605	1581	1614	1573	1607	1572	1576	1570
ν(C=C)	1581	1579	1589	1574	1576	1554	1580	1563	1567	1557	1556	1547
OH+CH	1286	1319	1281	1318	1331	1283	1335	1290	1332	1281	1331	1275
	1275	1271	1230	1258	1272	1243	1275	1245	1270	1242	1268	1243
in-plane			1216	1240	1234	1221	1260	1237	1245	1221	1248	1221
bending			1201	1222			1219	1198	1238	1200		
				1212			1206		1213	1189		
									1200			
ν(C–O)	1094	1109	1073	1087	1084	1111	1093	1116	1086	1112	–	1111
ν(V=O)	–	970	–	892	–	887	–	881	–	881	–	888
ν_a(V–O)	–	528	–	552	–	586	–	603	–	586	–	577
δ(O–V–O)	–	428	–	424	–	426	–	427	–	415	–	413
δ(C–O)	463	499	487	500	498	510	498	520	498	507	–	–
ν_s(V–O)	–	406	–	406	–	485	–	496	–	479	–	471
ν(V–N)	–	352	–	354	–	359	–	348	–	348	–	342

These comparisons show that the electronegativity of the ring substituents produces not only a decrease of the electronic density over the ring, generating a diminution in the ν(C=N)} stretching frequency, but also causes a lowering of the donor character of the N atom concerning its interaction with the V atom. The fact that in the case of *Q*H and its complex the difference between the respective ν(C=N) values is similar to those found for Cl*Q*H and ClI*Q*H and its complexes may be explained by a compensation of the two effects mentioned above.

Bands in the region between 1200 and 1300 $\mathrm{cm^{-1}}$ are assigned to Ar-OH in-plane bending modes, probably coupled to the adjacent C–H waggings [23, 25]. As the OH group is transformed to a C–O–V bond in the complexes, some differences can be observed in the positions and intensity in these bands.

The ν(C–O) modes in the ligands and in the complexes appear approximately at 1100 $\mathrm{cm^{-1}}$ in agreement with reported data [12, 26]. In every case, this mode lies at higher wavenumbers in the complex than in the free ligand, as can be also observed for the respective δ(CO) in-plane bending mode.

The characteristic ν(V=O) stretching mode is found at 970 $\mathrm{cm^{-1}}$ in the case of $\mathrm{VO}Q_2$, in agreement with previously reported data [20, 21, 26]. This band shifts to lower frequencies in the other compounds, and this situation renews an old discussion about which exists a wealth of conflicting and contradictory literature reports [21, 27–32]. This shift has usually been explained in terms of polymerization occuring by interaction of the vanadyl oxygen in one molecule with the open axial site of vanadium in another molecule [21, 27–30]. *Mathew et al.* [28] suggested that a low ν(V=O) frequency may be a diagnostic test for oxygen bridging in vanadyl(IV). On the other hand, they also suggested that vanadium complexes having colours other than green usually contain V=O polymeric units [28]. Interestingly, in many of the investigated cases in which also magnetic susceptibility measurements have been performed, the polymerization apparently generates no appreciable ferromagnetic interactions, at least at room temperature [27, 30]. Our own magnetic susceptibility measurements clearly demonstrate a similar behaviour.

Finally, in relation to this problem, it is worth commenting that the spectroscopic behaviour of the oxine complex is different, a fact that suggests that it remains monomeric, whereas all the other species are probably polymeric. However, as stated by *McCormick* and *Bozis* [27], the most obvious difference between the ligands that form monomeric complexes and those that give rise to extended structures is that the latter possess electron withdrawing groups. The electron density at the vanadium atoms may be reduced by these electron withdrawing groups to such an extent that the increased *Lewis* acidity of the vanadium atoms makes O=V–O=V bridging possible. On the other hand, pyridine adducts of 5,7-dihalogenated oxines exhibit appreciably higher ν(V=O) stretching bands than isolated complexes, suggesting that polymerization produces a dramatic weakening of this bond compared to the interaction of the axial position [21] with pyridine. All these arguments support the generation of polymeric species in all investigated vanadyl(IV) complexes containing halogen substituted ligands.

It is well known, ν(VO) vanadium-ligand vibrations appear at higher frequencies with respect to ν(NV) [10, 26, 33]. On this basis we have assigned ν_{as}(VO), ν_{s}(VO), and ν_{as}(VN) (Table 1). The corresponding ν_{s}(VN) mode probably lies below 300 cm^{-1} and could not be identified in our spectra. The assignment of the δ(OVO) bands are supported by results obtained from vanadyl(IV) complexes with oxygenated bidentate donors [34].

Interestingly, the ν(VO) modes of $\mathrm{VO}Q_2$ are located at lower frequencies than those in the other complexes. Once again, this fact is consistent with the increasing *Lewis* acidity at the vanadium atom caused by the presence of halogen in the ring, inducing a stronger π-retrodonation from vanadium to oxygen and reinforcing the V–O bonds.

5-Chloro-quinoline complexes with V(IV) and V(V)

As mentioned above, the vanadyl(IV) complex of 5-chloro-8-hydroxyquinoline is more sensible to oxidation than those derived from the other halogenated ligands. Therefore, we have investigated spectroscopically its behaviour under different experimental conditions. This study was undertaken with the following samples: pure V(IV) complex ($\mathrm{VO}(Q\mathrm{Cl})_2$), complex heated for two days at 100°C ($\mathrm{VO}(Q\mathrm{Cl})_2/100$), complex obtained by the same procedure as all other compounds and recovered after cooling at −20°C for two days ($\mathrm{VO}(Q\mathrm{Cl})_2/\mathrm{A}$), and the corresponding vanadium(V) complex ($\mathrm{VO}(Q\mathrm{Cl})_2\mathrm{OH}$).

The infrared data collected for all these complexes have been comparatively analyzed. Some typical vibrational modes from which the gradual transformation of V(IV) to V(V) can be observed, are shown in Table 2. As illustrative examples, the relevant parts of the IR spectra of three of the samples are presented in Fig. 2.

A band at 1038 cm^{-1} in the ligand is assigned to the Ar–Cl vibration [25]. This band is shifted to higher frequency in the vanadium(IV) complex, but retains its position in the vanadium(V) species.

The characteristic ν(V=O) stretching mode, located at 892 cm^{-1} in $\mathrm{VO}(Q\mathrm{Cl})_2$, is splitted into two bands during the oxidation process and finally converges to a unique band at 956 cm^{-1} in the fully oxidized $\mathrm{VO}(Q\mathrm{Cl})_2\mathrm{OH}$ species. This last value agrees very well with those reported for related vanadium(V) compounds [35, 36]. Another typical band in these systems is that located at 715 cm^{-1},

Table 2. Shifts of some typical IR bands during the transformation of V(IV) to V(V)

	Wavenumber (cm^{-1})^{a}			
	$\mathrm{VO}(Q\mathrm{Cl})_2$	$\mathrm{VO}(Q\mathrm{Cl})_2/100$	$\mathrm{VO}(Q\mathrm{Cl})_2/A$	$\mathrm{VO}(Q\mathrm{Cl})_2\mathrm{OH}$
ν(Ar–Cl)	1045 m	1045 m	1039 m	1039 m
ν(V=O)	892 s	892 s, 956 w	887 w, 956 s	956 s
$\nu(\mathrm{VO_2})$	–	920 sh	906 m	–
ν(V–OH)	–	719 sh	715 m	715 s
ν_a(V–O)	552 m	553 m, 545 sh	546 s	544 s
ν_s(V–O)	460 s	460 m	458 m	458 m
ν(V–N)	354 m	354 w, 374 vw	351, 373 w	351 w, 373 w
$\delta(\mathrm{VO_2})$	–	340 sh	335 vw, 311vw	345 sh, 307 w

^{a} S: strong, m: medium, w: weak, vw: very weak, sh: shoulder

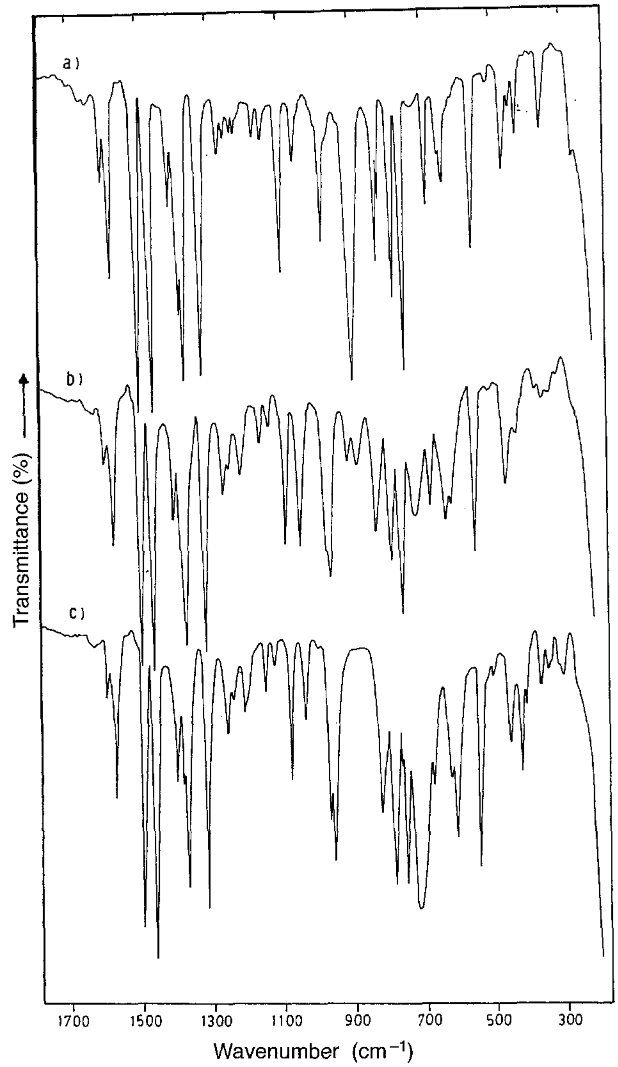


Fig. 2. Infrared spectra of VO(QCL)$_2$ (**a**), VO(QCl)$_2$/A (**b**), and VO(QCl)$_2$OH (**c**) between 1500 and 200 cm^{-1} of nomenclature, see text.

assigned to the V–OH stretching vibration. It is absent in the vanadium(IV) complexes and experiences enhancement with oxidation.

On the other hand, we can observe an intensity diminution of the typical 906 and 887 cm^{-1} bands that are absent in VO(QCl)$_2$OH. In some complexes of VO$_2L_2$ stoichiometry (L = bidentate organic ligand), the δ(VO$_2$) band occurs in the range between 322 and 344 cm^{-1} [37]. On this basis it is possible to assign either the band at 307 or the shoulder at 345 cm^{-1} to this mode in the vanadium(V) complex. According to the same reference, we assigned the band at 906 cm^{-1} in the partially oxidized species to a ν(VO$_2$) mode. This band may be overlapped with that at 956 cm^{-1} in VO(QCl)$_2$OH, the intensity of which increases with oxidation.

The ν(V–O) modes experience only small shifts during oxidation, whereas for the ν(V–N) modes two bands at 351 and 307 cm^{-1} replace the unique band found in the pure vanadyl(IV) complex at 354 cm^{-1}. Apart from this only mirror changes are observed in some of the ligand modes during oxidation.

To conclude, this analysis has shown that oxidation proceeds in the following order: $VO(QCl)_2$ < $VO(QCl)_2/100$ < $VO(QCl)_2/A$ < $VO(QCl)_2OH$. A sample heated at 70°C for two days shows an oxidation progress which allowed its intercalation between the first two compounds, whereas the material collected after volume reduction, using the general synthetic procedure, appears as more oxidized than sample *A*.

Magnetic properties

The magnetic susceptibilities of all prepared VO^{2+} complexes at room temperature (293 K) were found to be between 1.65 and 1.70 B.M., *i.e.* they lie clearly in the range which is characteritic for the spin only value of the d^1 system when the orbital contribution is completely quenched [38, 39]. As the magnetic orbitals of the VO^{2+} cations are of the *xy*-type [39], and these orbitals are not directed towards the bridging direction, the possibility for a magnetic coupling through interaction between these orbitals is relatively low.

Electronic spectra

The electronic spectra of the ligands and the complexes were measured in different solvents in the range between 800 and 200 nm. The compounds showed very low solubility in all tested solvents, and finally *DMF* and chloroform were selected. As the molar absorptivity coefficients (ε) were of the order 10^3–10^4 $dm^3 \cdot mol^{-1}$ cm^{-1} very diluted solutions (about 10^{-5} $mol \cdot dm^{-3}$) could be employed.

The results obtained with in chloroform solutions are very interesting, since the spectra as well as their colour change with time. The change was from yellow-orange to brownish, suggesting some reaction between the solvent and the complexes, probably caused by the small amounts of ethanol (about 2%) usually present in normal p.a. chloroform as a stabilizer.

Moreover, the complex of 5-chloro-8-hydroxyquinoline shows the highest reactivity and fastest colour changes. Therefore, we have chosen this compound to illustrate this behaviour and to analyze its origin. The modifications of the spectra of this complex with time are shown in Fig. 3 and compared with the spectrum of a freshly prepared solution of $VO(QCl)_2OH$.

In another series of experiments, $VO(QCl)_2$, $VO(QCl)_2/A$, and $VO(QCl)_2OH$ were dissolved in HPLC-quality chloroform totally free from ethanol; greenish solutions were obtained. In every case, a band at 650–660 nm appeared, and the band around 500 nm, present in p.a. chloroform solutions, was absent. Some comparative data are shown in Table 3. If the solution of $VO(QCl)_2/A$ in p.a. chloroform is stored during several days, its colour also turns to greenish, and a band at 640 nm appears, whereas that at 500 nm disappears.

It is very significant that the bands at 650 and 500 nm are absent in both *DMF* and freshly prepared p.a. chloroform solutions. These transitions must therefore arise from interactions between the solvent and the complexes.

Interestingly, the chemistry of a recently investigated system (VO^{2+}/maltol, maltol = 3-hydroxy-2-methyl-4-pyrone) closely resembles that of the VO^{2+}/QH system [40]. $VO(maltol)_2$ reacts in the presence of air with alcohols in chloroform

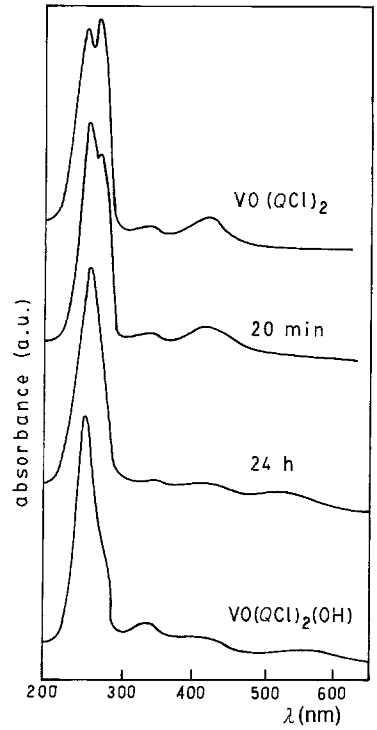


Fig. 3. Changes in the electronic spectra of pure VO(QCl)$_2$ in p.a. chloroform with time; the spectrum of a pure sample of VO(QCl)$_2$OH is also included for comparison

Table 3. Electronic spectra (nm) in p.a. chloroform (a) and HPLC quality chloroform (b)

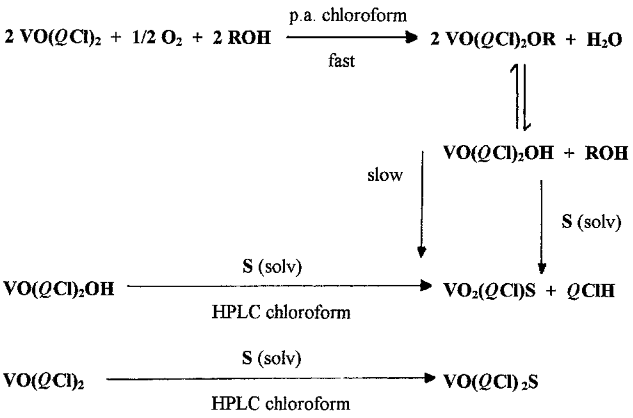
VO(QCl)$_2$		VO(QCl)$_2$/A		VO(QCl)$_2$OH	
a	b	a	b	a	b
250	252	250	252	248	252
266					
324		330		336	
340	342		342	398	342
414	396	404	386	414	398
		514		518	
	658		650		660

and also with alcohol free CH_2Cl_2, revealing some solvent coordination to vanadium [41].

On the other hand, it has been shown that dimeric vanadium(V) complexes of oxine and halogenated oxines of the type Q(VO)–O–(VO)Q are partially hydrolzed in chlorobenzene and give rise to species of QVO$_2$ stoichiometry [35, 42]. Consequently, for the present systems and on the basis of this behaviour, we can formulate the equilibria shown in Scheme 1.

The processes given in Scheme 1 allow to explain the spectroscopic behaviour. The esterification reaction additionally supports the formula suggested for the vanadium(V) complex of 5-chloro-8-hydroxyquinoline.

According to our previous results [12], the electronic transitions below 350 nm can be assigned to interligand transitions. These bands conserved their positions irrespectively of solvents and time and are also present in the spectra of the pure



Scheme 1

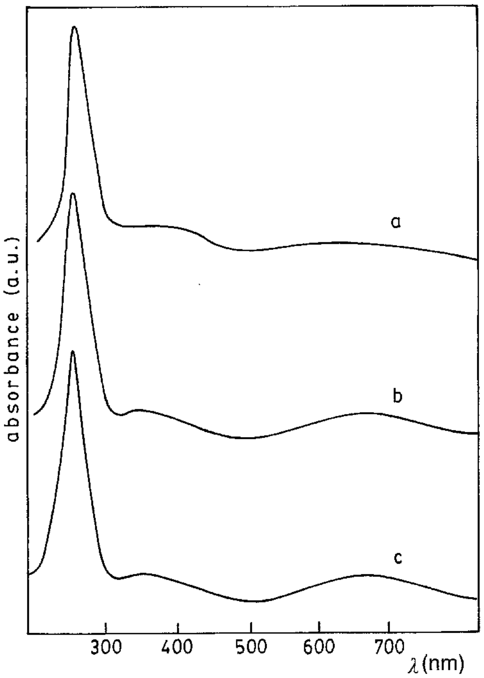


Fig. 4. Electronic spectra of different samples showing the band at approx. 650 nm: VO(QCl)$_2$ after 2 months in p.a. CH$_3$Cl (**a**), VO(QCl)$_2$ after dissolution in HPLC quality CH$_3$Cl (**b**), and VO(QCl)$_2$OH after dissolution in HPLC quality CH$_3$Cl (**c**)

ligands. The bands at higher wavelengths are assignable to charge transfer from the ligands to vanadium. This is in agreement with the shift to lower wavelenght with the rising oxidation state of the sample.

The two transitions located around 400 and 500 nm are characteristic of ester formation [43]. The latter one is present even in freshly prepared p.a. chloroform solutions of VO(QCl)$_2$OH (Fig. 3), and its intensity enhances with time. It also appears in all partially oxidized VO(QCl)$_2$ solutions in the same solvent. The band at around 640 nm, present in the HPLC quality chloroform solutions and in aged normal chloroform solutions, can be assigned to the Cl →V charge transfer, originating from solvent interaction. Some illustrative spectra are shown in Fig. 4.

Experimental

Materials

The halogenated oxines (Aldrich), 8-hydroxyquinoline (C. Erba), and $VOSO_4 \cdot 5H_2O$ (Merck) were used as supplied. HPLC quality chloroform was purchased from C. Erba. All other reagents and solvents were analytical grade products.

Syntheses

VOQ_2

This complex was prepared by reaction of a solution of $VOSO_4 \cdot 5H_2O$ (1.0 g in 5 cm^3 of water) with an ethanolic solution of the ligand (1.15 g in 5 cm^3) as previously described [20]. The synthesis was carried out under a N_2 flow in a totally isolated system. All further operations (filtration, washing, and drying) must also be performed under strict absence of air.

$VO(QCl_2)_2$

2.14 g of 5,7-dichloro-8-hydroxyquinoline were dissolved in a warm mixture of 150 cm^3 of ethanol and 50 cm^3 of *DMF* (water bath). 1.27 g of $VOSO_4 \cdot 5H_2O$, dissolved in 30 cm^3 of warm water, was added dropwise to the solution of the ligand. The precipitated complex was immediately filtered through a G4 glass filter, washed with *ca.* 200 cm^3 of hot ethanol, and dried for one weak at 60°C.

$VO(QBr_2)_2$

2.05 g of 5,7-dibromo-8-hydroxyquinoline were dissolved in a warm mixture of 200 cm^3 of ethanol and 200 cm^3 of *DMF* (water bath). 0.84 g of $VOSO_4 \cdot 5H_2O$, dissolved in 20 ml of warm water, were added dropwise to the ligand solution. In spite of the fact that the solution changes it colour, no precipitation is observed. After vigorous stirring and digestion of the mixture over the water bath for 20 min an orange-yellow spongy precipitate formed which was filtered through a G3 glass filter, washed with *ca.* 200 cm^3 of hot ethanol, and dried for 3 days at 60°C and for 3 more days at 100°C.

$VO(QI_2)_2$

0.50 g of $VOSO_4 \cdot 5H_2O$ were dissolved in 50 cm^3 of hot water (water bath). 1.60 g of 5,7-diiodo-8-hydroxyquinoline were dissolved in a warm mixture of 80 cm^3 of acetone and 60 cm^3 of *DMF*. The solution of the ligand was slowly added to the vanadyl solution. The precipitated complex was immediately filtered through a G3 glass filter, washed with *ca.* 200 cm^3 of hot ethanol, and dried for one week at 60°C.

$VO(QClI)_2$

This complex was obtained for the first time, using a similar procedure as those described above. 0.61 g of 5-chloro-7-iodo-8-hydroxyquinoline were dissolved in 150 cm^3 of warm ethanol (water bath). To this solution, 0.25 g of $VOSO_4 \cdot 5H_2O$, dissolved in 10 cm^3 of hot ethanol, were added dropwise. The solution quickly became dark and, the complex precipitated after short stirring. After short digestion over the water bath it was filtered, washed with *ca.* 100 cm^3 of ethanol and dried for 3 days at 60°C and for 3 more days at 100°C. $C_{18}H_8N_2O_3Cl_2I_2V$ (675.93); calcd.: C 31.91, H 1.18, N 4.14, V 7.54; found; C 31.80, H 1.27, N 4.26, V 7.66.

VO(QCl)$_2$

This complex was also prepared for the first time, following the procedure applied in the case of VOQ_2 (N_2-flow, strict absence of air). The dried, light-orange solid was stable in air. $C_{18}H_{10}N_2O_3Cl_2V$ (424.14); calcd.: C 50.94, H 2.36, N 6.60, V 12.03; found: C 50.35, H 2.20, N 6.30, V 12.20.

Attempts to obtain VO(*Q*Cl)$_2$ using the same procedure employed for the synthesis of the above mentioned dihalogen oxines, *i.e.* mixing ethanolic solutions of the ligand and the cation, failed. It was necessary to reduce drastically the volume of the reaction mixture or to cool it for two days in a freezer at −20° C in order to generate complex precipitation. The samples obtained this way are always partially oxidized.

VO(OH)(QCl)$_2$

This vanadium(V) complex was also obtained for the first time, using a similar procedure like that employed by *Blair et al.* for the synthesis of VO(OH)*Q*$_2$ [44], by addition of a solution of the ligand in diluted acetic acid to a weakly alkaline solution of sodium vanadate at 70°C. $C_{18}H_{11}N_2O_4Cl_2V$ (441.14); calcd.: C 48.98, H 2.49, N 6.35, V 11.56; found: C 49.18, H 2.34, N 6.15, V 11.50.

Spectroscopic and magnetic measurements

The infrared spectra were obtained with a Perkin Elmer 580 B spectrophotometer (KBr-pellets). Electronic absorption spectra of the complexes in different solvents were measured on a Hewlett-Packard 8452A diode array spectrophotometer. Magnetic susceptibilities were measured at room temperature with a Cahn 2000 instrument, calibrated in the usual way with $Hg[Co(SCN)_4]$. The used magnetic field strength was 6 kG.

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