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SYNTHESIS, PROPERTIES AND STRUCTURE OF VANADIUM(IV) SCHIFF BASE COMPLEX (VO)[SALPHEN]·CH_3CN

XIN WANG,* XIAO MIN ZHANG and HAI XIN LIU

Instrumental Analysis and Research Centre, Lanzhou 730000, P.R. China

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Abstract—$(C_2H_5)_4NVO_3$ reacts with the Schiff base Salphen (Salphen = N,N′-disalicylidene-*o*-phenylenediamine in acetonitrile to afford the title complex which has been characterized by elemental analysis, EPR, IR and Electronic absorption spectra and conductance measurement. The X-ray single crystal structure reveals that vanadium is coordinated in a square-pyramidal arrangement to the quadridentate ligand.

In recent years vanadium chemistry has aroused people's interest for its special structures and biological effects.[1,2] In order to understand better its structural, functional and mechanistic properties, it is necessary to study the coordination of vanadium in its various oxidation state. So far all the complexes containing VO(Schiff base dianion)$^{n+}$ ($n = 0$ or 1) moieties have been synthesized with materials of vanadium(IV) compounds. For example, [VO (Salen)] (Salen = N,N′-ethylenebis(salicylaldiminato) dianion),[3] $VO(Hsalahe)_2$ (Hsalahe = 2-salicylideneamino-1-hydroxyethane).[4] VO[N,N-propylenebis (salicylideneiminato)][5] VO-[bis-N (4-chlorophenyl) salicylideneiminato].[6]

Mazzanti *et al.*[3] have reported that $SalophenH_2$ reacted with an aqueous solution of $VOSO_4 \cdot 5H_2O$ to afford (VO)[Salophen] complex, but no crystal structure has been reported. In the present paper, we obtained (VO)[Salphen]·CH_3CN through reaction of $(C_2H_5)_4NVO_3$ with Salphen. The spectroscopic properties of the complex were measured and its structure was determined.

EXPERIMENTAL

Elemental analyses were measured on an Italy 1106 apparatus. IR spectra were recorded as KBr discs using a Nicolet 170sx spectrophotometer. EPR spectra were recorded on a Bruker-200D apparatus. Electronic spectra were recorded on a Beckman Du-7B spectrophotometer.

All chemicals were purchased commercially and used without further purification. The ligand Salphen was prepared by condensing salicylaldehyde with stoichiometric quantities of *o*-phenylenediamine in ethanol.

Synthesis of (VO)[*Salphen*]·CH_3CN

190.4 mg (0.8 mmol) of $(C_2H_5)_4NVO_3$ was added to 126.3 mg (0.4 mmol) of Salphen in 30 cm^3 acetonitrile. The resulting red solution was layered with ether to afford large red–black crystals. Found: N, 9.7; C, 62.2; H, 4.0. Calc. for (VO)[Salphen]·CH_3CN: N, 9.9; C, 62.5; H, 4.0.

Crystal structure determination

A selected single crystal with $0.15 \times 0.25 \times 0.30$ mm approximate dimensions was used for the analysis. All the intensity data were collected on an Enraf–Nonius CAD4 diffractometer using monochromated Cu-K_α radiation ($\lambda = 1.5418$ Å). The crystal was stable under irradiation. Cell dimensions were determined by least-squares refinement of the setting angles of 25 reflections in the range $12 < \theta < 19°$.

The structure analysis was performed on a PDP-11 computer with the SDP program. The positions of the vanadium and other non-hydrogen atoms were determined by direct methods. The positions of the hydrogen atoms were determined by difference Fourier synthesis. The crystal structure was refined by full-matrix least-squares to a final

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* Author to whom correspondence should be addressed.

Table 1. Crystal data for (VO)[Salphen]·CH_3CN

Formula	$C_{22}H_{17}N_3O_3V$
Formula weight	422.34
Cell constants	
a (Å)	9.398
b (Å)	19.161
c (Å)	11.256
β (°)	109.92
V (Å^3)	1905.7
D_{Calc} (g cm^{-3})	1.47
Molecules per cell, Z	4
System	monoclinic
Space group	$P2_1/n$
μ(Cu-K_α) (cm^{-1})	46.3
Wave length (Cu-K_α) (Å)	1.54184
Temperature (K)	293 ± 1
Data collected	3101
Data with $I > 3\sigma(I)$	2630
Discrepancy factor, R	0.052
$F(000)$	868
2θ max (°)	120
Scan rate (deg per min)	1–10
Corrections	Lorentz-polarization and empirical absorption

$R = 0.052$. Crystal data, bond distances and angles are listed in Tables 1 and 2, respectively. Tables of final atomic coordinates and the thermal parameters, together with bond distances and bond angles relating to the aromatic rings, have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.

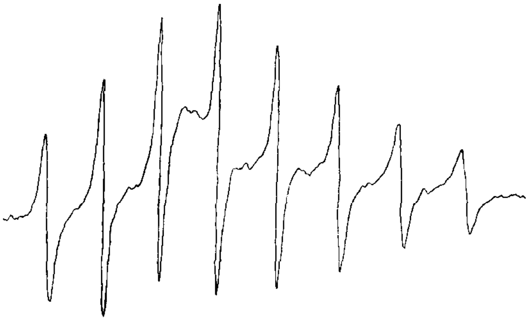

Fig. 1. Room-temperature EPR spectrum of (VO)(Salphen)·CH_3CN in acetonitrile.

RESULTS AND DISCUSSION

EPR spectra

Figure 1 shows the EPR spectrum of the vanadium compound dissolved in acetonitrile. The figure exhibits eight lines for (VO)[Salphen]·CH_3CN due to hyperfine coupling of ^{51}V whose nuclear spin number $I = 7/2$. This shows that a single vanadium is present in the molecule. Since there is rapid tumbling of molecules in solution at room temperature, the anisotropy is not observed. The $\langle g \rangle$ value determined from the magnetic field and frequency ($V = 9.78048 \times 10^9$ Hz) of the solution spectrum is 1.99, similar to the spin-only value suggesting little spin-orbit coupling. The solution spectra agree with the square–pyramidal structure for the vanadyl complex under study.[7]

IR spectra

From Table 3, we can see that the ν(OH) stretching frequencies are at about 3400 and 1400 cm^{-1},

Table 2. Selected bond distances (Å) and angles (°)

Bond distances (Å)			
V—O(1)	1.925(4)	N(1)—C(7)	1.314(6)
V—O(2)	1.930(3)	N(1)—C(8)	1.422(5)
V—O(3)	1.589(3)	N(2)—C(13)	1.418(5)
V—N(1)	2.062(4)	N(2)—C(14)	1.306(6)
V—N(2)	2.065(4)	C(6)—C(7)	1.420(6)
O(1)—C(1)	1.322(6)	C(14)—C(20)	1.413(7)
O(2)—C(15)	1.322(6)		
Bond angles (°)			
O(1)—V—O(2)	87.0(1)	O(3)—V—N(1)	103.8(2)
O(1)—V—O(3)	110.3(2)	O(3)—V—N(2)	104.4(1)
O(1)—V—N(1)	87.6(1)	N(1)—V—N(2)	77.9(1)
O(1)—V—N(2)	144.7(1)	C(7)—N(1)—C(8)	119.6(4)
O(2)—V—O(3)	109.5(2)	C(13)—N(2)—C(14)	120.4(4)
O(2)—V—N(1)	146.1(1)	N(1)—C(7)—C(6)	124.6(4)
O(2)—V—N(2)	87.5(1)	N(2)—C(14)—C(20)	125.3(4)

Table 3. IR and Electronic spectral (data for Salphen and (VO)[Salphen]·CH$_3$CN)

	IR (cm^{-1})					
	ν(OH)	ν(C=N)	ν(V=O)	ν(V—O)	ν(V—N)	
Ligand	3400	1613	—	—	—	
	1400	—	—	—		
Complex	—	1607	984	483	383	
	UV (nm) ε (M^{-1} cm^{-1}) CHCl$_3$ λ (ε)					
Ligand[a]	276.0 (18,200)	335.0 (19,000)	—	—	—	—
Complex[a]	263.5 (17,400)	318.5 (32,100)	408.0 (25,100)	556.0 (50)	593.0 (56.7)	712.5 (33.3)

[a] Values are λ_{max}.

the strong absorption at 1613 cm^{-1} due to the group (—C=N—) in the ligand. In the complex, the characteristic ligand band ν(C=N) (1607 cm^{-1}) displays a shift to lower frequency by (7 cm^{-1}) on complexation, and the ν(OH) band disappears, showing that it has been deprotonated.[8] The spectra show normal strong bands at 984 cm^{-1} assigned to ν(V=O).[9] The far infrared indicates that bands due to V—O and V—N stretching vibration occur at 483 and 383 cm^{-1}, respectively.

Electronic spectra

The spectra data measured in CHCl$_3$ are provided in Table 3. The UV spectrum of the vanadium compound is in the region 190–800 nm. By comparing characteristic bands of the two compounds, we find that the two optical bands in the ligand ($\lambda_{max} = 276$ nm, $\lambda_{max} = 335$ nm) make a shift to lower wavelength in the complex, respectively ($\lambda_{max} = 263$ nm, $\lambda_{max} = 318$ nm). The band in the complex at 408 nm ($\varepsilon = 25{,}100$ M^{-1} cm^{-1}) is regarded as the charge-transfer L → M between the ligand and vanadium.[7] By the method of molecular orbitals, we can see that the one d electron in VO^{2+} is placed in the b$_2$(d_{xy}) orbital. The predicted low intensity absorption are $b_2 \rightarrow e(d_{xz}, d_{yz})$, $b_2 \rightarrow b_1$ ($d_{x^2-y^2}$), and $b_2 \rightarrow a_1(d_z^2)$. The spectrum of (VO)[Salphen]·CH$_3$CN in CHCl$_3$ solution shows three crystal field bands at 712 nm ($\varepsilon = 33.3$ M^{-1} cm^{-1}), 593 nm ($\varepsilon = 56.7$ M^{-1} cm^{-1}) and 556 nm ($\varepsilon = 50$ M^{-1} cm^{-1}), which can be assigned to the transitions $b_2 \rightarrow e$, $b_2 \rightarrow b_1$, and $b_2 \rightarrow a_1$, respectively.[10]

Conductivity

The molar conductivity in acetonitrile (61 Ω^{-1} cm^2 mol^{-1}) is typical of a non-electrolyte.[11] The value agrees with the result of the X-ray structure analysis.

X-ray structure

The view of the molecular structure of the complex and its atomic numbering is shown in Fig. 2. The X-ray analysis of the complex establishes that in the mononuclear complex, Salphen serves as a doubly negative quadridentate ligand. The hydroxyl group in the complex is deprotonated and coordinated. The compound is a five-coordinate, distorted square pyramid in conformity with the coordination of vanadium(IV) schiff base complexes.[3,4] In the complex, the bond angles in the plane O(1)—V—O(2) 87.0(1)°, O(1)—V—N(1) 87.6(1)°, N(1)—V—N(2) 77.9(1)°, N(2)—V—O(2) 87.5(1)° are smaller than the regular angle 90°. But the vertex angles O(1)—V—O(3) 110.3(2)°, O(2)—V—O(3) 109.5(2)°, O(3)—V—N(1) 103.8(2)°, O(3)—V—N(2) 104.4° are bigger than the regular angle 90°. These are due to the central ion vanadium(IV) which lies a little above the plane.

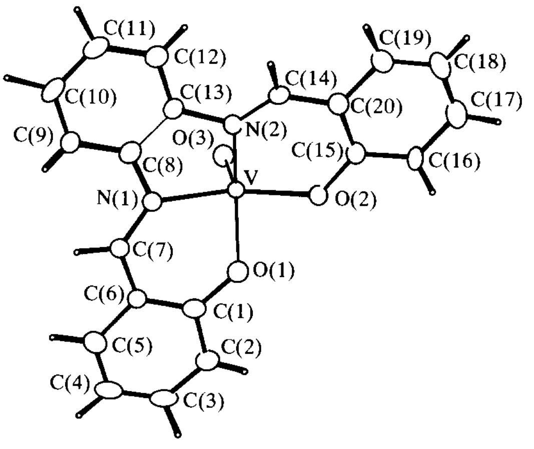

Fig. 2. Molecular structure of (VO)[Salphen]·CH$_3$CN showing the atom numbering.

The torsional angles show that the atoms of the complex except the oxygen atom on the vertex of the square pyramid are approximately in one plane. The relative bond lengths are V—O(1) 1.925(4) Å, V—O(2) 1.930(3) Å, V—N(1) 2.062(4) Å, V—N(2) 2.065(4) Å. These values are in the range seen for many other vanadium Schiff base complexes.[4–6] The short V—O bond length of 1.589(3) Å, which lies in the range observed for five-coordinate vanadium compounds (1.55–1.68 Å),[12] is typical of a five-coordinate vanadyl species.

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