# Crystal Structure of a Tris(dithiolene) Vanadium(IV) Complex Having Unprecedented $D_{3h}$ Symmetry

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(Received March 14, 1996)

The crystal structure of a tris(dithiolene)vanadium(IV) complex, $[V(S_2C_2H_2)_3]$ (**1**), was determined. This complex shows the first instance of the nearly perfect $D_{3h}$ geometry in tris(dithiolene) vanadium(IV) complexes. In comparison with **1**, the crystal structures of $(NEt_4)_2[V(bdt)_3]$ ($bdt^{2-}$ = 1,2-benzenedithiolate) (**2**) and $(NEt_4)_2[V(tdt)_3]$ ($tdt^{2-}$ = 3,4-toluenedithiolate) (**3**) having distorted *Oh* geometries were also determined by X-ray crystallography.

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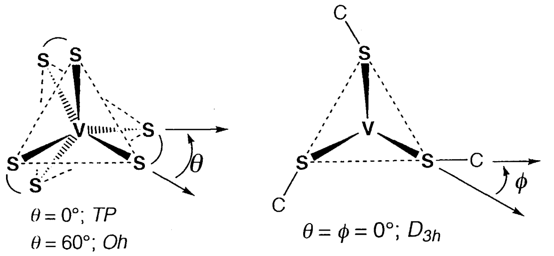
It is well known that tris(bidentate) metal complexes favor octahedral (*Oh*) geometry much more than trigonal prismatic (*TP*) coordination.[1-3] In contrast to the case of N- and O-donor ligands, both *TP* and *Oh* geometries are seen in tris(1,2-dithiolene) vanadium(IV) complexes, which have been so far well-characterized.[4-6] Symmetry of the entire molecule has shown the significant distortion from the regular $D_{3h}$, which is characterized as twist angle $\theta$ and the folding angle $\phi$ in Scheme.



It was believed that these distortions are intrinsic of the *TP* complexes because of the no instances of the regular $D_{3h}$.[7] Among these *TP* vanadium(IV) complexes, the distorted $D_{3h}$ geometry has been reported in $(BEDT\text{-}TTF)_3[V(dmit)_3]_2$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalenium; $dmit^{2-}$ = 2-thioxo-1,3-dithiole-4,5-dithiolato) ($\theta$ = av. 4.6°, $\phi$ = av. 22.3°),[5] $[V(DDDT)_3]\bullet DMF$ ($DDDT^{2-}$ = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) ($\theta$ = av. 8.5°, $\phi$ = av. 10.3°),[6] $[V(DDDT)_3]$ ($\theta$ = av. 15.7°, $\phi \sim 0°$)[6], and $[V(S_2C_2Ph_2)_3]$ ($\theta$ = av. 4.3°, $\phi \sim 0°$).[4] This paper shows the first example of the well-characterized tris(dithiolene) vanadium(IV) complex $[V(S_2C_2H_2)_3]$ (**1**) with the nearly perfect $D_{3h}$ symmetry ($\theta = \phi \sim 0°$). In comparison with **1**, crystal structures of $(NEt_4)_2[V(bdt)_3]$ ($bdt^{2-}$ = 1,2-benzenedithiolate) (**2**), and $(NEt_4)_2[V(tdt)_3]$ ($tdt^{2-}$ = 3,4-toluenedithiolate) (**3**) having distorted *Oh* geometries are also determined by X-ray crystallography.

Single crystals of **1** were obtained by the reaction of $VCl_3(thf)_3$ with sodium *cis*-ethenedithiolate. $VCl_3(thf)_3$ in a THF solution was added to a MeOH solution containing 4 equiv. of sodium *cis*-ethenedithiolate. After the solution was stirred for 2 h at room temperature, the obtained deep purple solution was evaporated under air to give black powder. Careful crystallization from THF resulted in the isolation of deep-purple single crystals in 10% yield.

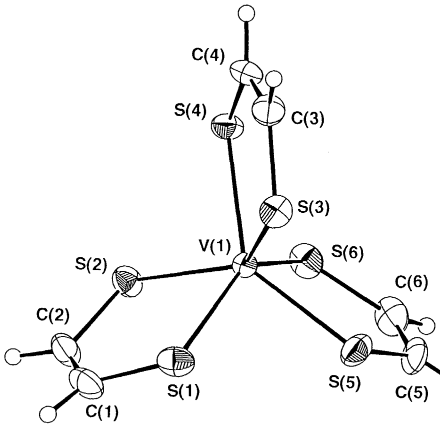
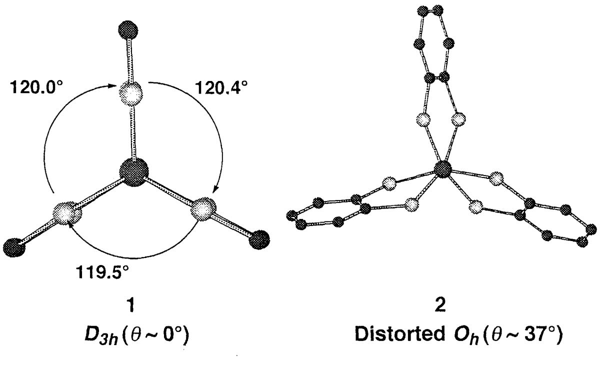


**Figure 1.** ORTEP drawing of **1**. Selected bond distances (Å) and angles(°): V(1)-S(1) 2.353(2), V(1)-S(2), 2.342(2), V(1)-S(3) 2.351(2), V(1)-S(4), 2.353(2), V(1)-S(5) 2.334(2), V(1)-S(6) 2.346(2), S(1)-C(1) 1.672(7), S(2)-C(2) 1.657(6), S(3)-C(3) 1.664(6), S(4)-C(4) 1.665(6), S(5)-C(5) 1.678(7), S(6)-C(6) 1.653(7), C(1)-C(2) 1.345(8), C(3)-C(4) 1.358(8), C(5)-C(6) 1.365(9), S(1)-V(1)-S(2) 82.49(6), S(1)-V(1)-S(3) 79.99(6), S(1)-V(1)-S(4) 135.31(7), S(1)-V(1)-S(5) 81.69(6), S(1)-V(1)-S(6) 138.25(7), S(2)-V(1)-S(3) 136.83(6), S(2)-V(1)-S(4) 82.57(5), S(2)-V(1)-S(5) 133.61(7), S(2)-V(1)-S(6) 80.55(6), S(3)-V(1)-S(4) 82.83(6), S(3)-V(1)-S(5) 82.08(6), S(3)-V(1)-S(6) 135.55(6), S(4)-V(1)-S(5) 135.98(7), S(4)-V(1)-S(6) 79.51(6), S(5)-V(1)-S(6) 83.00(7).

Figure 1 demonstrates the ORTEP drawing of the entire molecule of **1**.[8] The $VS_2C_2$ atoms of each ligand are in plane, and the three angles (120.4°, 119.5°, and 120.0°) between the $VS_2C_2$ planes are nearly equal to 120°. The *trans*-S-V-S bond angles (av. 135.9°)[7] are quite close to those of the regular *TP* form (*ca.* 136°). The molecule has a $C_3$ axis passing through the V atom as shown in Figure 2.



**1**
$D_{3h}$ ($\theta \sim 0°$)

**2**
Distorted $O_h$ ($\theta \sim 37°$)

**Figure 2.** The views of **1** and the anion moiety of **2** projected down the $C_3$ axis.

ESR measurement of **1** at 77 K in MeCN/DMF (4:1) shows an intense signal, characteristic of a vanadium(IV) center.[9] Comparison of the bond distances of the three $S_2C_2H_2{}^{2-}$ ligands indicates no appreciable differences between the corresponding distances (deviations within 0.05 Å). Because of the neutrality and the similar structures of the three $S_2C_2H_2$ ligands of **1**, the negative charge (-4) could be equally delocalized over the three $S_2C_2H_2$ ligands, indicating that **1** has not the structure of $[V^{IV}$(ethenedithiolate)$_2$(ethanedithial)] but a delocalized structure. Similar delocalization has been reported in $[V^{IV}(S_2C_2Ph_2)_3]$[4] or $[Ni^{II}(S_2C_2H_2)_2]$.[10]

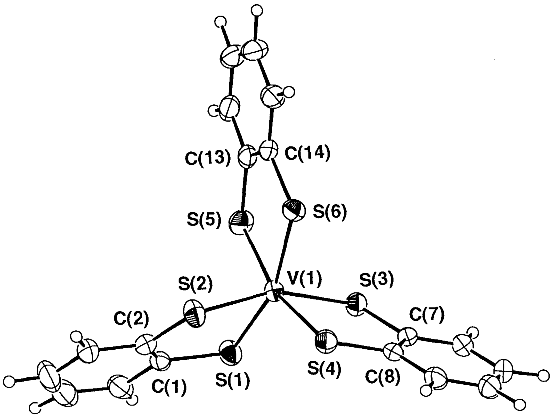


**Figure 3.** ORTEP drawing of **2**. Selected bond distances (Å) and angles (°): V(1)-S(1) 2.350(3), V(1)-S(2), 2.365(3), V(1)-S(3) 2.377(2), V(1)-S(4), 2.358(3), V(1)-S(5) 2.348(2), V(1)-S(6) 2.374(2), S(1)-C(1) 1.752(8), S(2)-C(2) 1.732(8), S(3)-C(7) 1.749(7), S(4)-C(8) 1.734(7), S(5)-C(13) 1.719(8), S(6)-C(14) 1.764(7), C(1)-C(2) 1.37(1), C(7)-C(8) 1.392(10), C(13)-C(14) 1.38(1), S(1)-V(1)-S(2) 83.52(8), S(1)-V(1)-S(3) 84.97(9), S(1)-V(1)-S(4) 112.20(9), S(1)-V(1)-S(5) 81.82(9), S(1)-V(1)-S(6) 161.20(9), S(2)-V(1)-S(3) 159.70(9), S(2)-V(1)-S(4) 85.31(9), S(2)-V(1)-S(5) 104.36(9), S(2)-V(1)-S(6) 90.96(9), S(3)-V(1)-S(4) 83.64(8), S(3)-V(1)-S(5) 90.44(9), S(3)-V(1)-S(6) 104.97(8), S(4)-V(1)-S(5) 164.10(9), S(4)-V(1)-S(6) 85.11(8), S(5)-V(1)-S(6) 82.18(8).

The crystal structures of **2** and **3** show distorted *Oh* geometries. These complexes were obtained by the modified synthetic methods for the literature.[11] The reaction of $VCl_3(thf)_3$ with 4 equiv. of $Li_2bdt{\bullet}dme$ in a THF/DME solution produced the deep red-purple dianionic vanadium(IV) complex $\{Li(dme)_2\}_2[V(bdt)_3]$, which was further converted to **2** by the cation exchange with $NEt_4Br$ (70% yield). The similar reaction of $VCl_3(thf)_3$ with $Li_2tdt$, $NEt_4Br$ produced **3** (57% yield). Figure 3 shows the ORTEP drawing of the anion moiety of **2**.[12] The view projected down the approximate $C_3$ axis is also illustrated in Figure 2. The structure of **3** is similar to that of **2**.[13] The dianionic **2** and **3** show typical ESR signals of vanadium(IV) centers. The twist angle $\theta$ of the regular *Oh* complex is restricted to *ca.* 48° (octahedral limit) as far as chelate ligands such as $bdt^{2-}$ are used.[7] The $\theta$ values are *ca.* 0° for **1**, *ca.* 37° for **2**, *ca.* 40° for **3**.

We first demonstrated that $S_2C_2H_2$ ligand is able to provide regular $D_{3h}$ tris-chelating vanadium(IV) compound and therefore the distortion is not intrinsic problem of the tris-type compounds. The similar structures of the three $S_2C_2H_2$ ligands reveal the equal delocalization of the negative charge (-4). On the other hand, distorted *Oh* geometries were demonstrated in the dianionic moieties of **2** and **3** with $bdt^{2-}$ and $tdt^{2-}$ chelates.

## References and Notes

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8 Crystal data for **1**: $C_6H_6S_6V$, $M$ =321.4, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 7.742(2), $b$ = 11.069(2), $c$ = 7.516(2) Å, $\alpha$ = 105.89(2), $\beta$ = 112.30(2), $\gamma$ = 85.75(2)°, $V$ = 572.9(2) Å$^3$, $D_{calcd}$ = 1.863 g/cm$^3$, MoK$\alpha$ ($\lambda$ = 0.71069 Å), $\mu$ = 19.07 cm$^{-1}$, $T$ = 295 K, 3353 reflections measured, 2640 independent, 1199 [$I > 3.0\ \sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms and isotropic refinement for hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 142 parameters $R$ = 0.034, $R_w$ = 0.026.

9 ESR parameters obtained by simulation, **1**: $g_x = g_y$ = 1.988, $g_z$ = 1.990 ($g_0$ = 1.989), $A_x = A_y$ = 0.0083 cm$^{-1}$, $A_z$ = 0.0003 cm$^{-1}$ ($A_0$ = 0.0056 cm$^{-1}$). **2**: $g_x$ = 1.971, $g_y$ = 1.973, $g_z$ = 1.993 ($g_0$ = 1.979), $A_x$ = 0.0095 cm$^{-1}$, $A_y$ = 0.0075 cm$^{-1}$, $A_z$ = 0.0010 cm$^{-1}$ ($A_0$ = 0.0060 cm$^{-1}$), **3**: $g_x$ = 1.972, $g_y$ = 1.975, $g_z$ = 1.993 ($g_0$ = 1.980), $A_x$ = 0.0092 cm$^{-1}$, $A_y$ = 0.0086 cm$^{-1}$, $A_z$ = 0.0012 cm$^{-1}$ ($A_0$ = 0.0063 cm$^{-1}$)

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12 Crystal data for **2**: $C_{34}H_{52}N_2S_6V$, $M$ =732.1, monoclinic, space group $P2_1/a$ (no. 14), $a$ = 21.32(1), $b$ = 11.38(1), $c$ = 30.85(1) Å, $\beta$ = 92.97(4), $V$ = 7479(8) Å$^3$, $D_{calcd}$ = 1.300 g/cm$^3$, MoK$\alpha$ ($\lambda$ = 0.71069 Å), $\mu$ = 6.26 cm$^{-1}$, $T$ = 295 K, 18686 reflections measured, 18172 independent, 5760 [$I > 3.0\ \sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms and not refined but included for hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 776 parameters $R$ = 0.056, $R_w$ = 0.065.

13 Crystal data for **3**: $C_{37}H_{58}N_2S_6V$, $M$ =774.2, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 12.240(5), $b$ = 16.444(6), $c$ = 11.430(4) Å, $\alpha$ = 108.71(3), $\beta$ = 90.17(4), $\gamma$ = 108.61(3)°, $V$ = 2050(1) Å$^3$, $D_{calcd}$ = 1.254 g/cm$^3$, MoK$\alpha$ ($\lambda$ = 0.71069 Å), $\mu$ = 5.74 cm$^{-1}$, $T$ = 295 K, 6153 reflections measured, 5782 independent, 1536 [$I > 3.0\ \sigma(I)$] included in the refinement, anisotropic and isotropic refinement for non-hydrogen atoms and not refined but included for hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 316 parameters $R$ = 0.067, $R_w$ = 0.055.