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Structures of Two Geometrical Isomers of Dioxo[(*S*)-*N*-salicylidene-3-aminopyrrolidine]vanadium(V)

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Synopsis. The title complex was prepared and the crystal structure was determined by the X-ray method. Two geometrical isomers are involved in a unit cell. For each isomer, the coordination polyhedron is a distorted square pyramid, and the two isomers differ from each other with respect to the mutual disposition of the basal chelate ligand and the apical V=O group.

In a previous paper,[1] we reported the preparation and characterization of vanadium(V) complexes containing tridentate $^{-}$O-N-O^{-}-type Schiff base ligands derived from salicylaldehyde and L-amino acids. These complexes tend to form a distorted octahedron with solvents or oxide ions. In order to study the structural variation of vanadium(V) complexes, we prepared a vanadium(V) complex with (*S*)-*N*-salicylidene-3-aminopyrrolidine (abbreviated to sal-(*S*)-apy), a tridentate $^{-}$O-N-N-type Schiff base ligand derived from salicylaldehyde and (*S*)-3-aminopyrrolidine.

Experimental

(*S*)-3-Aminopyrrolidine was purchased from Tokyo Kasei Kogyo Co. ^{1}H NMR and IR spectra were recorded on a Varian VXR 500 spectrometer and a JASCO IR-810 spectrometer, respectively.

Preparation of VO$_2$(sal-(*S*)-apy). To a dichloromethane solution (30 cm^3) containing (*S*)-3-aminopyrrolidine (0.43 g, 5 mmol) and salicylaldehyde (0.61 g, 5 mmol) was added a dichloromethane solution (40 cm^3) of VO(acac)$_2$ (1.32 g, 5 mmol; acac=2,4-pentanedionate ion). The mixture was stirred in air overnight to give a yellow precipitate, which was collected by filtration and recrystallized from methanol. Yield: 0.37 g. Found: C, 48.66; H, 4.83; N, 10.29%. Calcd for $C_{11}H_{13}N_2O_3V$: C, 48.54; H, 4.81; N, 10.29%.

Crystal Structure Determination. Crystals of VO$_2$(sal-(*S*)-apy)·CH$_3$CN were obtained by recrystallization from acetonitrile. A prismatic yellow crystal of approximate dimensions 0.3×0.35×0.8 mm^3 was used for the measurement. Crystal data: $C_{22}H_{26}N_4O_6V_2 \cdot 2CH_3CN$, FW 626.5, monoclinic, *C*2, a=23.073(4), b=11.814(2), c=12.160(3) Å, β=117.07(2)°, V=2951(1) Å^3, Z=4, D_x=1.41 g cm^{-3}, μ(Mo $K\alpha$)=5.11 cm^{-1}. Diffraction data were collected to 2θ=50° using graphite monochromatized Mo $K\alpha$ radiation (λ=0.71073 Å) and θ-2θ scan mode (scan range; 1.20+0.35 tan θ/°) on an Enraf Nonius CAD-4 diffractometer. Scan rate varied from 1.50 to 4.12° min^{-1} in θ. Lattice constants were determined from 25 2θ values ($22<2\theta<29°$). Three standard reflections were monitored every 2 h and showed 23% decay during data collection. The intensities were corrected for Lorents, polarization, and decay effects. All the calculations were carried out on a HITAC M-680H computer at the Computer Center of Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS-III.[2] The location of vanadium was determined using MULTAN 78[3] and the other non-hydrogen atoms were found by the usual Fourier methods. Structure determination and refinement were carried out using 4930 unique reflections with

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors ($B_{\mathrm{eq}}=4/3\{\sum_i\sum_j B_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j\}$)

Atom	x	y	z	B_{eq}/Å^2
V11	30071(2)	3230(5)	20440(4)	3.6
V21	30549(2)	−17083(5)	−29340(4)	3.6
O11	3399(1)	1223(2)	3152(2)	5.2
O12	2406(1)	−164(2)	2241(2)	6.1
O13	3532(1)	−1007(2)	2535(2)	5.7
O21	3488(1)	−2643(2)	−1941(2)	5.5
O22	2463(1)	−1316(2)	−2667(3)	6.7
O23	3587(1)	−390(2)	−2438(2)	5.7
N11	3224(1)	299(2)	512(2)	3.8
N12	2398(1)	1558(2)	782(2)	4.4
N21	3146(1)	−1500(2)	−4587(2)	3.5
N22	2443(1)	−2949(2)	−4205(2)	4.1
C101	3992(2)	−1445(3)	2268(3)	4.3
C102	4392(2)	−2304(3)	3068(3)	5.3
C103	4852(2)	−2784(3)	2774(4)	6.6
C104	4916(2)	−2495(3)	1720(4)	6.1
C105	4510(2)	−1712(3)	944(4)	5.3
C106	4045(1)	−1152(3)	1216(3)	3.8
C107	3648(2)	−286(3)	377(3)	4.0
C108	2862(2)	1174(3)	−428(3)	4.8
C109	2789(2)	2154(3)	284(3)	5.3
C110	2166(2)	771(4)	−1169(3)	5.6
C111	1856(2)	1039(3)	−325(3)	5.4
C201	4013(2)	90(3)	−2715(3)	3.8
C202	4457(2)	885(3)	−1937(3)	5.0
C203	4904(2)	1397(3)	−2221(4)	5.7
C204	4927(2)	1136(4)	−3282(4)	6.6
C205	4503(2)	357(3)	−4092(3)	5.1
C206	4037(1)	−166(2)	−3838(3)	3.5
C207	3583(1)	−904(2)	−4722(2)	3.3
C208	2692(2)	−2184(3)	−5633(3)	4.3
C209	2108(2)	−2333(3)	−5397(3)	5.0
C210	2958(2)	−3382(3)	−5480(3)	5.4
C211	2810(2)	−3866(3)	−4468(3)	5.0
N01	899(2)	−1674(6)	−17(6)	15.1
N02	762(2)	−329(5)	4491(6)	14.3
C01	889(2)	−1144(5)	785(6)	10.7
C02	857(3)	−466(6)	1680(6)	11.2
C03	828(2)	−641(5)	5444(5)	9.4
C04	893(3)	−1213(5)	6475(6)	11.0

$|F_o|>3\sigma(|F_o|)$. Block-diagonal least-squares refinement minimizing $\Sigma w(|F_o|-|F_c|)^2$ converged to R=0.038 and R_w=0.045. The atomic parameters of non-hydrogen atoms are listed in Table 1.[4]

Results and Discussion

Reaction of $V^{IV}O(acac)_2$ with H{sal-(*S*)-apy} in CH_2Cl_2 in air yields directly V^VO_2(sal-(*S*)-apy); the oxidizing agent should be atmospheric oxygen. The IR spectrum shows four strong bands in the V–O stretching region at 913, 930, 941, and 952 cm^{-1}, suggesting the presence of isomers. The X-ray analysis of the complex disclosed that two geometrical isomers, **A** and **B** exist in a unit cell (Fig. 1). Bond distances and selected bond angles are listed in Tables 2 and 3. Figure 1 shows perspective views of the isomers. The geometry around each vanadium atom can be described as a distorted square pyramid. The tridentate Schiff base ligand and one oxygen of the dioxo group occupy the basal positions, and the other oxygen of the dioxo moiety coordinates at the apical position. The two isomers differ from one another with respect to the mutual disposition of the Schiff base chelate and the apical V=O group. The vanadium atom in each isomer is displaced by 0.528(2) (**A**) or 0.523(2) Å (**B**) toward the apical oxo ligand from the best least-squares basal plane. The V11–O11 bond length (1.629(2) Å) in **A** is slightly longer than the other V–O (oxo ligand) bond lengths, the latter being very close to a typical V=O distance of 1.61 Å. The VO_2 group has the cis configuration in both isomers with an O–V–O angle varying from 107.5(1)° (**A**) to 109.9(2)° (**B**), to be compared with the value of 109.1(1)° found in tetraphenylphosphonium dioxo[4-(2-thiazolyl)resorcinolato]vanadate(V) monohydrate, the coordination polyhedron of which also has a distorted square pyramid.[5] Li et al.[6] reported the crystal structure of V^VO_2(HSHED) (HSHED=*N*-salicylidene-*N*′-(2-hydroxyethyl)etylenediamine), where the HSHED ligand serves as the same tridentate $^-$O–N–N-type chelate just as the sal-(*S*)-apy ligand. The VO_2(HSHED) complex takes a weakly associated dimeric structure; the two VO_2 units form a bis(μ-oxo)-bridged V(V) Schiff base dimer, $[VO_2(HSHED)]_2$ and each vanadium atom is hexacoordinated in a distorted octahedral arrangement.[6] In the present VO_2(sal-(*S*)-apy)·CH_3CN complex, there is no indication that any oxo group bridges two vanadium atoms. The acetonitrile molecule is not coordinated to the vanadium atom.

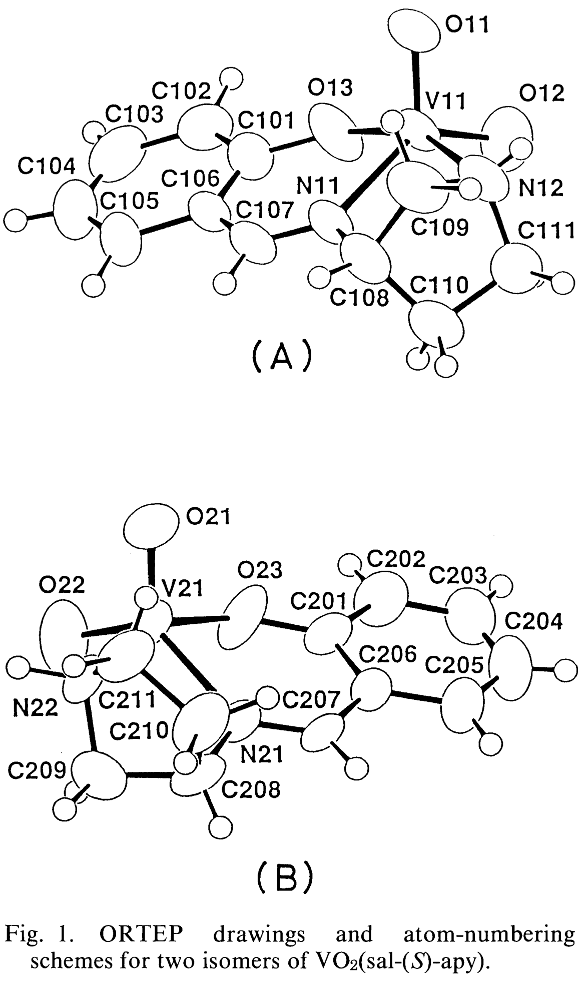

Fig. 1. ORTEP drawings and atom-numbering schemes for two isomers of VO_2(sal-(*S*)-apy).

Table 2. Bond Lengths (l/Å)

V(11)–O(11)	1.629(2)	V(21)–O(21)	1.605(2)
V(11)–O(12)	1.618(3)	V(21)–O(22)	1.610(3)
V(11)–O(13)	1.907(3)	V(21)–O(23)	1.903(3)
V(11)–N(11)	2.138(3)	V(21)–N(21)	2.128(3)
V(11)–N(12)	2.121(3)	V(21)–N(22)	2.132(2)
O(13)–C(101)	1.345(5)	O(23)–C(201)	1.306(5)
N(11)–C(107)	1.269(5)	N(21)–C(207)	1.298(4)
N(11)–C(108)	1.484(4)	N(21)–C(208)	1.469(3)
N(12)–C(109)	1.473(6)	N(22)–C(209)	1.486(4)
N(12)–C(111)	1.490(4)	N(22)–C(211)	1.496(5)
C(101)–C(102)	1.418(4)	C(201)–C(202)	1.395(4)
C(101)–C(106)	1.385(6)	C(201)–C(206)	1.424(5)
C(102)–C(103)	1.387(6)	C(202)–C(203)	1.367(6)
C(103)–C(104)	1.397(7)	C(203)–C(204)	1.352(7)
C(104)–C(105)	1.349(5)	C(204)–C(205)	1.377(5)
C(105)–C(106)	1.421(6)	C(205)–C(206)	1.392(6)
C(106)–C(107)	1.441(4)	C(206)–C(207)	1.410(4)
C(108)–C(109)	1.500(5)	C(208)–C(209)	1.509(6)
C(108)–C(110)	1.518(5)	C(208)–C(210)	1.521(5)
C(110)–C(111)	1.526(7)	C(210)–C(211)	1.532(6)

Table 3. Selected Bond Angles (ϕ/°)

O(11)–V(11)–O(12)	107.5(1)	O(21)–V(21)–O(22)	109.9(2)
O(11)–V(11)–O(13)	104.1(1)	O(21)–V(21)–O(23)	103.5(1)
O(11)–V(11)–N(11)	117.8(1)	O(21)–V(21)–N(21)	119.6(1)
O(11)–V(11)–N(12)	94.9(1)	O(21)–V(21)–N(22)	93.0(1)
O(12)–V(11)–O(13)	97.3(1)	O(22)–V(21)–O(23)	100.6(1)
O(12)–V(11)–N(11)	133.0(1)	O(22)–V(21)–N(21)	128.0(1)
O(12)–V(11)–N(12)	91.2(1)	O(22)–V(21)–N(22)	90.1(1)
O(13)–V(11)–N(11)	83.9(1)	O(23)–V(21)–N(21)	83.0(1)
O(13)–V(11)–N(12)	155.7(1)	O(23)–V(21)–N(22)	155.7(1)
N(11)–V(11)–N(12)	73.7(1)	N(21)–V(21)–N(22)	73.3(1)

The ^{1}H NMR spectrum of the complex in CD_3OD gives two singlet signals assignable to the imine proton at δ=8.96 and 8.59 in a relative ratio of 11 : 1, indicating the existence of the two isomers. On the other hand, the ^{1}H NMR spectrum in DMSO-d_6 shows only one imine signal at δ=8.99. From these results, we can conclude that the two isomers are interconvertible in solution and the equilibrium between the isomers varies with the kind of solvent.

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