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Crystal Structure and Spectroscopic Behaviour of Oxoetoxo-*bis*(5,7-dichloro-8-hydroxyquinolinato)vanadium(V)

Ana C. González-Baró[1], **Oscar E. Piro**[2], **Beatriz S. Parajón-Costa**[1], **Enrique J. Baran**[1,*], and **Eduardo E. Castellano**[3,#]

[1] Centro de Química Inorgánica (CEQUINOR), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina
[2] Departmento de Física y Programa PROFIMO, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1900 La Plata, Argentina.
[3] Instituto de Fisica de São Carlos, Universidade de São Paulo 13560 São Carlos (SP), Brazil

Summary. The title compound, a new example of an inorganic ester-like complex, was characterized by spectroscopic and X-ray crystallographic methods. It crystallizes in the triclinic space group $P\bar{1}$($a = 9.413(2)$, $b = 10.595(3)$, $c = 11.783(2)$ Å, $\alpha = 103.59(2)$, $\beta = 101.98(2)$, $\gamma = 99.40(2)°$, $Z = 2$). The structure was solved employing 2902 independent reflections with $I > 2\sigma(I)$ by direct and *Fourier* methods and refined by a full-matrix least-squares fit to $R_1 = 0.049$. Infrared and *Raman* spectra of the solid compound and the electronic absorption spectra of its acetonitrilic and ethanolic solutions were recorded and are briefly discussed.

Keywords. Vanadium(V); Inorganic etoxoester; Crystal structure analysis; Vibrational spectra; Electronic spectra.

Kristallstruktur und spektroskopisches Verhalten von Oxoetoxo*bis*(5.7-dichlor-8-hydroxychinolinato)vanadium(V)

Zusammenfassung. Die Titelverbindung, ein neues Beispiel eines anorganischen esterähnlichen Komplexes, wurde mit spektroskopischen und Röntgen-Einkristall-Methoden charakterisiert. Sie kristallisiert in der triklinen Raumgruppe $P\bar{1}$ $(a = 9.413(2), b = 10.595(3), c = 11.783(2)$ Å, $\alpha = 103.59(2), \beta = 101.98(2), \gamma = 99.40(2)°, Z = 2)$. Die Struktur wurde aus 2902 unabhängigen Reflexen mit $I > 2\sigma(I)$ durch direkte und *Fourier*-Methoden gelöst und durch einen *least-squares fit* zu $R_1 = 0.049$ verfeinert. Die Infrarot- und *Raman*spektren des Festkörpers und die Elektronenabsorptionsspektren seiner Lösungen in Acetonitril und Ethanol wurden aufgenommen und werden kurz besprochen.

[#] Dedicated to Prof. *Achim Müller* on the occasion of his 60th birthday.

Introduction

It is well known that a black, water insoluble complex of stoichiometry Q_2VO(OH) is generated by reaction of vanadium(V) with 8-hydroxyquinoline (QH) [1–3]. *Giacomelli et al.* suggested that this species should be considered as an inorganic analog of a carboxylic acid [4]. According to this proposal, the species of composition Q_2VO(OR), produced by its interaction with alcohols, may be classified as esters. Although many such esters have so far been prepared, most of them are only scarcely characterized [3–9].

In continuation of our studies on vanadium complexes containing halogenated derivatives of 8-hydroxyquinoline as ligands [9, 10], we have prepared esters derived from "acids" containing this type of ligands [9, 11]. Furthermore, in the case of the species derived from 5.7-dichloro-8-hydroxyquinoline, we have solved the crystal structure of the respective ethyl ester.

In this paper, we present the results of this structural study, complemented with some spectroscopic data.

Results and Discussion

Structural analysis

Crystal parameters and details of the applied refinement procedures are given in Table 1, whereas Fig. 1 shows an ORTEP plot [12] of the structure including the atom labelling of the non-hydrogen atoms and their vibrational ellipsoids.

Atomic fractional coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected interatomic bonding distances and angles are compiled in Table 3; Fig. 2 shows a projection of the crystal packing.

The only similar structure which has so far been reported is that of the isopropyl ester of oxohydroxo*bis*(8-hydroxyquinolinato)vanadium(V) [7]. This compound presents an analogous structural arrangement with the VO(O–*i*–Pr) group in *cis* configuration. The O–V–O angle of 101.9° is similar to that found in present study (102.7°). The V–O distances to the oxo and etoxo ligands are slightly shorter in the present case.

The coordination sphere around the central vanadium(V) atom is a distorted octahedron constituted by the oxygen atoms located at 1.590(3) Å (terminal V=O bond) and 1.746(3) Å (etoxo bond), the oxygen atoms of the organic ligand, presenting practically the same bond distances (1.910(3) and 1.924(3) Å), and the two nitrogen atoms of the ligands, whose bonding distances are significantly different. The V–N bond *trans* to the oxo ligand is longer (2.319(3) Å) than that located *trans* with respect to the etoxo ligand (2.203(3) Å). This behaviour is also similar to that found in the previously investigated structure [7] and has been explained as a consequence of a kind of *trans* effect generated by the ester linkage [7].

The C–O and C–N–C distances are somewhat shorter in the present case than in the isopropoxo complex; in general the ring C–C bonds are not very different in both compounds despite the presence of the two chlorine atoms in the present case. The four C–Cl bonds are practically identical.

Table 1. Summary of crystal data, X-ray measurements, and structure refinements

Empirical formula	$C_{20}H_{13}O_4N_2Cl_4V$
Formula weight	538.06
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.413(2)$ Å
	$b = 10.595(3)$ Å
	$c = 11.783(2)$ Å
	$\alpha = 103.59(2)^\circ$
	$\beta = 101.98(2)^\circ$
	$\gamma = 99.40(2)^\circ$
	$V = 1089.2(4)$ Å^3
Z	2
$\rho_{calc}(g \cdot cm^{-3})$	1.641
Absorption coefficient (mm^{-1})	0.977
Radiation, graphite monochr.	$MoK_\alpha(\lambda = 0.71069$ Å$)$
Θ-range for data collection	1.84 to 27.97°
F (000)	540
Index ranges	$-12 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 13, 0 \leqslant l \leqslant 15$
Reflections collected	5552
Independent reflections	4421 [R(int) = 0.055]
Observed reflections ($I > 2\sigma(I)$)	2902
Data/restraints/parameters	4421/0/284
Goodnes-of-fit on F^2	1.048
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0492, wR_2 = 0.1177$
R indices (all data)	$R_1 = 0.0882, wR_2 = 0.1421$

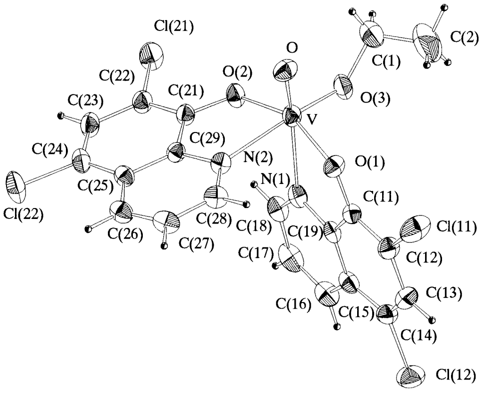

Fig. 1. ORTEP drawing of $C_{20}H_{13}O_4N_2Cl_4V$ showing the non-H labelling and the vibrational ellipsoids at 30% probability

Vibrational spectra

To further characterize this new inorganic ester, we have also recorded its infrared and *Raman* spectra. Both spectra are very complex. The proposed assignments, based on data or related compounds [9, 10, 13–16] and on some general literature information [17] are presented in Table 4 and shall be briefly discussed.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $C_{20}H_{13}O_4N_2Cl_4V$; U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
V	1958(1)	89(1)	8506(1)	44(1)
O	2146(3)	126(3)	9887(3)	55(1)
Cl(11)	6658(2)	3353(1)	9435(1)	81(1)
Cl(12)	5735(2)	2564(1)	4669(1)	74(1)
O(1)	3865(3)	1219(3)	8763(2)	46(1)
N(1)	2238(4)	−14(3)	6580(3)	44(1)
C(11)	4325(4)	1543(3)	7862(3)	41(1)
C(12)	5581(5)	2488(4)	8003(4)	50(1)
C(13)	6006(5)	2796(4)	7015(4)	56(1)
C(14)	5177(5)	2146(4)	5874(4)	51(1)
C(15)	3890(5)	1157(4)	5648(3)	47(1)
C(16)	2928(5)	439(5)	4517(4)	57(1)
C(17)	1693(6)	−485(5)	4454(4)	64(1)
C(18)	1382(5)	−671(4)	5504(4)	51(1)
C(19)	3482(4)	877(3)	6658(3)	40(1)
Cl(21)	−2309(1)	−3724(1)	6491(1)	72(1)
Cl(22)	1831(2)	−6653(1)	6459(1)	80(1)
O(2)	344(3)	−1434(2)	7686(3)	50(1)
N(2)	3108(3)	−1564(3)	8201(3)	42(1)
C(21)	611(4)	−2641(3)	7389(3)	41(1)
C(22)	−457(4)	−3787(4)	6831(4)	49(1)
C(23)	−69(5)	−5026(4)	6535(4)	53(1)
C(24)	1385(5)	−5115(4)	6799(4)	50(1)
C(25)	2544(4)	−3973(4)	7273(3)	43(1)
C(26)	4081(5)	−3914(4)	7696(4)	53(1)
C(27)	5056(5)	−2735(5)	8249(4)	54(1)
C(28)	4532(4)	−1562(4)	8490(3)	49(1)
C(29)	2115(4)	−2747(3)	7650(3)	39(1)
O(3)	813(3)	1205(3)	8317(3)	56(1)
C(1)	182(8)	1954(5)	9198(7)	101(2)
C(2)	918(11)	3338(7)	9591(8)	150(4)
H(13)	6859	3448	7138	
H(16)	3129	591	3814	
H(17)	1068	−984	3708	
H(18)	528	−1289	5447	
H(23)	−812	−5794	6154	
H(26)	4330	−4692	7527	
H(27)	6072	−2702	8470	
H(28)	5216	−756	8867	
H(1A)	−870	1864	8848	
H(1B)	276	1595	9889	
H(2A)	537	3798	10244	
H(2B)	741	3716	8924	
H(2C)	1970	3425	9887	

Table 3. Selected interatomic distances (Å) and bond angles (°) for $C_{20}H_{13}O_4N_2Cl_4V$

Bond distances			
V–O	1.590(3)	V–O(3)	1.746(3)
V–O(1)	1.910(3)	V–O(2)	1.924(3)
V–N(2)	2.203(3)	V–N(1)	2.319(3)
C(12)–Cl(11)	1.724(4)	C(14)–Cl(12)	1.736(4)
C(11)–O(1)	1.321(4)	C(18)–N(1)	1.311(5)
C(19)–N(1)	1.350(5)	C(11)–C(12)	1.371(5)
C(11)–C(19)	1.421(5)	C(12)–C(13)	1.398(6)
C(13)–C(14)	1.358(6)	C(14)–C(15)	1.399(6)
C(15)–C(19)	1.403(6)	C(15)–C(16)	1.405(6)
C(16)–C(17)	1.368(7)	C(17)–C(18)	1.379(7)
C(22)–Cl(21)	1.721(4)	C(24)–Cl(22)	1.726(4)
C(21)–O(2)	1.323(4)	C(28)–N(2)	1.312(5)
C(29)–N(2)	1.360(5)	C(21)–C(22)	1.367(5)
C(21)–C(29)	1.414(5)	C(22)–C(23)	1.405(5)
C(23)–C(24)	1.363(6)	C(24)–C(25)	1.411(6)
C(25)–C(29)	1.409(5)	C(25)–C(26)	1.404(6)
C(26)–C(27)	1.350(6)	C(27)–C(28)	1.400(6)
C(1)–O(3)	1.444(6)	C(1)–C(2)	1.435(9)
Bond angles			
O–V–O(3)	102.7(2)	O–V–O(1)	95.03(13)
O(3)–V–O(1)	100.22(13)	O–V–O(2)	102.72(14)
O(3)–V–O(2)	92.55(12)	O(1)–V–O(2)	155.28(12)
O–V–N(2)	91.62(14)	O(3)–V–N(2)	163.91(13)
O(1)–V–N(2)	85.48(12)	O(2)–V–N(2)	77.05(11)
O–V–N(1)	167.00(14)	O(3)–V–N(1)	87.86(13)
O(1)–V–N(1)	75.48(11)	O(2)–V–N(1)	84.03(12)
N(2)–V–N(1)	78.97(11)	C(11)–O(1)–V	121.6(2)
C(18)–N(1)–C(19)	118.4(4)	C(18)–N(1)–V	132.2(3)
C(19)–N(1)–V	109.1(2)	O(1)–C(11)–C(12)	124.4(3)
O(1)–C(11)–C(19)	118.8(3)	C(12)–C(11)–C(19)	116.8(3)
C(11)–C(12)–C(13)	121.8(4)	C(11)–C(12)–Cl(11)	119.7(3)
C(14)–C(13)–C(12)	120.1(4)	C(13)–C(14)–Cl(12)	118.8(4)
C(19)–C(15)–C(14)	116.9(4)	C(14)–C(15)–C(16)	127.0(4)
C(17)–C(16)–C(15)	119.6(4)	C(16)–C(17)–C(18)	119.6(4)
N(1)–C(18)–C(17)	122.9(4)	N(1)–C(19)–C(15)	123.4(3)
C(1)–O(3)–V	128.2(4)	C(2)–C(1)–O(3)	111.2(6)

The most important and characteristic vibrations of the organic ligand are not very different from those recently reported for the corresponding oxovanadium(IV) complex $VO(QCl_2)_2$ [10]. The stretching of the terminal V=O bond lies in the same range as that found in the "acid" derived from 8-hydroxyquinoleine (VOQ_2OH) and some of its esters [9, 14, 15]. Besides, it is practically identical to that observed in the parent acid $VO(QCl_2)_2OH$ [15]. The V–O stretching of the ester linkage can

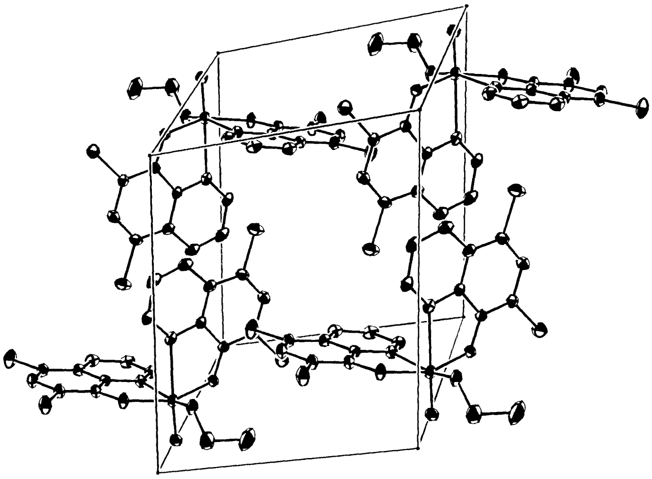

Fig. 2. ORTEP projection of $C_{20}H_{13}O_4N_2Cl_4V$ crystal packing along *a*; the *b* axis is horizontal

only be observed as a very weak *Raman* line at $744\,\mathrm{cm}^{-1}$ and as a shoulder ($745\,\mathrm{cm}^{-1}$) in the IR spectrum. The V–O and V–N metal-to-ligand vibrations are seen as very weak bands in the ranges expected for these modes [9, 10, 18, 19].

Some characteristic bands expected for the ethyl ester linkage [17] appear overlapped by ligand bands. Only two of them (not included in Table 4) could be identified in the IR spectrum: a weak band at $2973\,\mathrm{cm}^{-1}$, assignable to the CH_3 asymmetric stretch, and a shoulder at $1374\,\mathrm{cm}^{-1}$ related to the symmetric deformation of the same group.

Electronic spectra

The electronic absorption spectra of the ester in solutions of acetonitrile and ethanol are shown in Fig. 3. Both solutions are brown-reddish when freshly prepared, but their colour fades with time changing to green, probably caused by atmospheric humidity. The ethanolic solution is relatively more stable.

The two absorption bands at higher energies (210 and 258 nm in acetonitrile and 214 and 246 nm in ethanol) are assigned to intraligand transitions, probably superimposed by the O → V charge transfer involving the double bonded oxo group [13, 16, 20]. The other two bands are related to ligand-to-metal charge transfer transitions involving the organic ligand. The higher energy band (326 nm in acetonitrile and 324 nm in ethanol) essentially involves the oxygen atom, whereas the other one (374 nm in acetonitrile and 394 nm in ethanol) may be related to the nitrogen atom [13].

The higher intensity of the 324 nm band in ethanol as compared to the respective transition in acetonitrile can be explained by the fact that in ethanol the free ligand presents also a band in this region.

Table 4. Assignment of relevant IR and *Raman* bands (cm^{-1})

Infrared	*Raman*	Assignment
	3070 vw	
2929 w	2914 vw	ν(CH)
2859 w		
1595 w	1594 m	ν(C=N)
1579 sh / 1567 m	1580 s / 1568 m	ν(C=C)
1488 s	1489 s	
1456 vs	1456 m	
1396 w	1399 m	ring stretchings
1365 vs	1377 s	
1347 sh		
1236 m	1238 m	
1225 sh		out of plane CH
1200 w	1198 vw	deformations
1141 m		
1109 m	1113 w	ν(CO)
1084 m		
1029 m	1029 m	
973 m	973 w	in plane CH
907 m	908 m	deformations
894 m		
874 w / 866 w		
816 sh / 810 w		
962 s	963 m	ν(V=O)
745 sh	744 w	ν(V–O–(Et))
665 s	662 m	
658 sh	632 m	out of plane
631 w / 619 sh		ring deformation
593 m	598 w	in plane ring deformation
514 m / 478 w	513 m / 480 w	ν(V–O)
	418 w	δ(OVO)
333 w	375 w	ν(V–N)

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

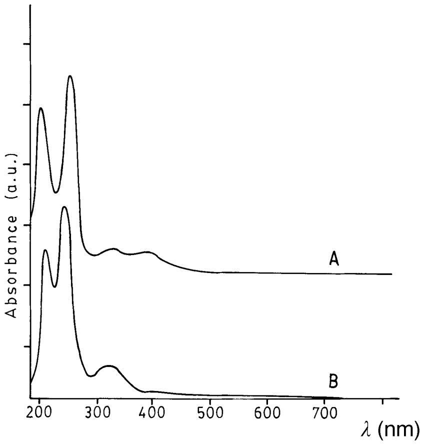

Fig. 3. Electronic absorption spectra of the ester in acetonitrile (**A**) and ethanol (**B**)

Experimental

Synthesis

$(QCl_2)_2VO(OH)$ ($HQCl_2 = $ 5,7-dichloro-8-hydroxyquinoline) was obtained by reaction of NH_4VO_3 and the ligand in acetic acid media employing standard techniques [1–3]. For the synthesis of the ethyl ester, 0.26 g of $(QCl_2)_2VO(OH)$ were refluxed with 40 ml of absolute ethanol for 2 hours. The generated wine-red solution was filtered and cooled to room temperature. After 24 h, crystal formation was observed. A number of well formed single crystals, suitable for a crystallographic study, were separated manually from the crystalline mass. The crystals were thermally stable up to *ca.* 220°C.

Crystal structure determination

Single crystal data collection was performed at 293(2) K on an Enraf-Nonius CAD-4 diffractometer using a dark red crystal plate of 0.05 mm in thickness parallel to $(10\bar{1})$. The plate was bounded by three pairs of opposite crystal faces: $(0, \pm1, 0), (\pm1, \pm2, \pm1)$, and $(\pm1, 0, \pm1)$, separated by 0.28, 0.21, and 0.20 mm, respectively. Unit cell parameters were refined by least-squares of $[\sin \Theta/\lambda]^2$, using 25 reflections in the $22.82 < 2\Theta < 39.28°$ range. Intensities were corrected for *Lorentz* and polarization effects as well as for absorption [21] (maximum and minimum transmission factors were 0.958 and 0.758). The crystal structure was solved by direct and *Fourier* methods and refined by full-matrix least squares techniques (programs used were SDP [22], SHELX-76 [23], SHELX-86 [24], and SHELX-93 [25]).

All hydrogen atoms of the ligands and one of the alcohol methyl group were located in a difference *Fourier* map. However, they were all positioned on a stereochemical basis and included in the refinement riding on the atom to which they are bonded (C-H distances of 0.93, 0.97, and 0.96 Å for CH, CH_2, and CH_3 groups, respectively) with three independent isotropic thermal parameters, one common to the quinoline hydrogens (which converged to $U = 0.053(4)$ Å^2), the second one common to the alcohol CH_2 hydrogens ($U = 0.20(3)$ Å^2), and a third one common to the methyl hydrogens ($U = 0.36(5)$ Å^2). During the refinement, the CH_3 hydrogen atoms were allowed to rotate as a rigid group around the corresponding alcohol C–C bonds as to maximize the sum of the electron density at the three calculated hydrogen positions. The somewhat large *U*-values for the alcohol hydrogens are consistent with the observed trend of an increase of thermal parameters of the carbon atoms to which they are attached towards the free end of the group, suggesting relatively large vibrational movements of the alcohol moiety.

Tables containing complete information on bond distances, angles, and anisotropic thermal parameters for the non-H atoms are available from the authors up on request and have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), from where they can be obtained referring to the deposition number CSD-59442, the names of the authors, and the citation of the paper.

Spectroscopic measurements

Infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer (KBr pellets). *Raman* spectra were obtained with an FRA 106 Raman accessory of a Bruker FTIR IF 66 spectrometer. The 1064 nm line of a Nd:YAG laser was used for excitation. Electronic absorption spectra were measured on a Hewlett-Packard 8453 diode array spectrophotometer using 1 cm quartz cells.

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