Table I. 360-MHz ^{1}H NMR Data^a for the [Co(acac)(dqpn')]$^+$ Diastereoisomers

isomer	acac^b CH$_3$	acac^b CH'$_3$	acac^b CH	dqpn^b CH$_3$	acac^c CH$_3$	acac^c CH'$_3$	acac^c CH	dqpn^c CH$_3$
Δ-β-exo	1.973	1.761	5.633	1.820 (J = 6.78)	1.998	1.772	5.683	1.626 (J = 6.74)
Δ-β-endo	2.092	1.783	5.670	0.437 (J = 6.77)	2.102	1.784	5.691	0.266 (J = 6.66)
Λ-β-exo	*d*	1.875	5.715	1.536 (J = 6.83)	2.067	1.882	5.755	1.352 (J = 6.62)
Λ-β-endo	*d*	1.977	5.770	1.573 (J = 5.79)	2.067	1.973	5.797	1.452 (J = 5.71)

^{a} Chemical shifts in ppm relative to Me$_4$Si as internal standard; coupling constants in Hz. ^{b} In acetone-d_6. ^{c} In Me$_2$SO-d_6. ^{d} Obscured by solvent signals.

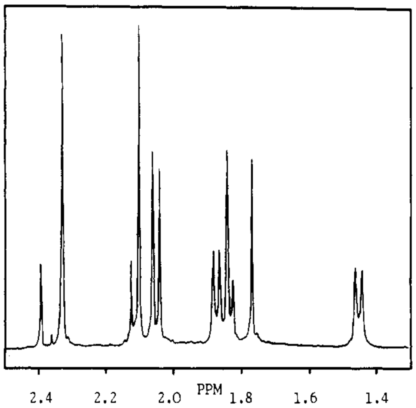

Figure 2. 360-MHz ^{1}H NMR spectrum of the methyl region of Δ,Λ-β-*exo,endo*-[Co(acac)(R-dqpn')]ClO$_4$ dissolved in 6.0 M DCl.

mers (and their mirror images) and these must be the species that have opposite absolute configuration for the nitrogen atom remote from the fold of the tetradentate. Reference to the reported[4] spectra of the latter complex in acetone-d_6 and 12 M DCl shows that only two such singlets are found. This observation is in accord with the conformational requirements of the R,R-chxn section of the ligand. Furthermore, the results show that under the conditions used to isolate [Co(acac)-(R,R-dqchxn')ClO$_4$, stereospecific coordination is enforced. This is analogous to findings for related Co(III) complexes of N,N'-di-2-picolyl-(R,R)-1,2-diaminocyclohexane.[8]

With these conclusions in mind, we recorded the 360-MHz ^{1}H NMR spectrum of [Co(acac)(R-dqpn')]ClO$_4$ in 6 M DCl, the aliphatic region of which is shown in Figure 2. Eight diastereomers are possible for β-[Co(acac)(R-dqpn)]$^{2+}$, of which only four are observed. Clearly the conformational preference, together with steric influences, dictates each isomer's preferred topology. In DCl solution eight separate acac methyl singlets are observed. Integration of the other signals arising from dqpn methyl resonances allows these to be assigned to corresponding isomers; two of these signals overlap at 1.872 ppm. Furthermore, the diastereoisomer distribution in 6 M DCl is found to be 0.23:0.76:0.48:0.52 ± 0.04, which is the same within experimental error as that for the deprotonated analogues. We thus conclude that no redistribution of the coordination spheres occurs. Assignments of chemical shifts in Table II are in accordance with this isomer distribution.

Table II. 360-MHz ^{1}H NMR Data^a for the [Co(acac)(R-dqpn)]$^{2+}$ Diastereoisomers in 6.0 M DCl

isomer	acac CH$_3$	acac CH'$_3$	dqpn CH$_3$
Δ-β-exo	2.059	1.768	1.831 (J = 5.53)
Δ-β-endo	2.038	1.839	1.872 (J = 6.25)
Λ-β-exo	2.327	2.100	1.450 (J = 6.74)
Λ-β-endo	2.392	2.123	1.872 (J = 6.25)

^{a} Chemical shifts in ppm relative to DSS as internal standard; coupling constants in Hz.

The dqpn methyl resonance of the Δ-β-exo complex shifts to lower field upon protonation. Molecular models show that if the in-plane amine nitrogen adopts the R configuration, the methyl group would still be significantly shielded. We thus conclude that the Δ-β-*endo*-S,S-[Co(acac)(R-dqpn)]$^{2+}$ ion forms stereospecifically with respect to the R,S isomer by virtue of the fact that no dqpn methyl resonances occur above 1.4 ppm. In contrast, the Δ-β-exo complex cannot adopt the S,S arrangement because of severe repulsive interactions between the methyl group, lying equatorially, and H(7) of the adjacent quinolyl ring. Quite the same interaction is evident in models of the Λ-β-endo complex, which is that species least populated in the crystal structure of the four [Co(acac)(R-dqpn')]$^+$ diastereomers. This may in fact be the reason for its low relative concentration. However, the R,R nitrogen arrangement minimizes the contact, and ligand strain, while allowing the dqpn methyl group to lie equatorially.

The fourth and most populous isomer is the Λ-β-*exo*-[Co-(acac)(R-dqpn)]$^{2+}$ ion, and it also is found to form stereospecifically with respect to nitrogen configurations in acid solution. Least strain in the tetradentate is suggested by molecular models to be in the R,R isomer, and we conclude that this complex ion has that configuration. Thus, the isomer distribution can be ascribed in these circumstances to steric effects in the tetradentate, especially due to the requirements of the optically active (R)-1,2-diaminopropane fragment.

Finally, we wish to emphasize that no redistribution of the coordination spheres of the diastereoisomers occurs in neutral or acidic solution. The four cocrystallized diastereoisomers persist in solution. We are continuing our studies on these and related complexes aimed at an understanding of the chiral discriminations responsible for the isomeric distributions observed.

Registry No. Δ-β-*exo*-[Co(acac)(R-dqpn')]ClO$_4$, 92542-44-4; Δ-β-*endo*-[Co(acac)(R-dqpn')]ClO$_4$, 92542-46-6; Λ-β-*exo*-[Co-(acac)(R-dqpn')]ClO$_4$, 92542-42-2; Λ-β-*endo*-[Co(acac)(R-dqpn')]ClO$_4$, 92473-49-9; Δ-β-*exo*-[Co(acac)(R-dqpn)]$^{2+}$, 92542-47-7; Δ-β-*endo*-[Co(acac)(R-dqpn)]$^{2+}$, 92542-48-8; Λ-β-*exo*-[Co(acac)-(R-dqpn)]$^{2+}$, 92542-49-9; Λ-β-*endo*-[Co(acac)(R-dqpn)]$^{2+}$, 92542-50-2.

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Preparation and Characterization of *trans*-Diiodotetra-*tert*-butoxytungsten(VI): The First Structurally Well-Characterized W^{VI}–I Bonds

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The hexa-*tert*-butoxyditungsten molecule[1a,b] has proved to be an extraordinarily versatile reactant, as attested by the

Table I. Crystallographic Parameters

formula	$WI_2(OCMe_3)_6$
fw	730.12
space group	$I4/m$
syst absences	hkl ($h + k + l = 2n$); $hk0$ ($h + k = 2n$); $00l$ ($l = 2n$)
a, Å	10.443 (1)
c, Å	10.483 (1)
V, Å	1143.2 (4)
Z	2
d_{calcd}, g/cm³	2.12
cryst size, mm	0.25 × 0.25 × 0.30
μ(Mo Kα), cm^{-1}	78.48
data collcn instrum	CAD-4
radiation (monochromated in incident beam)	Mo Kα
orientation reflcn range (2θ), deg	8–45
temp, °C	−104
scan method	ω–2θ
data collcn range (2θ), deg	5–55
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	776
no. of parameters refined	33
R^a	0.0266
$R_w{}^b$	0.0356
quality-of-fit indicator^c	1.088
largest shift/esd, final cycle	0.01
largest peak, e/Å³	0.70

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å²
W	0.000	0.000	0.000	1.076 (4)
I	0.000	0.000	0.26989 (5)	1.876 (8)
O(1)	−0.0624 (4)	−0.1648 (4)	0.000	1.34 (7)
C(1)	−0.1519 (6)	−0.2706 (6)	0.000	1.65 (9)
C(2)	−0.2866 (6)	−0.2168 (7)	0.000	2.6 (1)
C(3)	−0.1254 (6)	−0.3482 (5)	0.1204 (5)	2.89 (9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Some Bond Distances and Angles in $WI_2(OCMe_3)_4$

	Bond Distance, Å		
W-I	2.8293 (8)	C(1)-C(3)	1.525 (6)
W-O	1.840 (4)	-C(2)	1.515 (8)
O(1)-C(1)	1.448 (7)		
	Bond Angles, deg		
I-W-I	180.0 (0)	W-O(1)-C(1)	160.5 (4)
I-W-O(1)	90.0 (0)	O(1)-C(1)-C(3)	106.7 (3)
O(1)-W-O(1)	90.0 (0)	-C(2)	108.5 (5)
O(1)-W-O(1)	180.0 (0)		

results in recent publications by Chisholm,[1] Schrock,[2] and ourselves.[3] Much of this reaction chemistry had led to new di- or trinuclear compounds although oxidative additions leading to mononuclear tungsten(VI) compounds such as $(Me_3CO)_3W{\equiv}X$ (X = N, CR) are known. We report here the reaction of $W_2(OCMe_3)_6$ with iodine, whereby oxidation to tungsten(VI) also occurs but at the same time there is a transfer of *tert*-butoxy groups to give *trans*-$WI_2(OCMe_3)_4$. This molecule affords an excellent illustration of how oxygen to metal dative π bonding can stabilize an otherwise unfavorable situation, namely, tungsten(VI) to iodine bonding.

Experimental Section

Ditungsten hexa-*tert*-butoxide, $W_2(OCMe_3)_6$, was prepared[2] by the reduction of WCl_4 with sodium amalgam in THF, in the presence of $LiOCMe_3$, followed by recrystallization from hexane at −20 °C. All reactions were done under an argon atomosphere.

Reaction of $W_2(OCMe_3)_6$ with Iodine. A weighed amount of $W_2(OCMe_3)_6$ (406 mg, 0.5 mmol) was dissolved in 15 mL of toluene, and the solution was cooled to −40 °C. At this temperature 127 mg (0.1 mmol) of iodine was added. The reaction mixture was stirred at −40 to −20 °C for 2 h. The solvent was then removed under vacuum, and the residue was extracted with 8 mL of cold hexane. A brownish residue, which was insoluble in nonprotic solvents, has not been identified. Yellow rectangular crystals were formed from the hexane solution (20% yield) after 3 days at −20 °C. The crystalline compound is sensitive to oxygen and must be handled in a rigorously oxygen-free atmosphere.

Attempts To Form $W(OCMe_3)_6$. The iodide, $WI_2(OCMe_3)_4$, and $MOCMe_3$ (M = Li, Na) in 1:2 mole ratios were dissolved in THF, and the solution stirred for 2 days at room temperature. The THF was removed under vacuum and the residue extracted with hexane. This solution on storage at −20 °C deposited crystals of $WI_2(OCMe_3)_4$ and some unidentified white powder. The solution was then placed in another tube and the hexane stripped. The residue was redissolved in 1 mL of THF plus 5 mL of hexane. From this solution were isolated colorless crystals after 4 days at −20 °C. These crystals were identified by X-ray crystallography as $WO(OCMe_3)_4(THF)$, a compound to be described in a future paper.[4]

NMR Spectrum. The ^1H NMR spectrum of $WI_2(OCMe_3)_4$ was measured at room temperature in CD_3CN solution on a Varian EM-390 spectrometer. One sharp signal was seen at δ 1.2 (downfield from Me_4Si).

X-ray Crystallography. The crystal used for data collection was mounted on the tip of a glass fiber. Data were collected on an Enraf-Nonius CAD-4F diffractometer with the crystal maintained at −104 °C. General procedures used in determining the structure have been described elsewhere,[5] and details pertinent to this case are available in the supplementary material. Table I summarizes some relevant data and parameters.

The atomic positional parameters are listed in Table II, and a selected list of bond distances and angles is presented in Table III. Anisotropic thermal parameters, structure factors, and a complete list of bond lengths and angles are available as supplementary material.

Discussion

The reaction by which the title compound was prepared was undertaken to see whether a mild oxidation of the triply bonded $W_2(OCMe_3)_6$ might lead to a product in which a metal–metal bond, albeit of lower order, would be retained. Reactions of this type with $Mo_2(OCHMe_2)_6$ to give $Mo_2(OR)_6X_4$ products have been reported by Chisholm.[6] We have not been able to isolate such a product, but about 20% of the starting material appears as crystalline $WI_2(OCMe_3)_4$, which was identified by an X-ray crystal structure determination.

Having shown that we had $WI_2(OCMe_3)_4$ in hand and that the possibility of replacing the two iodine atoms by *tert*-butoxy groups did not appear to be sterically precluded, several attempts were made to prepare $W(OCMe_3)_6$ by reaction of $WI_2(OCMe_3)_4$ with lithium and sodium *tert*-butoxide. The $WI_2(OCMe_3)_4$ appeared to react only sluggishly if at all, and the only product we were able to identify was $WO(OCMe_3)_4$.

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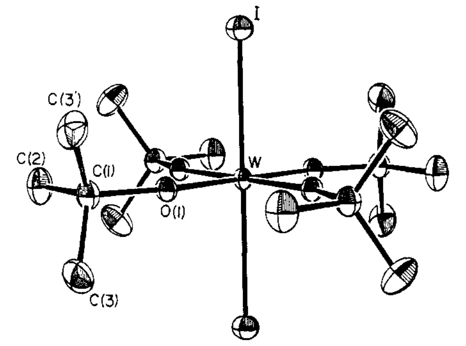

Figure 1. $WI_2(OCMe_3)_4$ molecule, with the atom-labeling scheme. The molecule has crystallographically imposed $4/m$ (C_{4h}) symmetry. Atoms are represented by ellipsoids of vibration at the 40% level.

Whether $W(OCMe_3)_6$ was an intermediate that decomposed to give $WO(OCMe_3)_4$ is unknown. It is also possible that $WO(OCMe_3)_4$ was formed by reaction with adventitious oxygen and/or water. In any event the challenge of preparing and identifying $W(OCMe_3)_6$ remains. The compound $WO(OCMe_3)_4$ is one we have isolated before in another way, and we shall report its structure and its chemical relationship to some other reactions of $W_2(OCMe_3)_6$ in a future publication.[4]

The structure of *trans*-$WI_2(OCMe_3)_4$ is shown in Figure 1. The molecule resides on a position of crystallographic $4/m$ or C_{4h} symmetry so that all angles around the tungsten atom are rigorously 90 or 180°, the two W–I distances are equal, and the four W–O distances are equal.

The $WI_2(OCMe_3)_4$ molecule is exceptionally interesting for several reasons. Perhaps most obvious is the fact that it is the only structurally characterized tungsten (or molybdenum) compound with the metal in oxidation state VI to contain metal to iodine bonds. The only adequately documented tungsten(VI) iodo compound in the literature appears to be WO_2I_2, first reported in 1966.[7,8] Since the structure is unknown beyond the statement that it is "a strongly disordered layer structure with a monoclinic unit cell", it is not certain whether there are discrete W–I bonds in this compound. It can be sublimed (but, to avoid decomposition to WO_2I, in the presence of excess I_2) so that some kind of molecule containing one or more W–I bonds does presumably exist. Obviously the dearth of iodo and bromo compounds of W^{VI} is attributable to the fact that there is normally an incompatibility between the oxidizing character of the metal in such a high formal oxidation state and the easy oxidizability of I^- or iodine covalently bonded. What, then, allows *trans*-$WI_2(OCMe_3)_4$ to be stable?

It would appear that we have here a very striking example of the fact that alkoxide groups can be strong π donors to the metal atoms to which they nominally form single bonds. Strong π donation from the oxygen atoms would moderate the oxidizing power of the metal atom so that iodide ions in proximity to the $W(OCMe_3)_4^{2+}$ unit could simply form covalent bonds by sharing electrons rather than losing them altogether to form I_2.

The structure of the $WI_2(OCMe_3)_4$ molecule provides direct evidence that strong $O \rightarrow W$ π bonding occurs. The W–O bond length, 1.840 (4) Å, is one of the shortest W–O or Mo–O "single" bond lengths yet reported.[9] This must, of course, be in part due to the small radius of W^{VI}, but it also indicates considerable strengthening of the W–O bonds by π bonding. We note, further that the W–O–C angles are 160.5 (4)°, which provides another strong and independent indication that both pairs of potential π electrons on each oxygen atom are being significantly donated to the metal atom.

The difference in the W–I and W–O bond lengths is 0.99 Å, whereas the difference between the commonly accepted single-bond covalent radii of the iodine and oxygen atoms is 0.67 Å. A large part of this "shortening" of the W–O bonds can be attributed to the strong $W \leftarrow O$ π interaction. Presumably in WO_2I_2 the oxygen atoms also donate π electron density over and above that needed to form W=O bonds to the tungsten atom, and this also is a major factor in allowing the existence of a tungsten(VI) iodo compound.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $W_2(OCMe_3)_6$, 57125-20-9; *trans*-$WI_2(OCMe_3)_4$, 92543-30-1; I_2, 7553-56-2; $WO(OCMe_3)_4(THF)$, 92543-29-8.

Supplementary Material Available: A more detailed account of the crystallographic work and tables of observed and calculated structure factors, anisotropic thermal parameters, and complete bond lengths and bond angles (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and
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A Novel Dinuclear Vanadium(II) Compound with Bridging Chlorine Atoms, Bridging Diphosphinomethane Ligands, and Bidentate Tetrahydroborate Ligands

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One of the major obstacles in developing the nonaqueous non-cyclopentadienyl chemistry of vanadium(II) has been the lack of soluble and easily prepared starting materials. At present the most readily available compound is a mixed vanadium–zinc complex $[V_2Cl_3(THF)_6]_2(Zn_2Cl_6)$.[1,2] While it can give rise to vanadium compounds that do not contain zinc atoms,[3] sometimes molecules incorporating both vanadium and zinc are obtained.[4]

It has been reported recently[5] that $LiBH_4$ can reduce vanadium in this V^{II} species to a +1 oxidation state, and in the presence of $PMePh_2$ an exotic, mixed V–Zn complex, $[V(PMePh_2)_2H_2ZnBH_4]_2$ has been isolated. We have found that under similar conditions but in the presence of $Ph_2PCH_2PPh_2$ (dppm) a different reaction occurs, which affords a zinc free product. The use of dppm and $NaBH_4$ instead of $PMePh_2$ and $LiBH_4$, respectively, produces a complex of the formula $[V(\mu\text{-}Cl)(\mu\text{-dppm})BH_4]_2$. We consider this compound to be of unusual interest because it has, by virtue of its central $V(\mu\text{-dppm})_2V$ frame, a potential for providing an entry into the chemistry of V^{II} dimers. At present no procedure for its isolation in a pure state is known, but we hope to solve that

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