X-ray Analysis of Bond Elongation in VO(acac)$_2$ at the Excited State

Manabu Hoshino, Akiko Sekine, Hidehiro Uekusa, and Yuji Ohashi*
Department of Chemistry and Materials Science, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551

(Received May 16, 2005; CL-050650)

X-ray crystal structural analysis of bis(acetylacetonato) oxovanadium(IV), VO(acac)$_2$, complex with photoirradiation at low temperatures clearly indicated the structural distortion caused by the production of the excited molecules with the elongated V=O and V–O bonds in the crystalline lattice.

Recently, several long-lived excited-state structures have been analyzed by X-ray structural analysis. Kim et al., Ozawa et al., and Coppens et al. reported the excited-state structures of $[Pt_2(pop)_3(popH)]^{3-}$ (pop is pyrophosphate, $(H_2P_2O_5)^{2-}$),[1] the derivative, $[Pt_2(pop)_2(popH)_2]^{2-}$,[2] and $[Rh_2(dimen)_4]^{2+}$ (dimen = 1,8-diisocyano-*p*-menthane),[3] respectively. These excited structures were analyzed using the synchrotron radiation.[2,4] But Yasuda et al. reported the excited state of $[Pt_2(pop)_2(popH)_2]^{2-}$ using the usual X-ray technique in the laboratory system.[5] They proposed that the crystal reached the equilibrium state between the ground and excited states on exposure to the Hg lamp and that the bond shortening of Pt–Pt and Pt–P at the excited state can be clearly observed in the structure at the equilibrium state. Recently, the same technique was applied to the Au complex, Au(PPh$_3$)$_2$Cl. At the equilibrium state, the bond distances of Au–Cl and Au–P decreased significantly.[6] In the above two molecules, the bonds of Pt–Pt, Pt–P, Au–P, or Au–Cl are shortened at the excited state. This caused the decrease of the unit cell at the equilibrium state.

Recently, we observed that the unit cell of the crystal of VO(acac)$_2$ (acac = acetylacetonato, $C_5H_7O_2^-$) expanded significantly when the single crystal was irradiated with the Xe lamp at low temperatures. The VO(acac)$_2$ complex was proposed to have the short-lived excited species, due to "d–d*" transition by visible light irradiation.[7] However, the lifetime is too short to observe the emission. Because the anisotropy in expansion of the unit cell by photoirradiation was clearly different from the thermal one, it is possible to observe the excited structure of the VO(acac)$_2$ complex at the equilibrium state. In this paper, we propose that the structural change can be observed if the bond elongation would occur at the excited state.

VO(acac)$_2$ was prepared by the method of Rowe and Jones.[8] The blue crystal suitable for X-ray measurement was obtained from a chloroform solution under diethyl ether atmosphere ($0.20 \times 0.20 \times 0.20\,mm^3$). The intensity data were collected on a Bruker SMART CCD diffractometer equipped with the Rigaku liquid-nitrogen cooling system at four temperatures (168, 160, 150, and 140 K) in the dark (light-off) and under photoirradiation (light-on).[9] The crystal data at the light-off and light-on stages at four temperatures are given in Table 1.[10] The crystal structure viewed along the *a* axis is shown in Figure 1.

At every temperature, the unit-cell volume significantly expanded at the light-on stage. However, the changes of the cell dimensions are different between the photoirradiation and warming. The differences of the cell dimensions between the light-off and light-on stages at 140 K are shown in the column of the pho-

Table 1. Crystallographic data of VO(acac)$_2$, at four temperatures at light-off and light-on stages, the photo change at 140 K and thermal changes between 140 and 168 K, and the ratio of photo changes to thermal changes

	168 K-off	168 K-on	160 K-off	160 K-on	150 K-off	150 K-on
$a/\text{Å}$	7.4028(3)	7.4077(1)	7.3913(2)	7.4030(2)	7.3721(2)	7.3863(2)
$b/\text{Å}$	8.1907(3)	8.1943(1)	8.1844(1)	8.1975(2)	8.1685(2)	8.1844(3)
$c/\text{Å}$	11.2311(4)	11.2383(2)	11.2270(2)	11.2417(3)	11.2110(3)	11.2320(3)
$\alpha/^\circ$	72.947(1)	72.973(1)	72.941(1)	72.960(1)	72.932(1)	72.920(1)
$\beta/^\circ$	72.088(1)	72.127(1)	72.127(1)	72.137(1)	72.199(1)	72.167(1)
$\gamma/^\circ$	66.845(1)	66.860(1)	66.883(1)	66.883(1)	66.924(1)	66.887(1)
$V/\text{Å}^3$	584.11(4)	585.35(2)	582.77(2)	585.46(2)	579.62(3)	582.71(3)
R_{int}	0.0274	0.0264	0.0258	0.0262	0.0264	0.0257

	140 K-off	140 K-on	Photo changes (PC)[a]	Thermal changes (TC)[b]	PC/TC[c]
$a/\text{Å}$	7.3582(2)	7.3759(2)	+0.0178(2)	+0.0447(3)	0.398
$b/\text{Å}$	8.1585(3)	8.1787(3)	+0.0202(3)	+0.0322(3)	0.627
$c/\text{Å}$	11.2035(2)	11.2308(4)	+0.0273(4)	+0.0276(4)	0.989
$\alpha/^\circ$	72.898(2)	72.902(1)	+0.004(2)	+0.049(2)	0.008
$\beta/^\circ$	72.199(2)	72.193(1)	−0.006(2)	−0.072(1)	0.083
$\gamma/^\circ$	66.950(2)	66.906(1)	−0.044(2)	−0.105(2)	0.419
$V/\text{Å}^3$	577.45(3)	581.52(3)	+4.07(3)	+6.66(4)	0.611
R_{int}	0.0258	0.0258			

[a]Difference between 140 K-on and 140 K-off. [b]Difference between 168 K-off and 140 K-off. [c]Ratio of PC to TC.

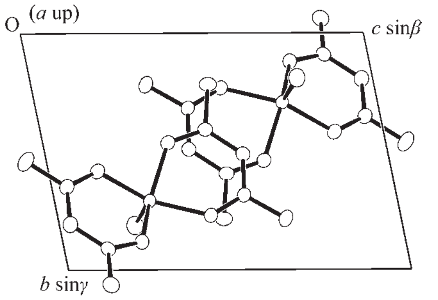

Figure 1. Crystal structure of VO(acac)$_2$ viewed along the *a* axis.

to change and the corresponding differences between the values at the light-off stages at 140 and 168 K are shown in the column of thermal change. The ratio of the photo change to the thermal change is shown in the final column.

It is clear that the expansion of the unit cell due to the photoirradiation is more anisotropic than that of the thermal expansion. This suggests that the change due to the photoirradiation is not caused by the thermal energy brought about by the radiationless transition in the process of deactivation from the excited state to the ground state, but is caused by the production of the excited molecules in the crystalline lattice.[11] It is clear that the crystal reached the equilibrium state composed of the ground and excited states. This is confirmed by the fact that essentially the same unit-cell expansion can be observed using the other crystals in the same conditions.[12]

Table 2. Change of each bond distances by photo-irradiation

	168 K	160 K	150 K	140 K
V=O/Å	+0.0012(9)	+0.0018(9)	+0.0027(8)	+0.0025(8)
V–O/Å	+0.0019(8)	+0.0032(8)	+0.0035(8)	+0.0049(8)
O–C/Å	+0.0003(14)	+0.0019(13)	+0.0020(13)	+0.0033(13)
C–C/Å	+0.0008(17)	+0.0020(16)	+0.0025(15)	+0.0031(15)

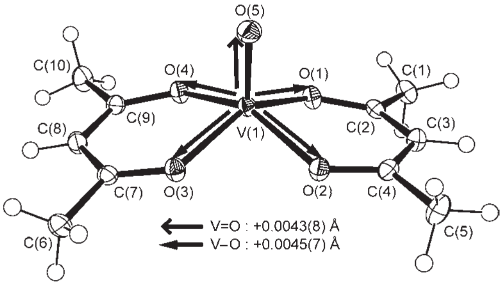

Figure 2. Elongation of V=O and V–O bonds at the excited state.

The differences in bond distances between the light-off and light-on stages at four temperatures are shown in Table 2. The V–O, O–C, and C–C distances in the chelate rings are averaged assuming C_{2v} symmetry. It is clear that essentially the same change of the bond distances can be observed at every temperature. As the temperature decreased, the amount of the change increased within the temperature range. This is probably due to the increased amount of the excited molecules at low temperatures. Although the elongation of the O–C and C–C bonds are within the experimental errors, the V=O and V–O bond distances significantly increase at the light-on stage at 150 and 140 K. The changes of the bond angles and the torsion angles are also within the experimental errors. The changes are schematically drawn in Figure 2. The similar bond elongations were observed again with the use of the other single crystal of VO(acac)$_2$ in the same conditions. The differences of V=O and V–O distances are +0.0043(8) and +0.0045(7) Å at 141 K.[11] Such bond elongations suggest that in the "d–d*" transition the electrons in the bonding orbital of the V–O bonds are transferred to the antibonding orbital of the V=O bond, as proposed by the theoretical calculation.[2,4]

In summary, it is possible to observe the structural change at the excited state even if the lifetime is very short, analyzing the crystal structure at the equilibrium state between the ground and excited states. The V=O and V–O bonds of VO(acac)$_2$ are significantly elongated at the excited state. The study to estimate the concentration of the excited molecules at the equilibrium state is in progress.

References and Notes

1 C. D. Kim, S. Pillet, G. Wu, W. K. Fullagar, and P. Coppens, *Acta Crystallogr.*, **A58**, 133 (2002).

2 Y. Ozawa, M. Terashima, M. Mitsumi, K. Toriumi, N. Yasuda, H. Uekusa, and Y. Ohashi, *Chem. Lett.*, **32**, 62 (2003).

3 P. Coppens, O. Gerlits, I. I. Vorontsov, A. Y. Kovalevsky, Y.-S. Chen, T. Graber, M. Gembickey, and I. V. Novozhilova, *Chem. Commun.*, **2004**, 2144.

4 P. Coppens, I. I. Vorontsov, T. Graber, M. Gembickey, and A. Y. Kovalevsky, *Acta Crystallogr.*, **A61**, 162 (2005).

5 N. Yasuda, H. Uekusa, and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, **77**, 933 (2004).

6 M. Hoshino, H. Uekusa, and Y. Ohashi, *Chem. Commun.*, **2005**, in contribution.

7 a) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962). b) S. D. Bella, G. Lenza, A. Gulino, and I. Fragalà, *Inorg. Chem.*, **35**, 3885 (1996).

8 R. A. Rowe and M. M. Jones, *Inorg. Synth.*, **5**, 113 (1957).

9 The light from a Hg lamp was brought to the crystal on the diffractometer using a glass fiber (emission lines are 410 and 443 nm, corresponding with the absorption band of VO(acac)$_2$).

10 Formula $C_{10}H_{14}O_5V_1$; $M_r = 265.15$; triclinic; space group $P\bar{1}$ (No. 2); $Z = 2$. Each structure was solved by the direct method (SHELXS-97) and refined by the full-matrix least-squares method (SHELXL-97). All atoms were found in the difference Fourier map. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 278182–278191. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

11 Since the crystal was stored in the cold N_2 gas stream and was in the thermodynamically equilibrium state, the temperature increase caused by the radiationless transition during the data collection may be a few degree, considering from the thermal conductivity of the crystal.

12 Crystal size = $0.25 \times 0.25 \times 0.10\,\text{mm}^3$, $T = 141(2)$ K. (light-off stage) $a = 7.3529(1)$, $b = 8.1521(2)$, $c = 11.1916(2)$ Å, $\alpha = 72.886(1)$, $\beta = 72.175(1)$, $\gamma = 66.911(1)°$, $V = 575.72(2)$ Å^3, $R\ [I > 2\sigma(I)] = 0.0256$, $Rw\ [I > 2\sigma(I)] = 0.0754$, Goodness of fit = 1.074. (light-on stage) $a = 7.3731(2)$, $b = 8.1726(2)$, $c = 11.2215(1)$ Å, $\alpha = 72.842(1)$, $\beta = 72.124(1)$, $\gamma = 66.866(1)°$, $V = 579.92(2)$ Å^3, $R\ [I > 2\sigma(I)] = 0.0254$, $Rw\ [I > 2\sigma(I)] = 0.0746$, Goodness of fit = 1.065. Data collection and structure analysis were performed in the same way.

Published on the web (Advance View) July 30, 2005; DOI 10.1246/cl.2005.1228