Synthesis and Crystal Structure of Polymeric Oxovanadium(V) Complexes with Tetradentate Schiff Base Ligands

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(Received, February 28, 2000; CL–000195)

New polymeric oxovanadium(V) complexes with tetradentate Schiff base ligands, [VO(Xsalen)]SbF_6 (H_2Xsalen: *N,N'*-di-Xsalicylidene-1,2-ethanediamine; X=5-MeO (methoxy) and H) were prepared from monomeric [VO(Xsalen)(H_2O)]NO_3·H_2O by changing the counter anion. X-Ray crystal structure analysis of [VO(5-MeOsalen)]SbF_6 showed that the complex has ···V^V=O···V^V=O··· chains in the crystals.

Synthesis of new linear chain polynuclear metal complexes is an attractive study for their physical properties (e.g. magnetism and electrical conductivity) and structural characteristics. Most oxovanadium(IV) complexes with tetradentate Schiff base ligands have monomeric structures with a five coordinate square-pyramidal geometry. However, several oxovanadium(IV) complexes like [VO(salpn)] (H_2salpn: *N,N'*-disalicylidene-1,3-propanediamine) have linear chain structures (···V^{IV}=O···V^{IV}=O···) with a distorted octahedral geometry in the solid state.[1] The mixed valence Schiff base-oxovanadium(IV)(V) complex [{VO(salen)}$_2$]I_5·CH_3CN also has a linear chain structure (···V^{IV}=O···V^V=O···) in the solid state.[2] On the other hand, only monomeric structures were reported for tetradentate Schiff base-oxovanadium(V) complexes. They have a distorted octahedral geometry with weak coordination of a solvent molecule[3] or a counter ion[4] *trans* to the oxo ligand. However, recently we have prepared polymeric oxovanadium(V) complexes from monomeric oxovanadium(V) complexes by changing the counter ion. This paper reports the first preparation and X-ray structure analysis of a polymeric Schiff base-oxovanadium(V) complex.

Monomeric oxovanadium(V) complexes [VO(Xsalen)(H_2O)]-NO_3·H_2O (X=5-MeO, H) were prepared by oxidation of [VO(Xsalen)] with $(NH_4)_2Ce(NO_3)_6$ in acetonitrile.[5] Crystalline dark blue complexes were obtained in 74–82% yields.[6] The IR spectra of the complexes show a V=O stretching band at 970 cm^{-1} for [VO(5-MeOsalen)(H_2O)]NO_3·H_2O and at 975 cm^{-1} for [VO(salen)(H_2O)]NO_3·H_2O, respectively. X-Ray structure analysis of [VO(5-MeOsalen)(H_2O)] NO_3·H_2O (I) was carried out.[7] The space group is $P2_1/c$ and Z = 8. The two independent complex cations in the unit cell have an almost identical structure. An ORTEP drawing of one of the independent complexes is shown in Figure 1. The complex has a distorted octahedral structure with weak coordination of a water molecule *trans* to the oxo ligand (V=O: distance: 1.584(2) and 1.587(2) Å, V···OH_2 distance: 2.307(2) and 2.268(3) Å). The water molecule coordinated to the vanadium atom is hydrogen bonded with the oxygen atoms of the NO_3^- ion and water of crystallization in the O···O range 2.715(4)—2.845(4) Å.

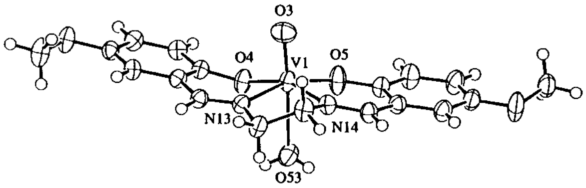

Figure 1. ORTEP drawing for the cation of [VO(5-MeOsalen)(H_2O)]NO_3·H_2O (I) with 50% probability ellipsoids. Selected bond lengths (Å) and angles(°): V(1)–O(3) 1.584(2), V(1)–O(4) 1.821(2), V(1)–O(5) 1.798(2), V(1)–O(53) 2.307(2), V(1)–N(13) 2.082(2), V(1)–N(14) 2.104(2). O(3)–V(1)–O(53) 169.0(1).

Polymeric [VO(Xsalen)]SbF_6 was prepared from monomeric [VO(Xsalen)(H_2O)]NO_3·H_2O by changing the counter anion. To an acetonitrile solution (300 cm^3) of [VO(Xsalen)(H_2O)]NO_3·H_2O (1.5 mmol) was added excess sodium hexafluoroantimonate (0.52 g, 3 mmol). The reaction mixture was stirred for 30 min, and evaporated to dryness. The residue was dissolved in acetonitrile (100 cm^3), and an undissolved part was removed by filtration. The filtrate was evaporated to dryness, and a dark blue residue was suspended with a small amount of ethanol (ca. 30 cm^3), and collected by filtration. Yields: 48—56%.[8]

The IR spectra of [VO(Xsalen)]SbF_6 did not show a V=O stretching band around 970 cm^{-1}. To assign a V=O stretching band, isotopic oxygen atom exchange reaction between the complexes and $H_2{}^{18}O$ was carried out.[9,10] To an acetonitrile solution (10 cm^3) of [VO(Xsalen)]SbF_6 (0.01 mmol) was added 0.02 cm^3 (ca.1 mmol) of $H_2{}^{18}O$ (95 > atom%). The solution was stirred at 25 °C under an argon atmosphere for 1 day, and evaporated to dryness. The IR spectra of the products showed a V=^{18}O stretching band at 829 cm^{-1} for [$V^{18}O$(5-MeOsalen)]SbF_6 and at 870 cm^{-1} for [$V^{18}O$(salen)]SbF_6, with a large decrease in intensity of a V=^{16}O stretching band at 878 cm^{-1} for [$V^{16}O$(5-MeOsalen)]SbF_6 and at 913 cm^{-1} for [$V^{16}O$(salen)]SbF_6, respectively. The fairly lower V=O stretching frequencies of the SbF_6 salts (878 and 913 cm^{-1}) than those of the monomeric NO_3 salts (970 and 975 cm^{-1}) suggest the formation of linear chain structures (···V^V=O···V^V=O···) in the SbF_6 salts.[1,11]

X-Ray crystal structure analysis of [VO(5-MeOsalen)]SbF_6 (II) was carried out.[12] The space group is $P\bar{1}$, and Z=2. The oxo ligands are located on inversion centers (O2A and O2B). There are positional disorders on the vanadium atom and the fluorine atoms of the SbF_6^- anion. All the non-hydrogen atoms were treated anisotropically. It was assumed that site occupancy factors of the disordered vanadium atom (V1A and V1B) are 50% each with sharing the Schiff base ligand, and those of the disordered fluorine atoms (F28A–F33A and F28B–F33B sets) are 60% and 40%, respectively. The oxygen atoms located on inversion centers (O2A and O2B) and the disordered vanadium atoms (V1A and V1B) are arranged almost linearly along the *c* axis (Figure 2). The positional disorder of the vanadium atoms can be interpreted with two possible orientations of the linear

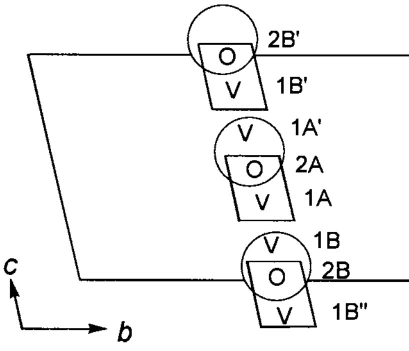

Figure 2. Schematic drawing of the arrangement of the V=O units in the crystals of [VO(5-MeOsalen)]SbF_6 (II).

chain represented as ···V1A=O2A···V1B'=O2B'··· (V=O units enclosed by parallelograms) and ···V1A'=O2A···V1B=O2B··· (V=O units enclosed by circles).

The structure of the complex cation in the linear chain of (II) in one of the orientations (V=O units enclosed by parallelograms) is shown in Figure 3. The molecule has a distorted octahedral geometry with weak coordination of the oxo ligand of the adjacent molecule at the sixth position. However, the V=O distances in (II) (1.577(2) and 1.571(2) Å) are a little shorter than those in (I) (1.584(2) and 1.587(2) Å), although the V=O stretching band of (II) is largely shifted to lower energy than that of (I). The short V=O distances in (II) may be an artifact due to the positional disorder of the vanadium atom. In any case, the V···V distance and the V=O stretching frequecy of (II) (3.83 Å and 878 cm^{-1}) indicate that the complex has a linear $\cdots V^V{=}O\cdots V^V{=}O\cdots$chain structure in which the V=O units are a little more weakly bonded to each other than those of [VO(salpn)](V···V distance: 3.78 Å, ν(V=O): 854 cm^{-1}).[1]

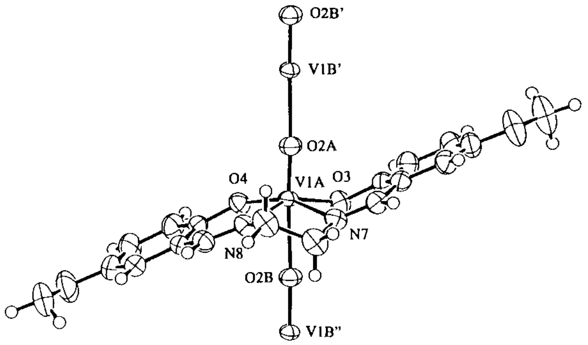

Figure 3. ORTEP drawing for the cation of [VO(5-MeOsalen)]SbF_6 (II) with 50% probability ellipsoids. The V=O moieties of the neighboring complex cations are also shown. Selected bond lengths (Å) and angles (°): V1A–O2A 1.577(2), V1A–O2B 2.262(2), V1A–O3 1.835(4), V1A–O4 1.775(3), V1A–N7 2.119(4), V1A–N8 2.085(4), V1B–O2A 2.266(2), V1B–O2B 1.571(2), O2A–V1A–O2B 171.97(10), O2A–V1B–O2B 172.96(10).

Polymeric [VO(Xsalen)]SbF_6 were prepared from monomeric [VO(Xsalen)(H_2O)]NO_3·H_2O by changing the counter anion as mentioned above. The formation of the polymeric structure in the SbF_6 salts may be attributed to a non-coordinating property of the SbF_6^- anion, weak Lewis basicity of acetonitrile used as a solvent, and crystal packing efficiency.

References and Notes

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6 [VO(5-MeOsalen)(H_2O)]NO_3·H_2O: Anal. Found: C, 44.01; H, 4.45; N, 8.70%. Calcd for $C_{18}H_{22}N_3O_{10}V$: C, 44.00; H, 4.51; N, 8.55%. [VO(salen)(H_2O)]NO_3·H_2O : Anal. Found: C, 44.73; H, 4.10; N, 9.91%. Calcd for $C_{16}H_{18}N_3O_8V$: C, 44.56; H, 4.21; N, 9.74%.

7 Crystal data: $C_{18}H_{22}N_3O_{10}V_1$, M = 491.33, monoclinic, space group $P2_1/c$ (no. 14), a = 24.718(4), b = 16.919(3), c = 10.295(3) Å, β = 101.88(2)°, U = 4212(1) $Å^3$, Z = 8, D_c = 1.549 g cm^{-3}, μ(MoKα)= 0.532 mm^{-1}, crystal size = 0.60 × 0.50 × 0.10 mm, 10212 reflections measured, 9670 unique reflections. Refinement was based on F with $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w^{-1} = \sigma^2(|F_o|) + 0.00119|F_o|^2$, against all the 9670 reflections. The R value $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.041 for the 6329 reflections with $I > 2\sigma(I)$. The R_w value was 0.067.

8 [VO(5-MeOsalen)]SbF_6: Anal. Found: C, 34.27; H, 2.79; N, 4.65%. Calcd for $C_{18}H_{18}N_2O_5F_6Sb_1V$: C, 34.37; H, 2.88; N, 4.45%. [VO(salen)] SbF_6: Anal. Found: C, 33.92; H, 2.36; N, 5.01%. Calcd for $C_{16}H_{14}N_2O_3F_6Sb_1V$: C, 33.78; H, 2.48; N, 4.92%.

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12 Crystal data: $C_{18}H_{18}N_2O_5F_6Sb_1V_1$, M = 629.03, triclinic, space group $P\bar{1}$ (no. 2), a = 11.653(1), b = 13.159(2), c = 7.659(2) Å, α = 103.02(2), β = 98.67(1), γ = 91.10(1)°, U = 1129.5(4) $Å^3$, Z = 2, D_c = 1.849 g cm^{-3}, μ(MoKα)= 1.689 mm^{-1}, crystal size = 0.50 × 0.50 × 0.10 mm, 5432 reflections measured, 5171 unique reflections. Refinement was based on F^2 with $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.0203P)^2 + 4.7006P$, where $P = (F_o^2 + 2F_c^2)/3$ against all the 5171 reflections. The R value $[\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o)^2]^{1/2}$ was 0.058 for the 4608 reflections with $I > 2\sigma(I)$. The R_w value was 0.134.