Bull. Chem. Soc. Jpn., **68**, 2847—2852(1995)

Dioxotungsten(VI) Complexes of ONO Donor Ligands and the X-Ray Crystal Structure of $[WO_2(o\text{-}OC_6H_4CH{=}NN{=}C(O)C_6H_5)(MeOH)]\cdot MeOH$

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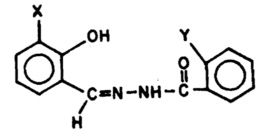
(Received March 22, 1995)

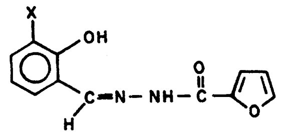
A general method for the preparation of dioxotungsten(VI) complexes of the type $[WO_2L(MeOH)]$ (where LH_2=the Schiff's base derived from salicylaldehyde or *o*-vanillin and benzoylhydrazide, salicylhydrazide, furoylhydrazide, and isonicotinoylhydrazide) using $[WO_2(acac)_2]$ (acacH=acetylacetone) as a precursor, is described. These complexes have been characterized by elemental analysis, electrical conductance, IR, electronic, and NMR spectral, electrochemical, and magnetic susceptibility measurements. The structure of $[WO_2(o\text{-}C_6H_4CH{=}NN{=}C(O)C_6H_5)(MeOH)]\cdot MeOH$ (**1a**·MeOH) has been determined by single-crystal X-ray diffraction analysis. **1a**·MeOH crystallizes in the space group $Pbc2_1$ with a=6.992(2), b=16.190(2), c=31.390(4) Å, V=3553.4(12) Å^3, Z=8, R_F=0.050, and R_w=0.054. The tungsten atom has a highly distorted octahedral coordination in which anionic oxygen atoms of the tridentate ligand are mutually *trans* and are *cis* to the *cis*-dioxo group.

Amongst the d^0 ions of chromium group metals, the chemistry of dioxomolybdenum(VI) complexes has been extensively studied possibly due to the presence of this cation in the oxidized form of certain molybdoenzymes.[1] The active site of oxo-transfer molybdoenzymes, viz. sulfite and aldehyde oxidase, xanthine oxidase, nitrate reductase, and xanthine dehydrogenase, has also been modeled using some *cis*-dioxomolybdenum(VI) complexes.[2] However, such dioxotungsten(VI) complexes are very limited; they are mostly organometallics[3] and only a few studies dealing with the dioxotungsten(VI) complexes of Schiff's base ligands[4—7] have been reported. The main reason for the lack of dioxotungsten(VI) complexes is the nonavailability of a suitable starting material. Yamanouchi et al.[4,5] have used WO_2Cl_2 or $WOCl_4$ as a starting material while we tried the reactivity of Na_2WO_4 towards Schiff's bases in aqueous medium with limited success.[6] Recently Yu and Holm[7] have successfully used $[WO_2(acac)_2]$ (acacH=acetylacetone) to prepare dioxotungsten(VI) complexes. The versatility of other similar precursors having coordinated acetylacetone groups, like $[MoO_2(acac)_2]$ for the synthesis of dioxomolybdenum(VI) complexes,[8] $[UO_2(acac)_2]$ for dioxouranium(VI),[9] and even $[Mo(NO)_2(acac)_2]$ for dinitrosylmolybdenum(0) complexes,[10] are well established and documented in the literature.

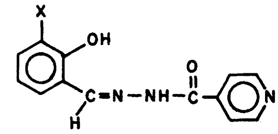
To establish the suitability of $[WO_2(acac)_2]$ as a precursor and explore the chemistry of several dioxotungsten(VI) complexes, we have studied its reactivity towards Schiff's bases **I**, **II**, and **III** (Chart 1). The dioxotungsten(VI) complexes studied here were isolated in a single-step process. A single-crystal X-ray analysis



(I)



(II)



(III)

No.	Ligand	X	Y	Abbreviation
1	I	H	H	H_2sal-BZH
2	I	OMe	H	H_2van-BZH
3	I	H	OH	H_2sal-SZH
4	I	OMe	OH	H_2van-SZH
5	II	H	—	H_2sal-FAH
6	II	OMe	—	H_2van-FAH
7	III	H	—	H_2sal-INH
8	III	OMe	—	H_2van-INH

Chart 1.

of one representative complex is also reported.

Experimental

General. All chemicals and solvents were procured from standard sources. Salicylaldehyde and acetylacetone were distilled under reduced pressure before use. [WO_2(acac)$_2$] was prepared following the method described by Yu and Holm.[7] The Schiff's bases were prepared by the literature methods.[11]

Preparation of [WO_2L(MeOH)]: A General Method. The appropriate Schiff's base (1 mmol) was dissolved in 25 cm^3 of methanol (Schiff's bases derived from salicylhydrazide required more solvent) by heating in a water bath. A solution of [WO_2(acac)$_2$] (0.44 g, 1 mmol) in 10 cm^3 of methanol was added to the above solution with vigorous shaking and then filtered. The filtrate was refluxed on a water bath for 6 h. After reducing the solvent to ca. 10 cm^3, the solution was cooled to 10 °C overnight and the colored precipitates which separated were filtered, washed with methanol, and dried in vacuo; yield: 90—95 %.

The analytical and physicochemical data of the complexes are presented in Tables 1, 2, and 3.

Measurements. Elemental analyses were performed by the microanalytical section of the National Chemical Laboratory. Details of other techniques are reported in our earlier papers.[12]

X-Ray Data Collection and Analysis. A single crystal of [WO_2(sal-BZH)(MeOH)]·MeOH suitable for X-ray structure determination was grown by slow evaporation of a MeOH solution of [WO_2(sal-BZH)(MeOH)] at room temperature. A bright yellow crystal having dimensions of 0.2×0.4×1.2 mm was mounted on a glass fiber for data collection. Accurate unit cell parameters were determined by a least squares fit of 25 machine-centered reflec-

Table 1. Analytical and Physicochemical Data of the Ligands and Complexes[a)]

S. no.	Compound stoichiometry	Color	Found (Calcd)/% C	 H	 N	Λ_M Ω^{-1} cm^2 mol^{-1}
1a	[WO_2(sal-BZH)(MeOH)] $C_{15}H_{14}N_2O_5W$	Yellow	36.91 (37.06)	2.95 (2.90)	5.52 (5.76)	11
2a	[WO_2(van-BZH)(MeOH)] $C_{16}H_{16}N_2O_6W$	Brown	37.41 (37.23)	3.33 (3.12)	5.19 (5.43)	20
3a	[WO_2(sal-SZH)(MeOH)] $C_{15}H_{14}N_2O_6W$	Yellow	35.97 (35.88)	2.63 (2.81)	5.32 (5.58)	13
4a	[WO_2(van-SZH)(MeOH)] $C_{16}H_{16}N_2O_7W$	Brown	36.35 (36.11)	3.14 (3.03)	5.33 (5.26)	12
5a	[WO_2(sal-FAH)(MeOH)] $C_{13}H_{12}N_2O_6W$	Yellow	32.59 (32.79)	2.54 (2.54)	5.87 (5.88)	14
6a	[WO_2(van-FAH)(MeOH)] $C_{14}H_{14}N_2O_7W$	Yellow	33.00 (33.22)	2.58 (2.79)	5.36 (5.54)	13
7a	[WO_2(sal-INH)(MeOH)] $C_{14}H_{13}N_3O_5W$	Yellow	34.50 (34.52)	2.61 (2.69)	8.45 (8.63)	12
8a	[WO_2(van-INH)(MeOH)] $C_{15}H_{15}N_3O_6W$	Orange	34.81 (34.84)	2.82 (2.92)	8.41 (8.13)	12

a) Abbreviations; As under Chart 1.

Table 2. IR and Electronic Spectral Data

Compound	IR/cm^{-1} ν(C=O)	 ν(C=N)	 ν_{sym}(O=W=O)	 ν_{asym}(O=W=O)	λ_{max} (ε/l mol^{-1} cm^{-1}) nm
1	1671	1604			380(3050), 327(30500), 298(38300), 286(36950)
1a		1601	928	896	392(4300), 326(24000), 297(29950), 286(30150)
2	1668	1622			348(16900), 317(33850)
2a		1595	944	890	380(13550), 362(19200), 349(19600), 315(31750)
3	1654	1617			380(21850), 362(28850), 349(29500), 301(22900)
3a		1602	949	899	381(4600), 333(14950), 290(14100)
4	1648	1606			380(28800), 365(40450), 349(41400), 316(48350)
4a		1594	917	875	368(5600), 313(14100)
5	1650	1605			328(18200), 300(23900), 289(21100)
5a		1599	910	880	378(2600), 328(18600), 300(25500), 289(23500)
6	1673	1611			341(26100), 311(69750), 303(74300)
6a		1599	951	908	341(15600), 312(35900), 302(38250)
7	1680	1610			332(19950), 300(20200), 289(21300)
7a		1601	930	915	402(2350), 330(21900), 298(24200), 288(27000)
8	1609	1603			342(21550), 305(46650)
8a		1600	948	909	412(1300), 336(12900), 303(30500)

Table 3. ^{1}H NMR Spectral Data (δ in ppm)[a]

Compound	–CH=N–	$–OCH_3$	$–CH_3$	–NH	–OH
1	8.60 (s, 1H)			11.30 (s, 1H)	12.10 (s, 1H)
1a	8.95 (s, 1H)		3.30 (s, 3H)		
3	8.76 (s, 1H)			10.86 (s, 1H)	11.64 (s, 2H)
3a	9.10 (s, 1H)		3.15 (s, 3H)		11.25 (s, 1H)
4	8.68 (s, 1H)	3.74 (s, 3H)		10.84 (s, 1H)	12.18 (s, 2H)
4a	9.05 (s, 1H)	3.85 (s, 3H)	b)		11.25 (s, 1H)
5	8.65 (s, 1H)			11.15 (s, 1H)	12.10 (s, 1H)
5a	8.95 (s, 1H)		3.20 (s, 3H)		
6	8.60 (s, 1H)	3.85 (s, 3H)		11.75 (b, 1H)	12.05 (b, 1H)
6a	8.85 (s, 1H)	3.80 (s, 3H)	3.15 (s, 3H)		
7	8.70 (s, 1H)			11.15 (b, 1H)	12.28 (b, 1H)
7a	9.05 (s, 1H)		3.20 (s, 3H)		
8	8.71 (s, 1H)	3.83 (s, 3H)		10.71 (s, 1H)	12.27 (s, 1H)
8a	9.00 (s, 1H)	3.85 (s, 3H)	3.20 (s, 3H)		

a) Letters given in parentheses indicate the type of signal. s=singlet, b=broad. b) CH_3 of MeOH resonance appears underneath of DMSO resonance.

tions 30<2θ<44°. Data were collected at 293 K on a Nonius CAD-4F single crystal X-ray diffractometer using Mo $K\alpha$ radiation (λ=0.7107 Å). Three standard reflections measured after every hour showed < 4% variation in average intensity. The structure was solved by direct methods using MULTAN-80. Least squares refinement of the scale factor and positional and anisotropic thermal parameters for nonhydrogen atoms converged to a final R=0.050. Weights based on counting statistics were used. Coordinates of hydrogen atoms were geometrically determined and held fixed during the refinement. The hydrogen atom scattering contribution was included in all subsequent calculations. For structure solution and refinement, NRCVAX programs were used.[13] The crystal data, data collection, and refinement parameters are summarized in Table 4. Final atomic parameters along with their esd's and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 5. Table 6 gives bond lengths and bond angles. The complete F_o-F_c data are deposited as Document No. 68048 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Synthesis of Metal Complexes. The use of $[WO_2(acac)_2]$ as a starting material for the dioxotungsten(VI) complexes has only recently been reported.[7] $[WO_2(acac)_2]$ undergoes ligand exchange reactions with the Schiff's bases **I**, **II**, and **III** in refluxing methanol to yield the corresponding dioxotungsten(VI) complexes of the type $[WO_2L(MeOH)]$ (where LH_2=a Schiff's base) as follows:

$$[WO_2(acac)_2] + LH_2 \xrightarrow{MeOH} [WO_2L(MeOH)] + 2\ acacH$$

Under the present reaction conditions, complete removal of two bidentate acetylacetone groups occurs; as the Schiff's bases are tridentate, the sixth position is occupied by the solvent. The analytical data support the above formulation of the complexes. These complexes are soluble in coordinating solvents like methanol, ethanol, pyridine, DMF, and DMSO.

Table 4. Crystal and Refinement Data for **1a**·MeOH

Molecular formula	$C_{16}H_{18}N_2O_6W$
Formula weight	518.2
Crystal dimension	0.2×0.4×1.2 mm
Crystal color	Bright yellow
Space group	$Pbc2_1$
Cell dimensions	
a/Å	6.992(2)
b/Å	16.190(2)
c/Å	31.390(4)
Cell volume/Å^3	3553.4(12)
Z	8
F(000)	1999
D_{calcd}/g cm^{-3}	1.937
Temperature/K	293
Radiation	Graphite monochromated Mo $K\alpha$ radiation (λ=0.7107 Å)
μ(Mo $K\alpha$)/mm^{-1}	6.67
Scan technique	ω–2θ
Scan speed/° min^{-1}	1
Scan width/°	0.80+0.35 tan θ
Scan range/°	0<2θ<47
Total no. of unique reflections	2659
Cut of observed data	3.5σ(I)
No. of observed reflections	2242
No. of parameters refined	450
R_F[a] and R_w[b]	0.050 and 0.054

a) $R_F=(\Sigma||F_o|-k|F_c||)/\Sigma|F_o|$. b) $R_w=[\Sigma w\ (|F_o|-k|F_c|)^2/\Sigma(|F_o|^2)]^{1/2}$. Weights based on counting statistics were used.

All the complexes are non-electrolytes (11—20 ohm^{-1} mol^{-1} cm^2) in DMF and are diamagnetic as expected for the 5d^0 tungsten ion. The thermal analysis data for $[WO_2(sal\text{-}INH)(MeOH)]$ shows a well-defined endothermic step at around 200 °C, corresponding to the loss of one molecule of methanol. This information

Table 5. Atomic Parameters x, y, z, and B_{iso} for **1a**·MeOH with esd's in Parentheses

Atom	x	y	z	$B_{\mathrm{iso}}/\mathrm{\AA}^2$
W1	.1667(1)	.21194(7)	.19047(0)	2.80(5)
O1	.240(2)	.129(1)	.1688(6)	3.9(9)
O2	.359(2)	.276(1)	.2037(6)	3.8(10)
O3	.128(3)	.157(1)	.2468(6)	5.1(11)
O4	.053(2)	.271(1)	.1424(6)	4.3(10)
O5	.003(3)	.317(1)	.2261(7)	4.8(10)
N1	−.141(2)	.166(1)	.1947(7)	2.5(9)
N2	−.172(3)	.117(1)	.2316(7)	3.1(10)
C1	−.098(4)	.261(2)	.1144(9)	3.2(13)
C2	−.085(4)	.308(2)	.0786(10)	4.0(14)
C3	−.250(5)	.303(2)	.0536(9)	4.4(16)
C4	−.415(4)	.259(2)	.0641(10)	4.5(16)
C5	−.412(4)	.213(2)	.1003(10)	4.0(15)
C6	−.258(4)	.213(2)	.1290(9)	3.5(14)
C7	−.265(3)	.166(2)	.1661(9)	3.2(13)
C8	−.022(4)	.118(2)	.2585(9)	3.3(14)
C9	−.025(4)	.076(2)	.2991(9)	3.3(13)
C10	−.201(5)	.046(2)	.3143(10)	4.7(16)
C11	−.199(4)	.004(2)	.3505(11)	5.0(17)
C12	−.034(6)	−.004(2)	.3753(12)	7.0(22)
C13	.143(5)	.024(2)	.3602(11)	5.9(20)
C14	.141(5)	.066(2)	.3216(11)	5.1(18)
C15	.081(5)	.377(2)	.2534(10)	5.3(18)
O6	.138(3)	.121(1)	.4755(8)	6.6(15)
C16	.086(5)	.199(2)	.4600(13)	7.2(22)
W1′	.3648(1)	.04101(7)	.99584(5)	2.67(4)
O1′	.295(3)	.126(1)	1.0179(7)	4.8(11)
O2′	.172(3)	−.021(1)	.9827(6)	3.9(9)
O3′	.408(3)	.101(1)	.9414(6)	4.5(10)
O4′	.472(3)	−.018(1)	1.0430(6)	4.0(10)
O5′	.521(3)	.938(1)	.9585(6)	3.6(9)
N1′	.665(2)	.084(1)	.9908(7)	2.8(10)
N2′	.714(3)	.128(2)	.9543(7)	3.6(12)
C1′	.622(4)	−.007(2)	1.0703(9)	3.8(15)
C2′	.609(4)	−.055(2)	1.1074(9)	4.2(16)
C3′	.767(4)	−.051(2)	1.1373(10)	4.6(17)
C4′	.925(4)	−.007(2)	1.1258(9)	4.0(15)
C5′	.942(4)	.038(2)	1.0882(9)	3.6(14)
C6′	.780(4)	.035(2)	1.0602(8)	2.7(12)
C7′	.802(4)	.082(2)	1.0204(8)	2.8(12)
C8′	.565(4)	.130(2)	.9295(9)	3.7(15)
C9′	.573(4)	.175(2)	.8885(9)	2.8(12)
C10′	.753(4)	.197(2)	.8703(10)	4.5(16)
C11′	.761(4)	.236(2)	.8317(11)	5.7(19)
C12′	.588(5)	.254(2)	.8116(10)	5.8(20)
C13′	.415(5)	.233(2)	.8267(10)	5.0(18)
C14′	.407(5)	.194(2)	.8658(10)	5.0(17)
C15′	.442(4)	.876(2)	.9369(10)	4.4(16)
O6′	.667(3)	.375(1)	.2077(8)	6.0(12)
C16′	.620(5)	.452(2)	.2242(13)	6.0(19)

is in agreement with the coordination of the methanol molecule at the sixth position of the metal complex.

Spectral Studies. A partial listing of the IR spectra of the ligands (**1**, **2**, **3**, **4**, **5**, **6**, **7**, and **8**) and their complexes (**1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a**, and **8a**) is given in Table 2. All the complexes exhibit two bands in the regions 910—950 and 875—920 cm^{-1}, due to the ν_{sym} and ν_{asym}(O=W=O) modes, respectively. These observations suggest the presence of a *cis*-$\mathrm{WO_2}$ structure as the *trans*-$\mathrm{WO_2}$ structure would show only one ν(O=W=O) band due to the asymmetric stretch.[8)]

The Schiff's bases exhibit a broad band at around 2700 cm^{-1} attributable to the intramolecularly hydrogen-bonded phenolic hydroxyl group. The absence of this band in the spectra of the complexes suggests the deprotonation of the phenolic group and subsequent coordination of the oxygen to the tungsten. A new broad band which appears in [$\mathrm{WO_2L(MeOH)}$] at around 3400 cm^{-1} may be due to the ν(OH) of the coordinated methanol. This is further supported by the appearance of another new band at 970—1000 cm^{-1} due to the ν(C–O) stretch; the ν(C–O) band in methanol occurs at 1034 cm^{-1}. The ν(C=N) band of the ligand which appears at 1603—1622 cm^{-1}, shifts to a lower frequency by 3—27 cm^{-1} in the complexes, indicating the coordination of the azomethine nitrogen.[14)] The Schiff's bases exhibit the ν(C=O) band at 1640—1680 cm^{-1} and this band is absent in the spectra of the complexes indicating the destruction of the carbonyl moiety due to enolization and subsequent proton replacement with the tungsten. A new band appearing in the region 1250—1275 cm^{-1} is assigned to the ν(C–O) (enolic) mode.

These Schiff's bases exhibit two to four electronic spectral bands which are also observed in the complexes (see Table 2). In addition, the complexes obtained from isonicotinoylhydrazone exhibit a new band at ca. 405 nm which is assigned to the ligand → metal charge transfer (lmct) transition between the lowest empty d-orbital of tungsten and the highest occupied ligand molecular orbital. However, in other complexes, such an lmct band could not be located, probably due to merging of this band with those of the ligand.

The ^{1}H NMR spectra of the Schiff's bases (**1**, **3**, **4**, **5**, **6**, **7**, and **8**) and their complexes (**1a**, **3a**, **4a**, **5a**, **6a**, **7a**, and **8a**) were recorded in DMSO-d_6. The chemical shifts (δ in ppm) relative to DMSO (2.40 ppm) are summarized in Table 3. All the Schiff's bases exhibit a signal at 10.71—11.30 ppm due to the –NH proton which suggests the ligands are in the keto form. Absence of this resonance upon complexation indicates the enolization of the keto group and subsequent coordination of the enolic oxygen after proton replacement. Similarly, the absence of the phenolic proton signal in the spectra of the complexes indicates the coordination of the phenolic oxygen atom. However, in the complexes obtained from salicylhydrazone Schiff's bases, the presence of a singlet at 11.2 ppm (1H) indicates the existence of one still-free hydroxyl group in these complexes. The sharp singlet due to the azomethine proton shifts downfield and suggests the coordination of the azomethine nitrogen.[15)]

Electrochemical Properties. The cyclic voltammograms (CV) of [$\mathrm{WO_2}$(sal-INH)(MeOH)] (**7a**) and [$\mathrm{WO_2}$(van-INH)(MeOH)] (**8a**) were recorded in DMF

Table 6. Bond Distances (Å) and Bond Angles (°) with esd's in Parentheses

W(1)–O(1)	1.59(2)	W(1′)–O(1′)	1.61(2)	O(5)–W(1)–O(3)	80.6(8)	O(5′)–W(1′)–O(3′)	81.3(8)
W(1)–O(2)	1.74(2)	W(1′)–O(2′)	1.73(2)	O(5)–W(1)–O(4)	79.4(8)	O(5′)–W(1′)–O(4′)	81.1(8)
W(1)–O(3)	2.00(2)	W(1′)–O(3′)	1.99(2)	O(2)–W(1)–N(1)	154.9(8)	O(2′)–W(1′)–N(1′)	154.4(9)
W(1)–O(4)	1.95(2)	W(1′)–O(4′)	1.92(2)	O(3)–W(1)–O(4)	147.6(8)	O(3′)–W(1′)–O(4′)	148.2(8)
W(1)–O(5)	2.34(2)	W(1′)–O(5′)	2.31(2)	O(3)–W(1)–N(1)	71.0(8)	O(3′)–W(1′)–N(1′)	69.0(8)
W(1)–N(1)	2.28(2)	W(1′)–N(1′)	2.22(2)	O(4)–W(1)–N(1)	79.5(8)	O(4′)–W(1′)–N(1′)	81.0(8)
O(3)–C(8)	1.27(3)	O(3′)–C(8′)	1.25(3)	O(5)–W(1)–N(1)	75.4(8)	O(5′)–W(1′)–N(1′)	75.1(8)
O(4)–C(1)	1.38(3)	O(4′)–C(1′)	1.37(3)	W(1)–O(3)–C(8)	126(2)	W(1′)–O(3′)–C(8′)	125(2)
O(5)–C(15)	1.40(3)	O(5′)–C(15′)	1.34(3)	W(1)–O(4)–C(1)	139(2)	W(1′)–O(4′)–C(1′)	136(2)
N(1)–N(2)	1.42(3)	N(1′)–N(2′)	1.39(3)	W(1)–O(5)–C(15)	127(1)	W(1′)–O(5′)–C(15′)	128(2)
N(1)–C(7)	1.25(3)	N(1′)–C(7′)	1.34(3)	W(1)–N(1)–N(2)	112(1)	W(1′)–N(1′)–N(2′)	117(2)
N(2)–C(8)	1.34(4)	N(2′)–C(8′)	1.30(3)	W(1)–N(1)–C(7)	128(2)	W(1′)–N(1′)–C(7′)	128(2)
C(1)–C(2)	1.36(4)	C(1′)–C(2′)	1.40(4)	N(2)–N(1)–C(7)	119(2)	N(2′)–N(1′)–C(7′)	115(2)
C(1)–C(6)	1.43(4)	C(1′)–C(6′)	1.34(4)	N(1)–N(2)–C(8)	113(2)	N(1′)–N(2′)–C(8′)	108(2)
C(2)–C(3)	1.40(4)	C(2′)–C(3′)	1.45(4)	O(4)–C(1)–C(2)	114(2)	O(4′)–C(1′)–C(2′)	113(3)
C(3)–C(4)	1.39(4)	C(3′)–C(4′)	1.36(4)	O(4)–C(1)–C(6)	117(2)	O(4′)–C(1′)–C(6′)	123(3)
C(4)–C(5)	1.36(4)	C(4′)–C(5′)	1.40(4)	C(2)–C(1)–C(6)	128(3)	C(2′)–C(1′)–C(6′)	122(3)
C(5)–C(6)	1.41(4)	C(5′)–C(6′)	1.43(4)	C(1)–C(2)–C(3)	112(3)	C(1′)–C(2′)–C(3′)	117(3)
C(6)–C(7)	1.39(4)	C(6′)–C(7′)	1.47(4)	C(2)–C(3)–C(4)	125(3)	C(2′)–C(3′)–C(4′)	118(3)
C(8)–C(9)	1.45(4)	C(8′)–C(9′)	1.48(4)	C(3)–C(4)–C(5)	117(3)	C(3′)–C(4′)–C(5′)	124(3)
C(9)–C(10)	1.41(4)	C(9′)–C(10′)	1.43(4)	C(4)–C(5)–C(6)	123(3)	C(4′)–C(5′)–C(6′)	116(2)
C(9)–C(14)	1.37(4)	C(9′)–C(14′)	1.40(4)	C(1)–C(6)–C(5)	113(3)	C(1′)–C(6′)–C(5′)	122(2)
C(10)–C(11)	1.32(4)	C(10′)–C(11′)	1.37(4)	C(1)–C(6)–C(7)	126(3)	C(1′)–C(6′)–C(7′)	123(2)
C(11)–C(12)	1.40(6)	C(11′)–C(12′)	1.40(5)	C(5)–C(6)–C(7)	121(3)	C(5′)–C(6′)–C(7′)	115(2)
C(12)–C(13)	1.40(5)	C(12′)–C(13′)	1.34(5)	N(1)–C(7)–C(6)	125(2)	N(1′)–C(7′)–C(6′)	122(2)
C(13)–C(14)	1.39(4)	C(13′)–C(14′)	1.38(4)	O(3)–C(8)–N(2)	118(2)	O(3′)–C(8′)–N(2′)	120(3)
O(6)–C(16)	1.40(4)	O(6′)–C(16′)	1.40(4)	O(3)–C(8)–C(9)	120(2)	O(3′)–C(8′)–C(9′)	118(2)
				N(2)–C(8)–C(9)	122(2)	N(2′)–C(8′)–C(9′)	120(2)
O(1)–W(1)–O(2)	110.8(9)	O(1′)–W(1′)–O(2′)	111.3(9)	C(8)–C(9)–C(10)	118(3)	C(8′)–C(9′)–C(10′)	120(2)
O(1)–W(1)–O(3)	92.4(9)	O(1′)–W(1′)–O(3′)	89.8(10)	C(8)–C(9)–C(14)	119(3)	C(8′)–C(9′)–C(14′)	122(2)
O(1)–W(1)–O(4)	102.3(9)	O(1′)–W(1′)–O(4′)	102.3(9)	C(10)–C(9)–C(14)	121(3)	C(10′)–C(9′)–C(14′)	118(3)
O(1)–W(1)–N(1)	93.0(8)	O(1′)–W(1′)–N(1′)	92.8(8)	C(9)–C(10)–C(11)	117(3)	C(9′)–C(10′)–C(11′)	120(3)
O(2)–W(1)–O(3)	99.2(8)	O(2′)–W(1′)–O(3′)	101.5(8)	C(10)–C(11)–C(12)	122(3)	C(10′)–C(11′)–C(12′)	117(3)
O(2)–W(1)–O(4)	102.2(8)	O(2′)–W(1′)–O(4′)	101.3(8)	C(11)–C(12)–C(13)	120(3)	C(11′)–C(12′)–C(13′)	124(3)
O(5)–W(1)–O(1)	167.8(8)	O(5′)–W(1′)–O(1′)	166.9(8)	C(12)–C(13)–C(14)	116(3)	C(12′)–C(13′)–C(14′)	118(3)
O(5)–W(1)–O(2)	80.3(8)	O(5′)–W(1′)–O(2′)	80.0(8)	C(9)–C(14)–C(13)	120(3)	C(9′)–C(14′)–C(13′)	120(3)

using 0.1 M tetrabutylammonium perchlorate (1 M=1 mol dm^{-3}) as a supporting electrolyte. Both complexes show a quasireversible wave with a peak separation of 260 and 480 mV at E_{pc} values of −1.48 and −1.0 V, respectively, vs. SCE. The cyclic voltammogram of **8a** is presented in Fig. 1. A comparison of the electrochemical data (peak potential) available for similar dioxotungsten(VI) complexes suggests that this is probably due to a W(VI)/W(IV) transition.[3b)] An attempt to do coulometry and isolate the W(IV) complexes was not successful due to decomposition of the latter.

Crystal Structure of [WO$_2$(sal-BZH)(MeOH)]·MeOH. The X-ray diffraction study of the complex [WO$_2$(sal-BZH)(MeOH)] (**1a**) revealed that the asymmetric unit consists of two molecules of the coordinated complex along with a solvated methanol and these are related by a pseudocenter. An ORTEP diagram of one of the molecules in the asymmetric unit along with a solvent molecule and the crystallographic numbering of the atoms is shown in Fig. 2. The complex contains a usual *cis*-dioxo group and a *mer* arrangement of the tridentate ONO donor ligand, whose anionic oxygen atoms are mutually *trans* and are *cis* to the two oxo ligands. A similar arrangement has also been found in [WO$_2$(5-*t*-butsal-OAP)(MeOH)] (where 5-*t*-butH$_2$sal-OAP=Schiff's base

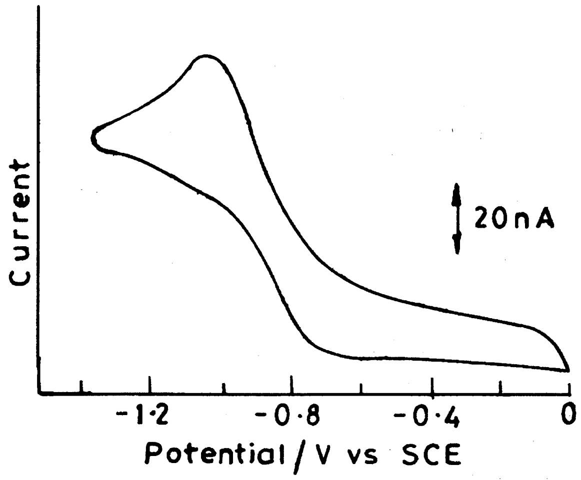


Fig. 1. Cyclic voltammogram (1×10^{-3} M in DMF) of [WO$_2$(van-INH)(MeOH)] at scan rate of 500 mV s^{-1}.

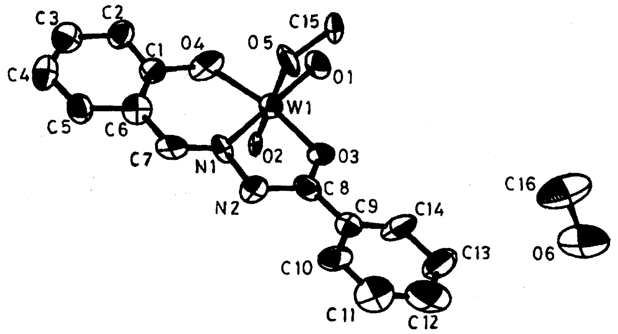


Fig. 2. ORTEP diagram of **1a**·MeOH (one of the two molecules in asymmetric unit) along with the crystallographic numbering. Ellipsoids are drawn with 50% probability.

derived from 5-*t*-butylsalicylaldehyde and *o*-aminophenol).[7] The X-ray structure also shows that the ligand H_2sal-BZH forms one five-membered ring and one six-membered ring. The sixth coordination site around the tungsten is occupied by a methanol molecule which is *trans* to the oxygen of the dioxo group. Thus, tungsten has a distorted octahedral coordination. The *cis* bond angles range from 79.4(8) to 111.3(9)° and the *trans* angles from 147.6(8) to 167.8(8)°. These distortions are probably due to the incorporation of tungsten into the five-membered ring. Thus, the structure also resembles that of the known *cis*-dioxomolybdenum(VI) complexes, [MoO_2(sal-INH)(MeOH)][16] and [MoO_2(5-*t*-butsal-OAP)(MeOH)].[17] The W–O single-bond distances are comparable to those found in other related complexes and even in W(VI) alkoxides.[7,18] The W=O bond lengths are 1.59(2) and 1.74(2) Å. An interesting feature is the 0.15 Å difference in the bond lengths of the two W=O bonds; a similar difference of 0.12 Å has also been observed in the structure of [WO_2(5-*t*-butsal-OAP)(MeOH)].[7] This structure is stabilized by intermolecular hydrogen bonding between the oxygen of the solvent molecule and that of the coordinated methanol [O(6′)···O(5) $(1+x, y, z)$=2.591(9) Å; O(6)···O(5′) $(\bar{x}, \bar{y}, 1/2+z)$=2.624(8) Å] and the bifurcated hydrogen bonding between the oxygen of the solvent methanol and the oxygen of one of the dioxo groups [O(6)···O(2′) $(\bar{x}, \bar{y}, 1/2+z)$=2.723(9) Å].

The authors are grateful to Dr. K. Vijaya Mohanan, National Chemical Laboratory, for carrying out the cyclic voltammetry measurements. M. R. M. acknowledges the encouragement received from the Head of the Chemistry Department.

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