Synthesis and Structural Characterization of 'Non-VSEPR' Structures of Oxo-Tungsten Complex

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Abstract: The crystal structure of $[(CH_3)_4N]_4 [WOCl_4F][WO_2Cl_4]$ was determined by single crystal X-ray diffraction technique. The crystal is monoclinic, space group C 2/m, with $a = 28.23(10)$ Å, $b = 11.60(4)$ Å, $c = 13.48(5)$ Å, $\beta = 118.43(7)^\circ$, $V = 3886(2)$ Å³, $Z = 4$. The structure was solved by direct methods and refined by least-squares methods to a final $R = 0.0512$ for 3825 observed reflections with $I > 2\sigma(I)$. In crystal there are two crystallographic distinct anions, both with cis geometry; the O-W-F and O-W-O angles are $97.5(3)^\circ$ and $103.1(3)^\circ$ respectively. All structures are cis configurations that confirm a preference for angles below 90° and 180° between cis and trans σ -donor ligands, respectively.

Keywords: X-ray crystal structure, Synthesis, IR spectra, Oxo- tungsten

Introduction

Under certain circumstances, metal complexes with a formal d^0 electronic configuration may exhibit structures that violate the traditional structure models, such as the VSEPR concept or simple ionic pictures. Some examples of the behavior, such as the bent gas phase structures of some alkaline earth dihalides or the trigonal prismatic coordination of some early transition metal chalcogenides or pnictides, have been known for a long time. However, the number of molecular examples for 'non-VSEPR' structures has increased dramatically during the past decade, in particular in the realm of organometallic chemistry. At the same time, various theoretical models have been discussed, sometimes controversially, to explain the observed, unusual structures. Many d^0 systems are important in homogeneous and heterogeneous catalysis, biocatalysis (*e.g.* molybdenum or tungsten enzymes).

The development of improved models for chemical bonding has always benefited from specific cases in which the existing models fail. One well-known example is the failure of the widely used valence-shell electron-pair-repulsion (VSEPR)¹ model and also of simple ionic models to predict the bent structures of some of the molecular dihalides of the heavy alkaline earth metals (Ca, Sr and Ba) in the gas phase²⁻¹⁰. Many more complexes with a formal d⁰ configuration of the central metal (and also with d¹ and d² configurations) have since been found, which do not conform to the simple structural models.

The increasing number of known non octahedral hexacoordinate d⁰, d¹ and d² complexes represents probably the most spectacular failure of the traditional structure models in this area of the periodic table. The octahedron, which is clearly favored by ligand repulsion¹¹, has been and still is by far the predominant geometry for this coordination number, both in main group and in transition metal chemistry.

Depending on the actual combination of σ -donor and π -donor ligands, we may expect a considerable variety of coordination arrangements. Very recently, Seppelt *et al.*¹² succeeded in carrying out initial solid-state structures determinations for four heteroleptic systems, [MoO(CH₃)₅], [WCl(CH₃)₅], [Mo(OCH₃)₂(CH₃)₄] and [MoCl(OCH₃)₂(CH₃)₃]. While the first three complexes are close to trigonal-prismatic limit, the latter complex appears to prefer a distorted octahedral arrangement, which resembles strikingly a low-lying transition state computed for [WCl₃(CH₃)₃]. The results of these studies confirm a preference for angles below 90° and 180° between cis and trans σ -donor ligands, respectively. For studying the effect of various kinds of π -donor and d⁰ system structures, we report here the synthesis and structures of oxo-tungsten.

Experimental

IR spectrum of the complex dispersed in KBr was recorded on a Shimadzu model 420 spectrophotometer. All reaction and air-sensitive product was manipulated in auto recirculating positive dry boxes, that purged by argon. Acetonitrile (Merck, PA) was twice distilled from phosphorus pentaoxide, to remove traces of moisture and stored over molecular sieves (type 4Å) activated at 390 °C. The (CH₃)₄NF·2H₂O was prepared from (CH₃)₄NOH and HF as described in the literature¹³.

Preparation of [(CH₃)₄N]₄[WOCl₄F][WO₂Cl₄].2CH₃CN (1)

Tungsten oxotetrachloride, WOCl₄, is very reactive compound. It reacted with oxygen if exposed to air. Inside a glove box purged by argon, a measured amount of tungsten (VI) oxotetrachloride (1 g) is dissolved in acetonitrile (25 mL) in a polyethylene beaker and stoichiometric amount of tetramethylammonium fluoride Dehydrate, (CH₃)₄NF, 2H₂O was added with stirring at room temperature. On refrigerating, solid product formed and gave suitable crystals after one week. Anal. Calcd for C₂₀H₅₄Cl₈FN₆O₃W₂ (%): C, 21.87; H, 4.92; N, 7.65. Found: C, 21.92; H, 4.89; N, 7.71.

X-ray crystallography

The intensity data for light green prism crystal of complex was measured on a Bruker SMART 1000 CCD area-detector, temperature 153(2) K, Mo K α radiation ($k=0.71073\text{\AA}^\circ$), graphite monochromator, ϕ and ω scans, Data collection and cell refinement with SMART¹⁴, data reduction with SAINT¹⁵, experimental absorption correction with SADABS¹⁶. Structure analysis and refinement: The structure was solved by direct methods (SHELXS-97)¹⁷; refinement was done by full-matrix least-squares on F² using the SHELXL-97 program suite¹⁷. Crystal data and structure refinement are given in Table 1.

Table 1. Crystal data and structure refinement for the complex

Empirical formula	C ₂₀ H ₅₄ Cl ₈ FN ₆ O ₃ W ₂
Formula weight	1096.99
Temperature (K)	153(2) K
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/m
Unit cell dimensions	
a (Å)	28.233(10)
b (Å)	11.606(4)
c (Å)	13.487(5)
α (°)	90
β (°)	118.437(7)
γ (°)	90
V (Å ³)	3886(2)
Z	4
D _{calc} , Mg m ⁻³	1.875
Absorption coefficient, mm ⁻¹	6.501
F(000)	2132
Crystal size, mm	0.25×0.12×0.10
θ range for data collection (°)	1.72 to 29.08
Index ranges	-38≤h≤38, -15≤k≤15, -18≤l≤18
Reflections collected	19690
Independent reflections	5353 [R(int) = 0.0345]
Completeness of theta. %	98.0%
Max./min. transmission	0.785 and 0.467
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5353 / 0 / 221
Goodness-of-fit on F ²	1.122
Final R indices [I>2σ(I)]	R1 = 0.0512, wR2 = 0.1032
R indices (all data)	R1 = 0.0701, wR2 = 0.1098

Results and Discussion

IR spectra

The assignments of IR bands are observed to be in good agreement with the X-ray structural data. The main stretching frequencies of the IR spectrum of the complex are tabulated in Table 2. The assignments of the IR spectrum in Table 2 refer to the cation and anion respectively. This type of hydrogen bonding in tetramethylammonium salts has been studied and reported by Harmon.

Table 2. The frequencies (cm⁻¹) and assignment of cation and anion of compound (1)

ν, cm ⁻¹	Assignment	Intensity	ν, cm ⁻¹	Assignment	Intensity
	(CH ₃) ₄ N ⁺		472	ν ₁₉	ms
3435	ν _{CH3} + ν ₁₉	(w, br.)	441	ν ₁₉	ms
3315	ν _{CH3} + ν ₈	(w, br.)	[WCl ₄ O ₂] ⁻³ , [WCl ₄ FO] ⁻		
3016	ν ₁₃	(w, br)	1024	ν _s (W = O)	
2625	ν ₁₁₄	(w, br.)	932	ν _s (W = O)	
1461	ν ₁₆	(s)	568	ν(W – F)	
953	ν ₁₈	(vs)			

The IR spectrum of this compound is similar to tetramethylammonium perchlorate salt. The IR spectrum shows the existence of hydrogen bonding. The comparison and studies of the IR spectrum are similar to in Harmon's study.

The IR spectrum of the ligand displays bands at 1024, 932 and 568 cm^{-1} , which may be assigned to ν_s (W = O), ν_s (W = O), ν (W – F) cm^{-1} for anions respectively. The complex spectrum shows band at around $\nu(\text{CH}_3 + \nu_{19})$ at 3435, $\nu(\nu\text{CH}_3 + \nu_8)$ at 3315, ν_{13} at 3016, ν_{14} at 2625, ν_{16} at 1461, ν_{18} 953, ν_{19} 472 and 441 cm^{-1} for cation. The results are also confirmed by the crystal structure analyses above.

Description of structures

Tungsten is one of the important transition metals in biological systems¹⁸. It is an integral component of the multinuclear M center of nitrogenases and the active sites of a group of oxotransferases¹⁹. Its unique properties appear to be due to its ability to exist in a number of different oxidation states and to coordinate with a variety of ligands. W(V) and W(VI) are generally thought to be the most likely oxidation states involved. Mixed Valence tungsten (V, VI) Compounds have been known several years ago. The mixed valence compounds commonly formed in preparation process^{20,21}. As seen crystal structure contains anionic Tungsten ions: a) tetrachlorofluorooxo ion b) tetrachlorodioxo. The coordination geometry about the molybdenum centre in each of these anions is essentially distorted octahedral. The X-ray data clearly demonstrate such inequality (Figures 1 and 2).

Figure 1. A view of the anionic $[\text{WCl}_4\text{O}_2]^{3-}$, $[\text{WCl}_4\text{FO}]^-$ and three independent $[\text{N}(\text{CH}_3)_4]^+$ cations and the acetonitrile solvent molecules. Displacement ellipsoids are shown at the 50% probability level

Figure 2. Crystal packing of the $[(\text{CH}_3)_4\text{N}]_4[\text{WCl}_4\text{F}][\text{WO}_2\text{Cl}_4]\cdot\text{CH}_3\text{CN}$

The trans W-Cl bonds to the oxygen atom [W(1)-Cl(1) = 2.583(2), W(1)-Cl(3) = 2.564(2) and W(2)-Cl(6) = 2.563(2)] are longer than the cis W-Cl distances to oxygen atom [W(1)-Cl(2) = 2.3715(18) and W(2)-Cl(4) = 2.201(3)] reflecting the greater trans influence of the oxygen atom as compared to the chlorine atom. The F atom in $[\text{WCl}_4\text{FO}]$ is oriented cis to the oxo ligands. The W-F bond length [W(2)-F(1) = 1.994(6)] is shorter than the sum of the single bond radii for W and the halides. The final atomic coordinates for the non-hydrogen atoms are given in Table 3 and selected bond lengths and angles are resumed in Table 4.

Table 3. Selected bond length [Å].

Bond	Length	Bond	Length
W(1)-O(2)	1.961(6)	W(2)-Cl(4)	2.201(3)
W(1)-O(1)	1.719(6)	W(2)-Cl(4)	2.465(4)
W(1)-Cl(2)	2.3715(18)	W(2)-Cl(5)	2.482(3)
W(1)-Cl(3)	2.564(2)	W(2)-Cl(6)	2.563(2)
W(1)-Cl(1)	2.583(2)	W(2)-O(3)	1.716(6)
W(2)-F(1)	1.994(6)		

Table 4. selected bond length [Å].

Bond	Angle	Bond	Angle
O(2)-W(1)-O(1)	103.1(3)	O(3)-W(2)-F(1)	97.5(3)
O(2)-W(1)-Cl(2)	94.51(4)	O(3)-W(2)-Cl(4)	99.50(11)
O(1)-W(1)-Cl(2)	94.24(5)	Cl(5)-W(2)-Cl(6)	84.22(8)
O(2)-W(1)-Cl(2)	94.51(4)	F(1)-W(2)-Cl(4)	97.20(10)
O(1)-W(1)-Cl(2)	94.24(5)	O(3)-W(2)-Cl(4)	90.12(11)
Cl(2)-W(1)-Cl(2)	165.89(8)	F(1)-W(2)-Cl(4)	89.25(10)
O(2)-W(1)-Cl(3)	88.2(2)	Cl(4)-W(2)-Cl(4)	167.58(10)
O(1)-W(1)-Cl(3)	168.6(2)	O(3)-W(2)-Cl(5)	90.2(3)
Cl(2)-W(1)-Cl(3)	84.73(4)	F(1)-W(2)-Cl(5)	169.28(15)
O(2)-W(1)-Cl(1)	168.8(2)	Cl(4)-W(2)-Cl(5)	88.87(9)
O(1)-W(1)-Cl(1)	88.1(2)	O(3)-W(2)-Cl(6)	170.95(19)
Cl(2)-W(1)-Cl(1)	84.52(4)	F(1)-W(2)-Cl(6)	87.22(16)
Cl(2)-W(1)-Cl(1)	84.52(4)	Cl(4)-W(2)-Cl(6)	87.52(8)

However there are also several cases with strong π -donor ligands, for which π bonding has been considered to increase the deviations from the VSEPR-type arrangements. Depending on the actual combination of σ -donor and single or double-faced π -donor ligand, we may expect a considerably variety of coordination arrangements²².

The results of these studies confirm a preference for angles below 90° and below 180° between cis and trans δ -donor ligands, respectively. At the same time, the distortions allow the competing π -donor ligands to enhance their bonding to the metal. These conclusions are consistent with more general notions about the alleviation, by structural distortions, of conflicts between different π -donor ligands (or between δ - and π -donor ligands) competing for a given set of metal d orbitals²³. The prototypical example for this type of competition is that discussed for distorted octahedral dioxotungsten complex, in which the two strong π -donor oxo ligand prefer a cisoid arrangement and the two weakest co-ligand is located trans to the oxo ligand, with typically small angles between them²⁴.

Conclusion

The $[(\text{CH}_3)_4\text{N}]_4[\text{WOC}_4\text{F}][\text{WO}_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$ complex was synthesized, the hydrogen bonds forming between the electronegative atom of anion and methyl hydrogens of the cation. The structure of this compound belongs to the non-VSEPR structures. CCDC, Nos 191520 contains the supplementary crystallographic data for this paper.

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