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Synthesis and characterization of 8-quinolinolato vanadium(IV) complexes

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ABSTRACT

Reaction of vanadium(III) chloride with 8-quinolinol (Hqn) gave a mononuclear vanadium(IV) complex, $[VOCl_2(H_2O)_2]$ **1**) · 2H₂qn · 2Cl · CH₃CN, and three dinuclear vanadium(IV) complexes: $[V_2O_2Cl_2(qn)_2(H_2O)_2]$ (**2**) · Hqn, $[V_2O_2Cl_2(qn)_2(C_3H_7OH)_2]$ (**3**), and $[V_2O_2Cl_2(qn)_2(C_4H_9OH)_2]$ (**4**). Reaction of vanadium(III) chloride with 5-chloro-8-quinolinol (HClqn) gave four dinuclear vanadium(IV) complexes: $[V_2O_2Cl_2(Clqn)_2(H_2O)_2]$ (**5**) · 2HClqn, $[V_2O_2Cl_2(Clqn)_2(C_3H_7OH)_2]$ (**6**), $[V_2O_2Cl_2(Clqn)_2(C_6H_5CH_2OH)_2]$ (**7**), and $[V_2O_2Cl_2(Clqn)_2(C_4H_9OH)_2]$ (**8**) · 2C₄H₉OH. Reaction of vanadium(III) chloride with 5-fluoro-8-quinolinol (HFqn) gave two dinuclear vanadium(IV) complexes: $[V_2O_2Cl_2(Fqn)_2(H_2O)_2]$ (**9**) · HFqn · 2H₂O and $V_2O_2Cl_2(Cqn)_2(C_3H_7OH)_2]$ (**10**). X-ray structures of **1** · 2H₂qn · 2Cl · CH₃CN, **3**, **4**, **6**, **7**, **8** · 2 *t*-BuOH, and **10** have been determined. As to the mononuclear species **1** · 2H₂qn · 2Cl · CH₃CN, **3**, **4**, **6**, **7**, **8** · 2 *t*-BuOH, and **10** to vanadium does not occur, but protonation to Hqn occurs to give H₂qn⁺, which links **1**'s through hydrogen bonding, while each of the dinuclear species has a terminal and a bridging qn (or Clqn, Fqn) ligand, giving rise to a (V-O)₂ ring. Magnetic measurements of **3**, **4**, **6**, **7**, and **10** in solid form show very weak antiferromagnetic behavior, and the effective magnetic moments are close to spin only value (2.44) of d¹-d¹ system, while ESR of **3** in THF shows dissociation to monomeric species. Change from mononuclear, **1**, to dinuclear, **2**, species was followed by the change of electronic spectrum.

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1. Introduction

8-Quinolinol (Hqn = C_9H_7NO) and its derivatives have been widely used as analytical reagents [1]; however, research on vanadium complexes with 8-quinolinol ligands or its derivatives is almost all on V(V). Guastini and coworkers reported the inter-conversion scheme of 8-quinolinolato vanadium(V) complexes (Scheme 1) [2], where $[VO(OH)(qn)_2]$ is the starting material, whose blue color in chloroform turns red due to the formation of $[VO(OR)(qn)_2]$ [3–5] with coordinated OR⁻ by the addition of ethanol (ROH). Dimerization of [VO(OR)(qn)₂] gives oxo-bridged dinuclear vanadium(V) species [6]. On the other hand, reports on 8-quinolinolato-V(III) or -V(IV) complexes are very limited (Chart 1), and $[V^{III}(qn)_3]$ (Chart 1b) [7] and $[V_2^{IV}O_2(qn)_4]$ [8] are the only complexes so far reported, with the structure of the latter being determined by elemental analysis and IR spectroscopy. As to V(IV) complexes with derivatives of 8-quinolinolate ligands, [V^{IV}O $(Meqn)_2$ (Chart 1d) [9] and $[V^{IV}O(L)_2]$ [10] (Chart 1e) were reported.

We report here the syntheses, X-ray structures, and characterization of dinuclear vanadium(IV) complexes with 8-quinolinol ligands obtained by the reaction of vanadium(III) chloride with 8-quinolinol via a mononuclear vanadium(IV) complex [VOCl₂

* Corresponding author. E-mail address: shiba@chem.ous.ac.jp (T. Shibahara). $(H_2O)_2$]. As for V(IV) complexes containing other ligands than 8quinolinol, several magnetic [11–14] and ESR [15] properties have been reported together with their X-ray structures. In addition, a simpler complex [VOCl₂(H₂O)₂] containing diethylether [16] or crown ether [17,18] has been reported.

2. Experimental

2.1. Materials and reagents

All the commercially available chemicals were used as received: VCl₃, Aldrich; 8-hydroxyquinoline (Hqn), nacalai Tesque; acetonitrile, nacalai Tesque; benzyl alcohol, nacalai Tesque; iso-propanol, nacalai Tesque; *t*-butanol, nacalai Tesque; 5-fluoro-8-hydroxyquinoline (HFqn), Tokyo Kasei; 5-chloro-8-hydroxyquinoline (HClqn), Merck.

2.2. Syntheses

[VOCl₂(H₂O)₂] · 2H₂qn · 2Cl · CH₃CN (1 · 2H₂qn · 2Cl · CH₃CN). Method 1. Dissolving VCl₃ (20.1 mg, 1.28×10^{-4} mol) in a mixture of acetonitrile (10 mL) and water (0.05 mL) by heating for 15 min at ca. 60 °C gave a pale dark-green solution, which was cooled to room temperature. Addition of Hqn (37.2 mg, 2.56×10^{-4} mol, Hqn/V = 2) to the solution resulted in a series of



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Scheme 1. 8-Quinolinolate vanadium(V) complexes.



Chart 1.

color changes: red \rightarrow orange \rightarrow green \rightarrow pale-green in ca. one minute. Standing the resultant solution for half an hour gave very paleblue, plate-like crystals of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$. As the crystals are very hygroscopic and become liquefied in a few seconds, they

Table 1

Crystallographic data.

were taken out of the mother liquid under a dinitrogen atmosphere: yield, 35.2 mg (48%).

Method 2. A similar procedure to that described in method 1 gave a pale-green solution: the only difference was the use of conc. HCl (0.05 mL) instead of water (0.05 mL). Standing the resultant solution for one day gave very pale-blue, plate-like crystals of $1 \cdot 2H_2$ qn $\cdot 2Cl \cdot CH_3$ CN: yield 37.6 mg (51%).

 $[V_2O_2Cl_2(qn)_2(H_2O)_2] \cdot Hqn (2 \cdot Hqn)$. A similar procedure to that described in method 1 for the synthesis of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$ were followed: only the amount of water was increased from 0.05 mL to 0.15 mL. From the resultant pale-green solution, pale-green, thin-layered crystals of $2 \cdot$ Hqn were deposited in an hour: yield, 19.0 mg (36%). *Anal.* Calc. for $C_{27}H_{23}Cl_2N_3O_7V_2$: C, 48.09; H, 3.44; N, 6.23. Found: C, 48.24; H, 3.64; N, 6.22%.

 $[V_2O_2Cl_2(C_9H_6NO)_2(C_3H_7OH)_2]$ (3). Similar procedures to those for the synthesis of 2 Hqn were followed: except for the fact that under dinitrogen atmosphere, iso-propanol (10 mL) was added immediately after the addition of Hqn (Hqn/V = 2). Palegreen, thin-layered crystals of 3 were obtained by slow air oxidation through keeping the solution in a loosely sealed vessel for several days: yeild, 18.3 mg (47%). Anal. Calc. for C₂₄H₂₈Cl₂N₂O₆V₂: C, 47.00; H, 4.60; N, 4.57. Found: C, 46.98; H, 4.34; N, 4.52%.

 $[V_2O_2Cl_2(qn)_2(C_4H_9OH)_2]$ (4). Similar procedures to those for the synthesis of **3** were followed: *t*-butanol was used instead of iso-propanol: yield: 14.98 mg (37%). *Anal.* Calc. for $C_{26}H_{32}Cl_2N_2O_6V_2$: C, 48.69; H, 5.03; N, 4.37. Found: C, 48.61; H, 4.74; N, 4.33%.

 $[V_2O_2Cl_2(C_9H_5CINO)_2(H_2O)_2] \cdot (C_9H_6CINO)_2 (5 \cdot 2HClqn)$. Similar procedures to those for the synthesis of **2** · Hqn were followed: HClqn was used instead of Hqn: yield: 34.39 mg (56%). *Anal.* Calc. for C₃₆H₂₆Cl₆N₄O₈V₂: C, 45.17; H, 2.74; N, 5.85. Found: C, 44.97; H, 2.89; N, 5.86%.

 $[V_2O_2Cl_2(C_9H_5ClNO)_2(C_3H_7OH)_2]$ (6). Similar procedures to those for the synthesis of **3** were followed: HClqn was used instead of Hqn: yield: 20.38 mg (47%). *Anal.* Calc. for $C_{24}H_{26}Cl_4N_2O_6V_2$: C, 42.26; H, 3.84; N, 4.11. Found: C, 42.17; H, 3.74; N, 4.11%.

 $[V_2O_2Cl_2(C_9H_5ClNO)_2(C_6H_5CH_2OH)_2]$ (7). Similar procedures to those for the synthesis of **3** were followed: HClqn and benzyl alcohol were used instead of Hqn and iso-propanol, respectively: yield: 26.85 mg (54%). *Anal.* Calc. for C₃₂H₂₆Cl₄N₂O₆V₂: C, 49.39; H, 3.37; N, 3.60%. Found: C, 49.52; H, 3.36; N, 3.56(3.60).

	$\bm{1}\cdot 2H_2qn\cdot 2Cl\cdot CH_3CN$	3	4	6	7	8 · 2 <i>t</i> -BuOH	10
Formula	C ₂₀ H ₂₃ Cl ₄ N ₃ O ₅ V	$C_{24}H_{26}Cl_2N_2O_6V_2$	$C_{26}H_{32}Cl_2N_2O_6V_2$	$C_{24}H_{24}Cl_4N_2O_6V_2$	$C_{32}H_{26}Cl_4N_2O_6V_2$	$C_{34}H_{50}Cl_4N_2O_8V_2$	C24H20Cl2F2N2O6V2
F.W.	578.17	611.27	641.34	680.16	778.26	858.47	643.22
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	trigonal	monoclinic
Space Group	$P2_1/m$ (#11)	$P2_1/n$ (#14)	C2/c (#15)	$P2_1/c$ (#14)	C2/c (#15)	R3 (#148)	$P2_1/n$ (#14)
a (Å)	7.599(3)	9.978(15)	16.609(8)	9.004(5)	28.688(10)	31.730(17)	8.407(6)
b (Å)	20.875(8)	16.23(2)	10.412(5)	15.873(9)	7.572(2)	31.730(17)	16.019(11)
c (Å)	7.719(3)	16.51(2)	16.418(8)	20.049(11)	18.157(5)	10.442(4)	19.933(14)
β (°)	91.235(4)	105.06(3)	91.090(5)	98.478(9)	127.964(4)	90.000	98.691(12)
V (Å ³)	1224.2(8)	2582(6)	2839(2)	2834(3)	3109.8(16)	9105(8)	2653(3)
Ζ	2	4	4	4	4	9	4
D _{calc} (g/cm ³)	1.568	1.572	1.501	1.594	1.662	1.409	1.610
μ (Mo K $lpha$) (cm $^{-1}$)	8.777	9.725	8.884	10.771	9.935	7.736	9.613
Reflections collected	13998	24750	15863	27710	17243	35245	29478
Unique reflections	3566	5821	4129	6333	4496	5865	7708
$[R_{(int)}]$	0.098	0.066	0.046	0.099	0.069	0.039	0.031
Goodness-of-fit (GOF)	1.005	1.064	0.996	0.994	0.990	1.069	1.060
$R_1 (I > 2.00\sigma(I))$	0.0428	0.1048	0.0311	0.0952	0.0346	0.0436	0.0409
R; wR ₂	0.0495;0.1016	0.1429; 0.2463	0.0341; 0.0885	0.1442; 0.2538	0.0450; 0.0881	0.0512; 0.0954	0.0477; 0.1098

 $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$

 $wR2 = [\sum (w(F_0^2 - F_c^2)^2) / \sum w(F_0^2)^2]^{1/2}.$



Chart 2. 8-Quinolinolato vanadium(IV) complexes.

 $[V_2O_2Cl_2(C_9H_5CINO)_2(C_4H_9OH)_2] \cdot 2C_4H_9OH (8 \cdot 2 t-BuOH)$ Similar procedures to those for the synthesis of **3** were followed: HClqn and benzyl alcohol were used instead of Hqn and *t*-butanol, respectively: yield: 23.51 mg (47%). *Anal.* Calc. for $C_{34}H_{50}Cl_4N_2O_8V_2$: C, 47.57; H, 5.87; N, 3.26. Found: C, 47.41; H, 5.80; N, 3.39%.

 $[V_2O_2Cl_2(C_9H_5FNO)_2(H_2O)_2] \cdot C_9H_6FNO \cdot 2H_2O(9 \cdot HFqn \cdot 2H_2O).$ Similar procedures to those for the synthesis of **3** were followed: HFqn was used instead of Hqn: yield: 33.60 mg (69%). *Anal.* Calc. for $C_{27}H_{24}Cl_2F_3N_3O_9V_2$: C, 42.43; H, 3.17; N, 5.50. Found: C, 42.31; H, 2.46; N, 5.35%.

 $[V_2O_2Cl_2(C_9H_5FNO)_2(C_3H_7OH)_2]$ (10). Similar procedures to those for the synthesis of **3** were followed: HFqn was used instead of Hqn: yield: 15.88 mg (38%). *Anal.* Calc. for $C_{24}H_{26}Cl_2F_2N_2O_6V_2$: C, 44.40; H, 4.04; N, 4.31. Found: C, 44.48; H, 3.77; N, 4.13%.

2.3. X-ray crystallography and solution of structures

Structural determinations of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, **3**, **4**, **6**, **7**, **8** $\cdot 2t$ -BuOH, and **10**. Data were collected on a Rigaku/MSC Mercury CCD diffractometer. Suitable crystals were attached to the tip of a glass capillary using silicone grease and transferred to the goniostat, where they were cooled for data collection, using graphite monochromated Mo K α radiation. The structures were solved using a combination of Patterson method (DIRDIF99 PATTY) [19], and all the remaining non-hydrogen atoms were located from difference Fourier maps [20]. The hydrogen atoms of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, **4**, **7**, **8**, and **10** were located from difference Fourier maps, and their positions were fixed. Those of **3** and **6** were located at calculated positions. All of the isotropic thermal parameters of hydrogen atoms were constrained to $1.2U_{eq}$ to which they were attached. The program package Crystal Structure [21] was used, SHELXL being used for the refinement. Crystallographic data are summarized in Table 1.

2.4. Measurements

Electronic spectra were measured using a Hitachi U-2000 double-beam spectrophotometer. X-ray diffraction data were collected with a Rigaku CCD diffractometer and analyzed using the teXsan System. Elemental analyses were determined with a Perkin–Elmer 240 NCH analyzer. Variable-temperature magnetic susceptibility measurements of **3**, **4**, **6**, **7**, and **10** were carried out on powdered samples on an MPMS XL5 SQUID magnetometer in the range of 1.9–300 K in a 1 T applied field. The diamagnetic corrections were carried out using Pascal's constant [22]. ESR spectrum was obtained for a solution of **3** in THF with a JEOL JES-FE2XG spectrometer.

3. Results and discussion

Designations of compounds	
$[VOCl_2(H_2O)_2] \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$	$1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$
$[V_2O_2Cl_2(qn)_2(H_2O)_2] \cdot Hqn$	2 · Hqn
$[V_2O_2Cl_2(qn)_2(C_3H_7OH)_2]$	3
$[V_2O_2Cl_2(qn)_2(C_4H_9OH)_2]$	4
$[V_2O_2Cl_2(Clqn)_2(H_2O)_2] \cdot 2HClqn$	5 · 2HClqn
$[V_2O_2Cl_2(Clqn)_2(C_3H_7OH)_2]$	6
$[V_2O_2Cl_2(Clqn)_2(C_7H_7OH)_2]$	7
$[V_2O_2Cl_2(Clqn)_2(C_4H_9OH)_2] \cdot 2C_4H_9OH$	8 · 2 <i>t</i> -BuOH
$[V_2O_2Cl_2(Fqn)_2(H_2O)_2] \cdot H5Fqn \cdot 2H_2O$	$9 \cdot \mathrm{HFqn} \cdot \mathrm{2H_2O}$
$[V_2O_2Cl_2(Fqn)_2(C_3H_7OH)_2]$	10

3.1. Syntheses and electronic spectra

Reaction of vanadium(III) chloride with 8-quinolinol (Hqn), 5chloro-8-quinolinol (HClqn), or 5-fluoro-8-quinolinol (HFqn) gave one mononuclear vanadium(IV) complex and eight dinuclear vanadium(IV) complexes listed below, and X-ray structures of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, **3**, **4**, **6**, **7**, **8** $\cdot 2$ *t*-BuOH, and **10** have successfully been determined (Chart 2). No X-ray structures of monomeric and dimeric V(IV) complexes with qn ligands have been reported so far.



Fig. 1. Electronic spectral change in the course of the reaction from $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$ to $2 \cdot Hqn$ in acetonitrile (every 5 min).

The reaction of VCl₃ with Hqn in acetonitrile–water or acetonitrile–concentrated HCl gives mononuclear V(IV) species **1**, which turns to dinuclear V(IV) species **2**, when coordination of qn⁻ occurs. Smaller amounts of water and higher acidity retard the reaction rate from **1** to **2**. Probably deprotonation of H₂qn⁺ is one of the important processes. **1** · 2H₂qn · 2Cl · CH₃CN is very hygroscopic and becomes liquefied within a few seconds when the crystals are taken out of the mother liquid in the air, and therefore the composition is according to that determined by X-ray crystallography. Electronic spectral change of **1** to **2** was observed by dissolving **1** · 2H₂qn · 2Cl · CH₃CN in acetonitrile under dinitrogen atmosphere (Fig. 1). Further oxidation of **2** proceeds to give V(V) species in the air (Fig. 2), but the rate is low and any air-free technique is required to obtain crystals of **2**.

Addition of propanol or butanol in the synthesis of $2 \cdot Hqn$ results in the formation of alcohol-coordinated species $[V_2O_2Cl_2(qn)_2(ROH)_2]$ ($R = C_3H_7$, **3**; C_4H_9 , **4**), respectively, which are air-oxidized to give V(V) species much more easily than the water-coordinated complex **2**, and a mild air-free condition is required for the isolation of **3** and **4**; leaving the solution containing the crystals of iso-propanol-coordinated species **3** for a few days longer causes resolution of the deposited crystals and change of color of the solution from pale-green to dark red. This indicates the formation of V(V) complex [3–5]. The use of HClqn (**5**, **6**, **7**, and **8**) or HFqn (**9** and **10**) instead of Hqn gave respective complexes.

Electronic spectral data of **1–10** are shown in Table 2. Electronic spectral change of **1** to **2** was observed by means of dissolving $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$ in acetonitrile under dinitrogen atmosphere (Fig. 1); coordination of 8-quinolinol (Hqn) to **1** gives **2**, which accompanies the peak shift from 720 to 670 nm. Further electronic spectral change indicates slow air oxidation of **2** · Hqn to give V(V) species in acetonitrile (Fig. 2).



Fig. 2. Electronic spectral change in the course of the air oxidation of $2 \cdot$ Hqn in acetonitrile (every 30 min).

Table 2

Electronic spectral data of 1-10 in acetonitrile.

Compound	$\lambda_{\text{max, nm}} \left(\epsilon / M^{-1} \text{ cm}^{-1} \right)$
$1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$	355 (6220), 720 (40.4)
2	372 (5560), 670 (108)
3	375 (4570), 672 (103)
4	393 (5960), 675 (113)
6	375 (4590), 673 (99.3)
7	390 (5660), 671 (97.5)
8 · 2C ₄ H ₉ OH	401 (6210), 679 (120)
9	374 (4550), 670 (105)
10	380 (5490), 672 (98.0)

3.2. X-ray structures

ORTEP drawings of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, **3**, **4**, **6**, **7**, **8**, and **10** are shown in Fig. 3. Atomic distances are listed in Tables 3 and 4, respectively. Fig. 3a. $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$ shows that a crystallographic mirror plane passes through V1, O1, O2, O3, C21, C22, N21, and H221. A feature of this compound is that coordination of Hqn to vanadium does not occur; however, protonation to Hqn occurs to give H_2qn^+ , which is linked to [VOCl₂-(H₂O)] through hydrogen bonding: H10···Cl2, 2.32 Å; Cl2···H2, 2.15 Å.

X-ray structures of five compounds containing the mononuclear vanadium complex, [VOCl₂(H₂O)] (1), have been reported so far: $1 \cdot 2Et_2O$ [16], $1 \cdot 15$ -crown-5 [17], $1 \cdot benzo-15$ -crown-5 [17], $1 \cdot 18$ -crown-6 [18], and $1 \cdot 2C_{10}H_{10}N_3 \cdot Cl_2$ ($C_{10}H_{10}N_3 = bis\{2-(2-pyridylamino)pyridinium\}$) [23], where diethyl ethers (in the former four complexes) connect 1's through hydrogen bonding, which cause interaction between the complexes. The dimensions of 1 in $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$ are not so different from those of the reported complexes (see Table 4).

Complexes **3**, **4**, **6**, **7**, **8**, and **10** are dimeric species having four membered anti-coplanar $(V-O)_2$ rings. Possible structures of $[VO(\mu-OR)_2VO]^{2+}$ are shown in (Chart 3). Crystallographic (**4**, **7**, and **8**) or pseudo crystallographic (**3**, **6**, and **10**) centers of symmetry reside on the centers of the rings. The V–O distances trans to the terminal oxo ligands are substantially longer than those cis to the terminal oxo ligands (Table 3) due to V=O trans effect. The V–V distances will be discussed in the magnetic properties section below.

3.3. Magnetic properties

The magnetic data of **3**, **4**, **6**, **7**, and **10** were treated by applying the Bleaney–Bowers equation [24] (Eq. (1)), calculated for two S = 1/2 centers under a 2JS1 × S2 spin Hamiltonian, using a non-linear least-squares fitting routine (*N* α , 0.0001).

$$\chi_{\rm M} = \frac{2Ng^2\beta^2}{kT} \left(\frac{1}{3+x^2}\right) + N\alpha, \quad \text{where } x = \exp(-J/kT) \tag{1}$$

The results are summarized in Table 5. The compounds in solid state are experiencing a very weak antiferromagnetic interaction between the metal centers, and the effective magnetic moments are close to spin only value (2.44) of the d^1 - d^1 system. Fig. 4 shows temperature dependence of magnetic susceptibility of **3**. ESR spectrum of **3** at 270 K in THF and its simulation (Fig. 5) indicate that the dimeric species **3** dissociates to give monomeric species; the g value (2.03) obtained in the solution differs distinctly from that obtained in solid state (Table 5).

Much discussion has focused on the magnetic properties of dinuclear oxo-vanadium complexes, and it is suggested that metal-metal interactions of complexes with syn-orthogonal, syncoplanar, and twist structures are strong, while those of complexes with anti-coplanar ones are weak [11,12,13]. The complexes **3**, **4**, **6**, **7**, and **10** are of anti-coplanar structure, and the above discussion is well applied.

4. Conclusion

Reaction of vanadium(III) chloride with 8-quinolinol (Hqn) gave a mononuclear vanadium(IV) complex, $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, and three dinuclear vanadium(IV) complexes: $2 \cdot Hqn$, 3, and 4. Reaction of vanadium(III) chloride with 5-chloro-8-quinolinol (HClqn) gave four dinuclear vanadium(IV) complexes: $5 \cdot 2HClqn$, 6, 7, and $8 \cdot 2$ *t*-BuOH. Reaction of vanadium(III) chloride with 5-fluoro-8-quinolinol (HFqn) gave two dinuclear vanadium(IV) complexes: $9 \cdot HFqn \cdot 2H_2O$ and 10. X-ray structures of $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, **3**, **4**, **6**, **7**, **8** $\cdot 2$ *t*-BuOH, and **10** have been determined. All the dinuclear complexes reported here have $(V-O)_2$ rings.

Magnetic measurements of **3**, **4**, **6**, **7**, and **10** in solid state show very weak antiferromagnetic behavior, and the effective magnetic moments are close to spin only value (2.44) of the d^1-d^1 system, while ESR of **3** in THF shows dissociation to monomeric species.



g) 10

Fig. 3. ORTEP drawings of 1 · 2H₂qn · 2Cl · CH₃CN, 3, 4, 6, 7, 8 · 2C₄H₉OH, and 10 with thermal ellipsoids at 50% probability (see text). Uncoordinated *t*-butyl alcohol molecules in 8 are omitted for clarity.

Table 3

Selected bond lengths	(Å) for	$1 \cdot 2H_2qn \cdot 2Cl$	· CH3CN, 3, 4,	6, 7	. 8	· 2C ₄ H ₉ OH, and 10 .
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1		3	4	6	7	8 · 2 <i>t</i> -BuOH	10
V–N		2.09[1]	2.103(1)	2.102[7]	2.112(1)	2.107(2)	2.103[2]
V-O ^b		1.99[1]	1.9956(8)	1.9855[3]	1.999(1)	1.999(1)	1.9913[5]
V–V V–Cl 2.	.3085(9)	3.349(2) 2.370[6]	3.3860(2) 2.3721(3)	3.338(2) 2.368[4]	3.3537(5) 2.3677(5)	3.3778(3) 2.3761(5)	3.3392(3) 2.371[1]
V=0 1. $\angle V-0^c-C$ $\angle V-0^d-V$.576(2)	1.592[5] 130.0[2] 107.25[4]	1.5953(8) 139.53(7) 108.25(3)	1.585[6] 123.9[9] 107.0[2]	1.604(2) 126.5(2) 106.57(4)	1.596(1) 131.4(1) 107.85(6)	1.5935[7] 129.1[4] 107.1[2]

^a Oxygen of qn *trans* to terminal oxygen.

^b Oxygen of qn *cis* to terminal oxygen.

^c Oxygen of alcohol.

^d Oxygen of qn.

Table 4

Selected bond lengths (Å) and angles (°) of $[VOCl_2(H_2O)_2]$ (1).

	$\bm{1}\cdot 2H_2qn\cdot 2Cl\cdot CH_3CN^a$	$\bm{1}\cdot Et_2O^b$	1 · 15C5 ^c	$1 \cdot B15C5^d$	1 · 18C6 ^e	$\boldsymbol{1}\cdot 2C_{10}H_{10}N_3\cdot Cl_2{}^f$
V=0	1.576(2)	1.574(1)	1.570(2)	1.567(3)	1.568(3)	1.5719(19)
V–Cl	2.3085(9)	2.318[5]	2.3050[7]	2.299[5]	2.31[2]	2.310[5]
V–O ^g	2.011[1]	1.997(1)	2.005[2]	2.022[5]	2.00[2]	1.977[1]
O ^b –V–Cl	106.18(2)	105.78[3]	108.7[4]	107.6[1]	105.0[2]	104.6[7]
O ^b –V–O ^b	105.5[4]	106.32(3)	103.4[1]	103.1[2]	103.7[2]	106.5[3]
Cl-V-Cl	147.64(2)	148.4(1)	142.73(4)	144.80(5)	150.1(3)	150.85(3)
Cl–V–O ^g	85.7[1]	85.6[1]	85.8[2]	86.1[3]	86.5[7]	85.90[7]
0 ^g –V–0 ^g	149.07(9)	147.36(7)	153.2(1)	153.8(1)	152.3(1)	147.0(1)
$V \cdots V^h$	7.719	7.282	8.206	7.910		7.838

^a This work.

^b Ref. [16].

^c Ref. [17]: 15C5 = 15-crown-5.

^d Ref. [17]: B15C5 = benzo-15-crown-5.

^e Ref. [18]: 18C6 = 18-crown-6.

f

Ref. [23]: $C_{10}H_{10}N_3$ = bis{2-(2-pyridylamino)pyridinium}.

^g Coordinated water molecule.

^h The shortest V····V distance.



Chart 3. Possible structures of $[VO(\mu-OR)2VO]^{2+}$.

Table 5

Effective magnetic moments, g-, and J-values of 8-quinolinolato dinuclear vanadium(IV) complexes.

Complex	$\mu_{ m eff}$ (300 K)	g	$J(cm^{-1})$
3	2.43	1.89 (2.03 ^a)	-2.0
10	2.53	2.01	-0.9
6	2.49	1.94	-0.6
4	2.50	2.06	-0.3
7	2.45	2.00	-0.1

^a Determined by ESR spectrum.



Fig. 4. Temperature dependence of magnetic susceptibility of **3**. χA vs. *T* plot (\bigcirc) and μ_{eff} vs. T plot (\Box), 1 T, 1.9–100 K.



Fig. 5. ESR spectrum of 3: (A) measured at 270 K in THF; (B) the simulated spectrum.

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Appendix A. Supplementary material

CCDC 711089, 711090, 711091, 711092, 711093, 711094 and 711095 contain the supplementary crystallographic data for $1 \cdot 2H_2qn \cdot 2Cl \cdot CH_3CN$, **3**, **4**, **6**, **7**, **8** $\cdot 2C_4H_9OH$ and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.02.025.

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