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Note

Synthesis, characterization and crystal structures of two *cis*-dioxo vanadium(V) complexes of monoanionic tridentate Schiff base ligands

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Abstract

Reaction of Sal-L (Sal = salicylaldehyde; L = Girard reagent P or T) with $(C_2H_5)_4NVO_3$ yielded the title complexes, which have been characterized by elemental analysis, ^{1}H NMR, IR spectra and conductance measurement. The X-ray crystal analyses of the compounds reveal that the molecules possess a VO_2^+ unit which is in *cis*-configuration. From the structures, we can also see that the ligands are present as tridentate donors coordinating through the atoms of ONO, which form a distorted trigonal bipyramid configuration in complex **II** and a square pyramid in complex **I**.

Keywords: Crystal structures; Vanadium complexes; Oxo complexes; Schiff base complexes

1. Introduction

Vanadium chemistry has aroused considerable interest in recent years in view of its special structures and biological effects [1,2]. The heightened interest in the biological chemistry of vanadium is due to the recent discovery of the first two vanadoenzymes (nitrogenase and bromoperoxidase [3–5]). Vanadium nitrogenase may contain a V–Fe–S cluster that is a structural analogue of the molybdenum enzyme [6,7]. The bromoperoxidases are thought to contain a mononuclear vanadium(V) active site [8]. A large number of vanadium Schiff base complexes are known. They all have a square pyramid or octahedron configuration.

There have been a lot of vanadium complexes with Schiff bases reported in previous papers, but so far no *cis*-dioxo vanadium(V) with a Schiff base complex monomer. Scheidt et al. and Giacomelli et al. have reported the crystal structures of $[O_2VA]^{3-}$ (A = EDTA), $[O_2V(OX)_2{}^{3-}]$ (OX = oxalate) and $[Q_2VO_2]^-$ (Q = 8-quinolinato anion) [9–11]. These anions contain a *cis*-VO_2^+ unit, and vanadium is in the octahedron configuration. We first synthesized two *cis*-dioxo vanadium(V) monomers $[VO_2(\text{Sal-P})]\cdot CH_3OH$ and $[VO_2(\text{Sal-T})]$. In the present paper, we describe the syntheses and spectroscopic characterizations of the title complexes. X-ray diffraction analyses have been performed on the title complexes.

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2. Experimental

Girards reagents T and P ($T = NH_2NHCOCH_2N(CH_3)_3Cl$; $P = NH_2NHCOCH_2NC_5H_5Cl$) were obtained from the British Drug Houses Ltd. All other reagents were purchased commercially and used without further purification. The ligands Sal-P and Sal-T were prepared by condensing salicylaldehyde with stoichiometric quantities of Girards reagent P and T in ethanol, respectively. The vanadium material $(C_2H_5)_4NVO_3$ was synthesized in a similar method to that given in the literature [12]. IR spectra were recorded as KBr discs on a NIC-5DX spectrophotometer. Elemental analyses were measured on an Italy 1106 apparatus. Molar conductivities were measured on a DDS-11A conductivity set. ^{1}H NMR spectra were recorded on a Varian FT-80A spectrometer.

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2.1. Preparation of *[VO_2(Sal-P)]·CH_3OH (I)*

Sal-P (291.5 mg, 1 mmol) was dissolved in methanol (50 cm^3) and $(C_2H_5)_4NVO_3$ (229 mg, 1 mmol) was added at room temperature. The solution immediately became yellow. After slow evaporation of the solvent, single yellow crystals were isolated. Yield 70%. *Anal.* Found: C, 48.8; H, 4.4; N, 11.5; Calc. for $C_{15}H_{16}N_3O_5V$: C, 48.8; H, 4.4; N, 11.4%.

2.2. Preparation of *[VO_2(Sal-T)] (II)*

Complex **II** was prepared by a similar procedure to that of **I**. Sal-T was dissolved in methanol, followed by addition of $(C_2H_5)_4NVO_3$ to afford **II**. Yellow crystals of **II** were obtained after slow evaporation. Yield 75%. *Anal.* Found: C, 45.3; H, 5.0; N, 13.2; Calc. for $C_{12}H_{16}N_3O_4V$: C, 45.4; H, 5.1; N, 13.2%.

2.3. *X-ray structure determinations for compounds I and II*

A selected single crystal of **I** with dimensions 0.05×0.20×0.30 mm was sealed in a glass fibre tube together with a small amount of mother liquor, as the crystal was sensitive to loss of solvent. A suitable crystal of **II** with dimensions 0.20×0.20×0.40 mm was mounted on a glass fibre. All the intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Cu Kα radiation (λ=1.54184 Å). The scan mode was ω-2θ. Crystal data and collection and processing parameters are given in Table 1.

Table 1
Crystallographic data for complexes I and II

Complex	I	II
Formula	$C_{15}H_{16}N_3O_5V$	$C_{12}H_{16}N_3O_4V$
M_r	369.25	317.22
Colour	yellow	yellow
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.542(2)	7.778(2)
b (Å)	9.942(2)	16.155(3)
c (Å)	11.745(3)	11.178(2)
α (°)	82.48(2)	
β (°)	105.23(2)	100.31(0)
γ (°)	108.33(3)	
U (Å^3)	805.87	1381.9
Z	2	4
D_c (g cm^{-3})	1.522	1.53
μ (cm^{-1})	54.8	62.3
F(000)	380	660
2θ Limits (°)	2–120	2–120
Total reflections measured	2530	2260
Unique data used ($I>3\sigma(I)$)	2524	2153
R	0.066	0.055
R_w	0.063	0.054

The structure analyses were performed on a PDP11/44 computer with the SDP program [13]. The positions of the vanadium atoms were determined by direct methods. The positions of the other non-hydrogen atoms were revealed by difference Fourier synthesis. The positions of the hydrogen atoms were calculated as idealized contributions. Full-matrix least-squares was used to refine the structures.

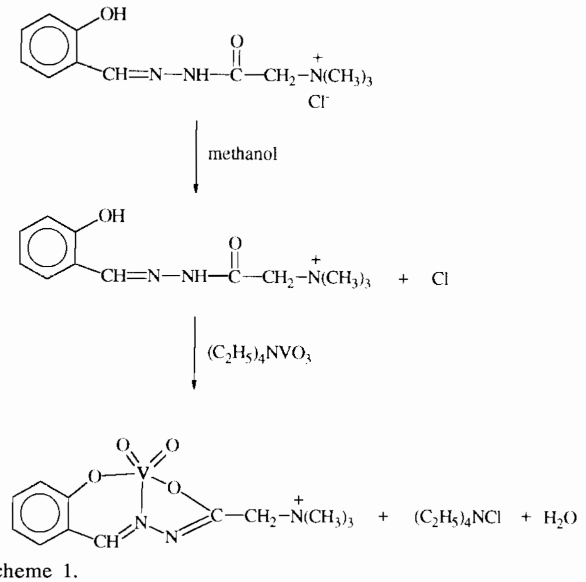
3. Results and discussion

3.1. *Synthesis, conductivity and spectroscopic properties*

The title complexes were synthesized in methanolic solution at room temperature. In the reaction, the ligands Sal-P and Sal-T lost their chloride anions as internal salts, so neutral complexes were obtained. As the two reaction procedures are similar, we show only the synthesis of [VO_2(Sal-T)] in Scheme 1.

The molar conductivity for complexes **I** and **II** was measured in methanol. The values for **I** and **II** are 54.2 and 56.3 Ω^{-1} cm^2 mol^{-1}, respectively, which are typical of non-electrolytes [14]. The results agree with the X-ray structures of both complexes.

The IR spectral data of the ligands and complexes are provided in Table 2. The characteristic ligand bands ν(C=N) (1630 (P), 1623 (T) cm^{-1}) display a shift to lower frequency (1616 (**I**), 1609 (**II**) cm^{-1}, respectively), by bonding to vanadium [15]. The ν(C=O) bands (1708 (P), 1701 (T) cm^{-1}) of the ligands disappear in the complexes suggesting enolization of the ligand and reaction of the enol form with the elimination of a proton. Bands due to V–O stretching vibration occur at 456 (**I**) and 463 (**II**) cm^{-1} [15]. The ν(OH) stretches disappear in the spectra of the complexes, which indicate



Scheme 1.

Table 2
IR and ^{1}H NMR spectral data

Compound	IR (cm^{-1})					
	Phenolic ν(C–O)	ν(OH)	ν(C=N)	ν(C=O)	ν(V=O)	ν(V–O)
Sal-P(P)	1279	3360 1412	1630	1708		
Sal-T(T)	1272	3149 1406	1623	1701		
Complex **I**	1307		1616		924 903	456
Complex **II**	1307		1609		937 912	463
	^{1}H NMR (δ ppm)					
	Aromatic	–CH=N	$-CH_2-$	$-N^+C_5H_5$	$-N^+(CH_3)_3$	$-OCH_3$
Complex **I**	8.70–8.11	9.1	5.61	7.54–6.68		3.14–3.08
Complex **II**	7.6–7.3	8.93	6.8		3.2	

that both hydroxyl groups are involved in coordination of the oxygens to vanadium [16]. The phenolic ν(C–O) bands (1279 (P), 1272 (T) cm^{-1}) of the ligands shift to a higher frequency (1307 cm^{-1}) in the complexes [17]. The IR spectrum of the *cis*-MoO_2 moiety has been reported; it exhibits two strong bands at 905–948 and 875–914 cm^{-1} [18,19]. The IR spectra of the complexes show two new strong bands (924, 903 cm^{-1} in complex I; 937, 912 cm^{-1} in complex **II**), which we assign to sym. ν(O=V=O) and asym. ν(O=V–O), respectively.

The ^{1}H NMR spectra of the complexes were recorded in DMSO-d_6 using TMS as the internal standard. The related data are given in Table 2. As expected, OH resonances bonding to aromatic ring are absent in the complexes. The azomethine proton signals (–CH=N) appear at δ 9.1 ppm in complex **I** and δ 8.93 ppm in complex **II** [20]. The peaks at δ 5.61 (**I**) and 6.8 (**II**) ppm are assigned to ($-CH_2-$). The peak at δ 3.2 ppm (**II**) is attributed to $-N^+(CH_3)_3$. The proton signal which appears at δ 3.14–3.08 ppm (**I**) is assigned to $-OCH_3$. The OH resonance in complex **I** has not been observed due to a broad proton signal, which is submerged in noise.

3.2. *Structural studies*

The atomic positional parameters and selected bond lengths and angles are given in Tables 3, 4 and 5, respectively. The structures of complexes **I** and **II** are displayed in Figs. 1 and 2. The X-ray analyses of the two complexes establish that both ligands actually serve as mono negative ligands in the mononuclear complexes (see Scheme 1) and bond to the *cis*-VO_2 moiety through ONO as tridentates. The N(1)–C(7) (1.287(7)–1.292(6) Å) and N(2)–C(8) (1.279(6)–1.290(7) Å) distances in the complexes are typical double bonds (normal single bond is 1.364 Å [18]). The O(2)–C(8) bond (1.298(6) (**I**), 1.291(6) (**II**) Å) has the partial double character of the C=O bond. In both complexes the structural data concerning the VO_2 moiety are very close, with an O–V–O angle varying from 108.2(2)° in complex **I**

Table 3
Atomic coordination and thermal parameters for non-hydrogen atoms of complex **I**

Atom	x	y	z	B_{eq} [a] (Å^2)
V	0.2068(1)	0.33409(9)	0.85956(8)	2.49(2)
O(1)	0.3216(5)	0.2131(4)	0.8125(3)	3.19(8)
O(2)	0.2257(5)	0.4522(4)	0.9865(3)	3.33(8)
O(3)	−0.0232(5)	0.2755(4)	0.8042(4)	3.8(1)
O(4)	0.2946(5)	0.4741(1)	0.7792(3)	3.62(9)
O(5)	0.7366(9)	0.1745(7)	0.5962(6)	3.6(2)
N(1)	0.2402(5)	0.2061(4)	1.0208(4)	2.33(9)
N(2)	0.2402(6)	0.2654(4)	1.1234(4)	2.64(9)
N(3)	0.2353(6)	0.4256(4)	1.2997(4)	2.60(9)
C(1)	0.3038(7)	0.0753(5)	0.8358(5)	2.8(1)
C(2)	0.3409(8)	0.0017(6)	0.7558(5)	3.6(1)
C(3)	0.3291(8)	−0.1406(6)	0.7770(6)	3.8(1)
C(4)	0.2824(8)	−0.2139(6)	0.8806(6)	3.7(1)
C(5)	0.2491(8)	−0.1418(5)	0.9609(5)	3.2(1)
C(6)	0.2585(7)	0.0033(5)	0.9412(5)	2.5(1)
C(7)	0.2406(7)	0.0756(5)	1.0331(5)	2.6(1)
C(8)	0.2329(7)	0.3933(5)	1.0923(5)	2.5(1)
C(9)	0.2357(8)	0.4922(6)	1.1790(5)	3.2(1)
C(10)	0.3862(8)	0.3795(6)	1.3593(5)	3.2(1)
C(11)	0.3916(9)	0.3185(6)	1.4720(6)	3.9(1)
C(12)	0.239(1)	0.3062(6)	1.5220(6)	4.4(2)
C(13)	0.0851(9)	0.3531(7)	1.4589(6)	4.5(2)
C(14)	0.0844(8)	0.4135(6)	1.3457(5)	3.6(1)
C(15)	0.763(1)	0.0407(9)	0.5961(8)	12.4(3)

[a] $B_{eq}=4/3[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$.

Table 4
Atomic coordination and thermal parameters for the non-hydrogen atoms of complex **II**

Atom	x	y	z	B_{eq}[a] (Å^2)
V	0.1518(1)	0.09498(6)	0.23093(8)	3.85(2)
O(1)	0.2146(7)	0.1426(3)	0.0897(4)	6.3(1)
O(2)	0.0747(5)	0.0038(2)	0.3297(3)	4.60(9)
O(3)	−0.0222(6)	0.1512(3)	0.2300(4)	6.0(1)
O(4)	0.3099(7)	0.1271(3)	0.3337(5)	8.2(1)
N(1)	0.1787(5)	−0.0169(2)	0.1357(4)	3.19(9)
N(2)	0.1418(6)	−0.0899(3)	0.1943(4)	3.59(9)
N(3)	0.1967(6)	−0.1699(3)	0.4644(4)	3.64(9)
C(1)	0.2660(7)	0.1202(4)	−0.0106(5)	4.0(1)
C(2)	0.3028(7)	0.1808(4)	−0.0929(6)	4.4(1)
C(3)	0.3546(7)	0.1593(4)	−0.1977(6)	4.7(1)
C(4)	0.3703(8)	0.0760(4)	−0.2297(5)	4.9(1)
C(5)	0.3324(8)	0.0163(4)	−0.1508(5)	4.3(1)
C(6)	0.2777(7)	0.0357(3)	−0.0426(5)	3.5(1)
C(7)	0.2343(7)	−0.0284(3)	0.0347(5)	3.5(1)
C(8)	0.0896(7)	−0.0712(3)	0.2932(4)	3.4(1)
C(9)	0.0420(7)	−0.1394(3)	0.3712(5)	4.0(1)
C(10)	0.270(1)	−0.0990(4)	0.5457(6)	6.0(2)
C(11)	0.1310(9)	−0.2350(4)	0.5401(5)	5.0(1)
C(12)	0.3323(8)	−0.2061(5)	0.4020(6)	5.8(2)

[a] $B_{eq}=4/3[a^2B_{11}+b^2B_{22}+c^2B_{33}+ac(\cos\beta)B_{13}]$.

Table 5
Important bond distances and angles in complexes **I** and **II**

	I	II
Bond distances (Å)		
V–O(1)	1.894(4)	1.897(4)
V–O(2)	1.966(4)	1.996(3)
V–O(3)	1.626(4)	1.627(3)
V–O(4)	1.635(4)	1.611(4)
V–N(1)	2.143(5)	2.128(3)
O(1)–C(1)	1.332(7)	1.307(6)
O(2)–C(8)	1.298(6)	1.291(6)
N(1)–N(2)	1.409(7)	1.403(5)
N(1)–C(7)	1.287(7)	1.292(6)
N(2)–C(8)	1.290(7)	1.279(6)
Bond angles (°)		
O(1)–V–O(2)	144.2(2)	155.1(1)
O(1)–V–O(3)	107.0(2)	96.1(2)
O(1)–V–O(4)	96.4(3)	100.7(2)
O(1)–V–N(1)	82.3(2)	82.2(1)
O(2)–V–O(3)	103.5(2)	94.8(2)
O(2)–V–O(4)	91.5(2)	96.3(2)
O(2)–V–N(1)	73.4(2)	73.6(1)
O(3)–V–O(4)	108.2(2)	110.7(3)
O(3)–V–N(1)	101.7(2)	128.8(2)
O(4)–V–N(1)	149.0(2)	120.0(3)
N(2)–N(1)–C(7)	115.7(4)	114.7(4)
N(1)–N(2)–C(8)	106.3(4)	109.2(4)
O(1)–C(1)–C(6)	122.5(5)	121.7(4)
N(1)–C(7)–C(6)	122.8(5)	125.3(4)
O(2)–C(8)–N(2)	125.6(5)	123.7(4)

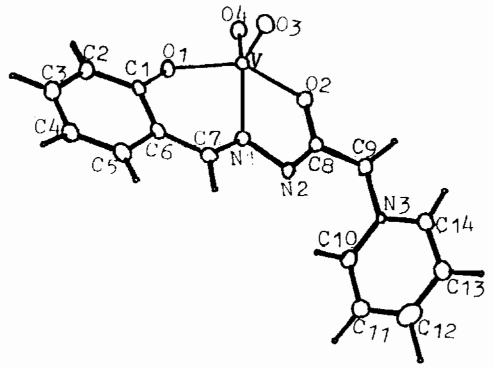


Fig. 1. Crystal structure of complex **I**.

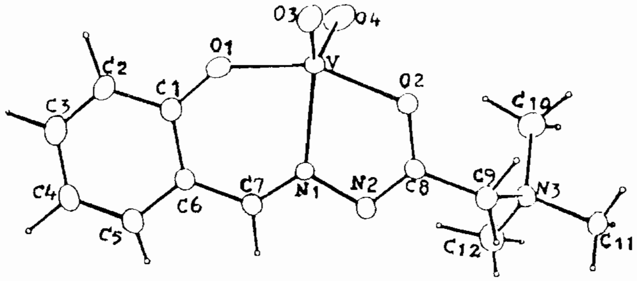


Fig. 2. Crystal structure of complex **II**.

to 110.7(3)° in complex **II**, while the V–O bond distances have a double-bond character (1.626(4) and 1.635(4) Å in complex **I**; 1.627(3) and 1.611(4) Å in complex **II**). The two VO_2 groups in complexes **I** and **II** possess the *cis*-configuration according to the literature [9,10]. The bonds of the other two oxygen atoms bonding to the vanadium atom V–O(1) (1.894(4) (**I**), 1.897(4) (**II**) Å) and V–O(2) (1.966(4) (**I**), 1.996(3) (**II**) Å) are in the range of vanadium–Schiff base complexes. The V–N(1) bonds for complex **I** and **II** are 2.143(5) and 2.128(3) Å, respectively. The torsional angles of C(7)–N(1)–N(2)–C(8) (−177.78° in complex **I**; 179.45° in complex **II**) and N(1)–N(2)–C(8)–O(2) (0.45° in complex **I**; 0.15° in complex **II**) indicate that C(7) N(1) N(2) C(8) and N(1) N(2) C(8) O(2) are in one plane in both complexes. It is clear from the very large differences in the bond angles between equivalent atoms in **I** and **II** (O(3)–V–O(4) = 108.2(2)° (**I**), 110.7(3)° (**II**); O(3)–V–N(1) = 101.7(2)° (**I**), 128.8(2)° (**II**), O(4)–V–N(1) = 149.0° (**I**), 120.0(3)° (**II**)), that the almost 120° angles for **II** are consistent with a trigonal bipyramid geometry while **I** can be regarded as a square pyramid.

References

[1] N.D. Chasteen (ed.), *Vanadium in Biological Systems*, Kluwer Dordrecht, Netherlands, 1990.
[2] D. Rehder, *Angew. Chem., Int. Ed. Engl., 30* (1991) 148.

[3] R.L. Robson, R.R. Eady, T.H. Richardson, R.W. Miller, M. Hawkins and J.R. Postgate, *Nature (London), 322* (1986) 388.
[4] H. Vilter, *Phytochemistry, 23* (1984) 1387.
[5] E. de Boer, Y. Vankooyk, M.G.M. Tromp, H. Plat and R. Wever, *Biochim. Biophys. Acta, 869* (1986) 48.
[6] J.A. Kovacs and R.H. Holm, *Inorg. Chem., 26* (1987) 702, 711.
[7] J.M. Arber, B.R. Dobson, R.R. Eady, P. Stevens, S.S. Hasnain, C.D. Garner and B.E. Smith, *Nature (London), 325* (1987) 372.
[8] E. de Boer, M.G.M. Tromp, H. Plat, G.E. Krenn and R. Wever, *Biochim. Biophys. Acta, 872* (1986) 104.
[9] W.R. Scheidt, R. Countryman and J.L. Hoard, *J. Am. Chem. Soc., 93* (1971) 3878.
[10] W.R. Scheidt, Chun-che Tsai and J.L. Hoard, *J. Am. Chem. Soc., 93* (1971) 3867.
[11] A. Giacomelli, C. Floriani, A. Ofir de S. Duarte, A. Chiesi-Villa and C. Guastini, *Inorg. Chem., 21* (1982) 3310.
[12] K.F. Jahr, J. Fuchs and R. Oberhauser, *Chem. Ber., 101* (1968) 482.
[13] B.A. Frenz, The Enraf-Nonius CAD4 SDP, a real-time system for concurrent X-ray data collection and crystal structure determination, in H. Schenk, R. Olthaf-Hazekamp, H. Vankoningsveld and G.C. Bassi (eds.), *Computing in Crystallography,* Delft University Press, Delft, 1978, p. 64.
[14] W.G. Geary, *Coord. Chem. Rev., 7* (1971) 81.
[15] S.M. Abu-El-Wafa and R.M. Issa, *Bull. Soc. Chim. Fr., 127* (1990) 64.
[16] R.K. Parashar, R.S. Sharma, R. Nagar and R.C. Sharma, *Curr. Sci., 56* (1987) 518.
[17] N.S. Biradar and V.H. Kulkarni, *Rev. Roum. Chim., 16* (1971) 1203.
[18] C. Bustos, O. Burckhardt, R. Schrebler, D. Carrillo, A.M. Arif, H. Cowley and C.M. Nunn, *Inorg. Chem., 29* (1990) 3996.
[19] M.W. Bishop, G. Butler, J. Chatt, J.R. Dilworth and G.J. Leigh, *J. Chem. Soc., Dalton Trans.,* (1979) 1843.
[20] N. Kanoongo, R. Singh and J.P. Tandon, *Transition Met. Chem., 14* (1989) 221.