

If the second moments of the two structures are different, because of different internuclear distances or coordination numbers, then it is much difficult to make a correlation by using the one-electron model. It would predict, for example, that the system with the larger second moment is always the more stable, a result which is not at all reliable. Such one-electron ideas really only come into their own with structural problems that share the same second moment.

A Vital Difference

Solids and molecules, however, do differ in one very important respect. While zero- and small-gap molecules invariably distort (respectively via first- and second-order Jahn-Teller effects), metals (with zero gaps) are well-known in solids. In these cases it is not possible to lower the energy of usually two- and three-dimensional systems by distortion. While the energy at one point in the Brillouin zone may be lowered, the energy rises at another point. Thus whereas the correlation between the HOMO-LUMO gap and more stable structure applies to both coloring and distortional problems in molecules, in solids the distortion route is often frustrated.

Acknowledgment. This research was supported by the Office of Naval Research and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Appendix

The solid-state calculations employed the extended Hückel implementation of the tight-binding method. The atomic parameters used are given in Table II. In the band structure calculations, typically 20 k points were used in the irreducible wedge of the Brillouin zone. The geometries of the crystals were fixed at the values consistent with atomic sizes and the parent structure. The cubic unit cell edges used in the computations were as follows: sphalerite, $a_0 = 5.56 \text{ \AA}$; rock salt, $a_0 = 4.50 \text{ \AA}$; spinel, $a_0 = 10.627 \text{ \AA}$. In the case of the defect ReO_3 structure for the manganese oxide ($\text{MnO}_{2.5}\square_{0.5}$) a unit cell with an Mn-O distance of 1.87 \AA was employed.

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Redox-Catalyzed Condensation of Hexaammineosmium(II) with Acetone

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Received June 1, 1988

The nucleophilic activity of a transition-metal-coordinated ligand has both biological and synthetic significance. In the course of investigating the reactivity of $[\text{Os}(\text{NH}_3)_6](\text{OTf})_2$ ($\text{OTf} = \text{CF}_3\text{SO}_3^-$) in nonaqueous media,¹ it was discovered that under anaerobic conditions this species condenses with acetone to yield a 2-propanimine complex of Os(II).² Spectroscopic and electrochemical data³ of the resulting compound $[\text{Os}(\text{NH}_3)_5(\text{NHC}(\text{CH}_3)_2)](\text{OTf})_2$ (**1**) indicate that the imine ligand is terminally bound, in contrast to the isoelectronic acetone analogue in which π coordination is observed.⁴ A ^1H NMR spectrum of **1** displays inequivalent methyl resonances at 1.90 (3 H, s) and 2.09 ppm (3 H, s) and a broad peak at 12.65 ppm (1 H) corresponding to the imine proton. Trans- and cis-amine resonances (4.05 and 3.73 ppm) appear in close proximity, contrary to what is observed for pentaammineosmium(II) complexes containing η^2 -bound ligands.⁵ A cyclic voltammogram of this material features a reversible couple at $E_{1/2} = -0.61 \text{ V}$ (NHE), which, in consideration of the electrochemical data reported for other pentaammineosmium(II) complexes,⁵ would be inconsistent with η^2 coordination. The infrared spectrum of **1** includes absorptions at 1587 and 1432 cm^{-1} , the latter of which is assigned to the C-N stretch and is similar to that found for the complex $[\text{Ru}(\text{NH}_3)_5(\text{NHCHPh})]^{2+}$ (1440 cm^{-1}).⁶ When a sample of **1** is dissolved in MeOD for 1 h and reclaimed, its infrared spectrum no longer includes the higher energy absorption, indicating isotopic exchange. This 1587- cm^{-1} feature is tentatively ascribed to an N-H deformation.⁷ When $[\text{Os}(\text{NH}_3)_5(\text{NHC}(\text{CH}_3)_2)]^{2+}$ is generated by dissolving $[\text{Os}(\text{NH}_3)_6](\text{OTf})_2$ in acetone- d_6 , a ^1H NMR spectrum of the reaction mixture shows ammine resonances similar to those described above, but the peaks at 1.90 and 2.09 ppm are absent. In addition, a broad singlet is present at 2.86 ppm, which we ascribe to the formation of H_2O , consistent with the stoichiometry

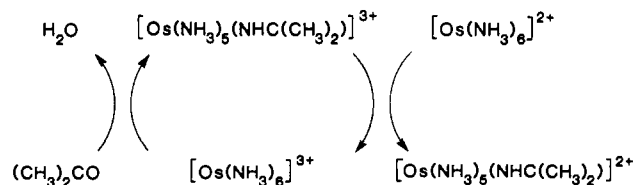


Figure 1. Redox-catalyzed condensation reaction of hexaammineosmium(II) with acetone.

$(\text{CH}_3)_2\text{CO} + [\text{Os}(\text{NH}_3)_6]^{2+} =$
 $[\text{Os}(\text{NH}_3)_5(\text{NHC}(\text{CH}_3)_2)]^{2+} + \text{H}_2\text{O}$ (1)

A significant driving force for this reaction comes from the ability of the imine ligand to stabilize the Os(II) metal center through π -back-bonding.⁸

Reaction 1 is catalyzed by trace amounts of $[\text{Os}(\text{NH}_3)_6]^{3+}$ and is inhibited by acid. From these observations the formation of **1** is thought to occur through nucleophilic attack by an amidopentaammineosmium(III) intermediate (Figure 1), an observation that has previously been reported for Ru(III) and Pt(IV).⁹ In the presence of trace amounts of Os(III),¹⁰ **1** shows further reactivity in acetone over time. Cyclic voltammetry indicates that the reversible couple assigned to this species is slowly replaced by one at -0.42 V (NHE), suggesting further imine formation at the osmium center.

When a 0.5 N NaTFMS/DME solution of $[\text{Os}(\text{NH}_3)_6](\text{OTf})_2$ is treated with excess acetaldehyde and trace amounts of Na^+MeO^- ,¹¹ an intense orange color immediately develops. Cyclic

(3) IR (KBr): 1587, 1432 cm^{-1} . ^1H NMR (acetone- d_6): 1.90 (3 H, s), 2.09 (3 H, s), 3.73 (12 H, b), 4.05 (3 H, b), 12.65 ppm (1 H, b). ^1H NMR (acetonitrile- d_3): 1.78 (3 H, s), 2.10 (3 H, s), 3.13 (12 H, b), 3.44 (3 H, b), 11.94 ppm (1 H, b). Cyclic voltammetry (scan rate 100 mV/s; acetone/0.5 N NaOTf; Pt⁹ working electrode): $E_{1/2} = -0.61 \text{ V}$ (NHE).

(4) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

(5) Typically, pentaammineosmium(II) complexes containing a π -bound sixth ligand have $3+/2+$ couples with $E_{1/2}$ greater than 0.0 V (NHE). See: Harman, W. D. Ph.D. Dissertation, Stanford University, 1987.

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(9) Evans, I. P.; Everett, G. W., Jr.; Sargeson, A. P. *J. Chem. Soc., Chem. Commun.* **1975**, 139.

(10) A trace of $[\text{Os}(\text{NH}_3)_6]^{3+}$ is added, which is thought to generate $[\text{Os}(\text{NH}_3)_5(\text{NHC}(\text{CH}_3)_2)]^{3+}$ in acetone. This latter species may be susceptible to further condensation.

(1) $[\text{Os}(\text{NH}_3)_6](\text{OTf})_2$ has been used in our laboratories as a potent one-electron-reducing agent ($E_{1/2} = -0.78 \text{ V}$; H_2O ; NHE). Synthesis: $[\text{Os}(\text{NH}_3)_6](\text{OTf})_3$ (250 mg) dissolved in acetone (10 mL) was stirred along with 5 g of activated magnesium under argon. After 2 h the resulting suspension was pipetted from the magnesium and filtered. The isolated yellow solid was washed with a 1:1 acetone/ether solution, dried under vacuum, and recrystallized from methanol and ether. $[\text{Os}(\text{NH}_3)_6](\text{OTf})_2$ was prepared from the direct reaction of $[\text{Os}(\text{NH}_3)_5(\text{OTf})_3]$ in liquid ammonia. The synthesis of $[\text{Os}(\text{NH}_3)_5(\text{OTf})_2]$ has been reported by: Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.

(2) Under anaerobic conditions, $[\text{Os}(\text{NH}_3)_6](\text{OTf})_2$ (50 mg) was stirred in acetone (5 mL) for 6 h. Formation of the product was monitored by cyclic voltammetry ($E_{1/2} = -0.61 \text{ V}$ in acetone). Treatment with ether precipitated the final product. Anal. Calcd for $[\text{Os}(\text{NH}_3)_5(\text{NHC}(\text{CH}_3)_2)](\text{OTf})_2$: C, 9.52; H, 3.52; N, 13.33. Found: C, 9.95; H, 3.33; N, 12.92.

voltammograms reveal an initial reaction analogous to that observed for acetone and hexaammineosmium(II); the hexaammine 3+/2+ couple at -0.84 V is initially replaced by one at $E_{1/2} = -0.53$ V, which, in light of the previous discussion, suggests the formation of $[\text{Os}(\text{NH}_3)_5(\text{NHCHCH}_3)]^{2+}$. This species rapidly decomposes, however, resulting in several electroactive products. Treatment of this reaction mixture with excess ether results in a precipitate whose infrared spectrum includes an intense absorption near 2200 cm^{-1} . This observation suggests that a coordinated nitrile may be one of the reaction products.¹² Schug et al.^{6,13} have reported similar findings with $[\text{Ru}(\text{NH}_3)_6]^{3+}$, which under basic conditions reacts with aldehydes to give the corresponding Ru(II) nitrile complex. The oxidation of an imine to a nitrile would require either an external oxidant or elimination of hydrogen, however, neither of which have been detected.¹⁴

Acknowledgment. Support of this work by National Science Foundation Grants CHE85-11658 and CHE84-14329 (400-MHz NMR) and National Institutes of Health Grant GM13638-20 is gratefully acknowledged.

- (11) When this reaction is repeated without the addition of base, no reactivity is detected by cyclic voltammetry after 1 h, even upon addition of $[\text{Os}(\text{NH}_3)_6](\text{OTf})_3$.
 (12) E.g., the C-N stretch for $[\text{Os}(\text{NH}_3)_5(\text{CH}_3\text{CN})](\text{OTf})_2$ occurs at 2186 cm^{-1} : Sekine, M.; Harman, W. D.; Taube, H. *Inorg. Chem.*, in press. Also see ref 12.
 (13) Schug, K.; Guengerich, C. P. *J. Am. Chem. Soc.* **1975**, *97*, 4135.
 (14) For additional reports of imine complexes see: Joss, S.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 3487. Elsbernd, H.; Beattie, J. K. *J. Chem. Soc. A* **1970**, 2598. Lane, C. C.; Lester, J. E.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1971**, 1618.

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Structure of (Pentamethylcyclopentadienyl)((pentamethylcyclopentadienyl)oxy)dioxotungsten(VI), $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$. Structural Evidence for the Strong Trans Influence of the Oxo Ligand

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Received March 4, 1988

The chemistry of organometallic compounds containing oxo, alkoxo, and peroxy ligands is an area of increasing interest with potential relevance to selective catalytic oxidation of hydrocarbons. Compounds of the middle transition elements could exhibit reactivity that would provide a basis for catalytic systems, since these metals are less oxophilic than the early transition metals and yet readily attain high formal oxidation states. We have therefore recently explored synthetic routes to oxo derivatives of permethyltungstenocene, e.g. $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}=\text{O}$.¹ Herein we report the structure of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$, obtained by the reaction of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}=\text{O}$ with O_2 . The two oxo ligands exhibit a strong trans influence resulting in a coordination geometry of the $\eta^5\text{-C}_5\text{Me}_5$ ligand, which is more properly described as $\eta^1, \eta^4\text{-C}_5\text{Me}_5$.

Experimental Section

(i) **Preparation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$.** A solution of $\text{Cp}^*_2\text{W}=\text{O}$ (200 mg) in pentane (10 cm^3) at $-78\text{ }^\circ\text{C}$ was placed under O_2 (1 atm) and was stirred as it was allowed to warm to room temperature. Upon reaching room temperature, the initially green solution

Table I. Crystal and Intensity Collection Data

| | |
|--|--|
| formula: $\text{WO}_3\text{C}_{20}\text{H}_{30}$ | CAD-4 diffractometer |
| fw: 502.31 | 2θ range: $2\text{--}50^\circ$ |
| cryst color: pale yellow | absences: $h0l, h + l = 2n + 1;$ |
| habit: irregular, chunky | $0k0, k = 2n + 1$ |
| $a = 14.987(2)\text{ \AA}$ | $\mu = 60.22\text{ cm}^{-1}$ ($\mu_{\text{r,max}} = 1.63$) |
| $b = 7.459(1)\text{ \AA}$ | $\theta\text{--}2\theta$ scan |
| $c = 19.422(3)\text{ \AA}$ | octants collcd: $\pm h, k \pm l; \pm h, -k, l$ |
| $\beta = 110.59(1)^\circ$ | no. of reflns measd: 12144 |
| $V = 2032.5(5)\text{ \AA}^3$ | no. of indep reflns: 3556 |
| $Z = 4$ | no. of reflns with $F_o^2 > 0$: 3373 |
| $\lambda = 0.71073\text{ \AA}$ | no. of reflns with $F_o^2 > 3\sigma(F_o^2)$: 2861 |
| space group: $P2_1/n$ | goodness of fit for merging data: 1.14 |
| cryst size: $0.19 \times 0.19 \times 0.47\text{ mm}$ | final R index: 0.0318 |
| graphite monochromator | final goodness of fit: 1.57 |

Table II. Final Parameters for the Heavy Atoms ($\times 10^4$)

| atom | x | y | z | $U_{\text{eq}}^a\text{ \AA}^2$ |
|-------|------------|------------|------------|--------------------------------|
| W | 4288.7 (1) | 1542.3 (2) | 1912.0 (1) | 345 (0.4) |
| O(1) | 3766 (2) | 3217 (4) | 1146 (2) | 478 (9) |
| O(2) | 4932 (2) | 17 (5) | 1612 (2) | 660 (10) |
| O(3) | 3350 (2) | 371 (5) | 1992 (2) | 623 (9) |
| C(1) | 3121 (3) | 3125 (6) | 393 (2) | 440 (12) |
| C(2) | 3518 (3) | 2003 (6) | -79 (2) | 420 (11) |
| C(3) | 2881 (3) | 743 (6) | -412 (2) | 422 (11) |
| C(4) | 2055 (3) | 871 (6) | -163 (2) | 407 (11) |
| C(5) | 2192 (3) | 2197 (6) | 321 (2) | 425 (11) |
| C(6) | 2977 (5) | 5079 (8) | 135 (4) | 638 (17) |
| C(7) | 4460 (5) | 2398 (11) | -154 (4) | 670 (17) |
| C(8) | 2938 (5) | -607 (10) | -967 (3) | 625 (17) |
| C(9) | 1226 (4) | -382 (10) | -422 (4) | 625 (16) |
| C(10) | 1585 (5) | 2830 (12) | 730 (4) | 678 (18) |
| C(11) | 5203 (3) | 1718 (6) | 3162 (2) | 393 (10) |
| C(12) | 5807 (3) | 2481 (7) | 2804 (2) | 412 (11) |
| C(13) | 5381 (3) | 4077 (6) | 2472 (2) | 418 (11) |
| C(14) | 4542 (3) | 4363 (6) | 2646 (2) | 414 (11) |
| C(15) | 4449 (3) | 2933 (6) | 3080 (2) | 393 (10) |
| C(16) | 5403 (5) | 35 (8) | 3618 (3) | 614 (16) |
| C(17) | 6718 (4) | 1665 (12) | 2796 (4) | 674 (17) |
| C(18) | 5712 (5) | 5327 (11) | 2003 (4) | 749 (19) |
| C(19) | 3867 (5) | 5930 (8) | 2407 (5) | 679 (19) |
| C(20) | 3687 (5) | 2694 (12) | 3411 (4) | 685 (18) |

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*) (\bar{a}_i \bar{a}_j)]$$

became colorless. The solution was concentrated after 30 min and cooled to $-78\text{ }^\circ\text{C}$, giving white (or very pale yellow) crystals of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}(\text{O})_2(\text{OC}_5\text{Me}_5)$ (200 mg, 93%). Anal. Found (calcd): C, 47.5 (47.8); H, 5.8 (6.0). The crystals used in the X-ray analysis were obtained by slow evaporation from a mixture of pentane and benzene.

(ii) **X-ray Structure Analysis.** The crystals were thick needles, clear to pale yellow, and were cleaved with a razor blade to give irregular chunks that were mounted in capillary tubes. The maximum dimensions of the crystal used for data collection, measured with a micrometer microscope, were about $0.19 \times 0.19 \times 0.47\text{ mm}$, but the grease used to fix the crystal in the capillary obscured the edges and both the size and the shape of the crystal may have been incorrectly estimated. The data (Table I) were collected on a CAD-4 diffractometer using monochromated $\text{Mo K}\alpha$ radiation, and the cell dimensions were obtained from 25 reflections with $11.5^\circ < \theta < 14^\circ$. Three equivalent quadrants ($\pm h, k, l; \pm h, k, -l; \pm h, -k, l$) were collected to $\theta = 25^\circ$, with $\theta\text{--}2\theta$ scans at 4° (in θ)/min. With data uncorrected for absorption, the GOF for merging equivalent reflections was 1.16; with corrected data ($\mu = 60.22\text{ cm}^{-1}$), 1.21. Structure refinements based on both data sets indicated that the absorption corrections were probably too large, so the final data set was based on $\mu = 45\text{ cm}^{-1}$; the GOF of merging was 1.14.

The structure was derived from Patterson and Fourier maps. The conformations of the methyl groups were indicated clearly and unambiguously on difference maps calculated in the planes of the H atoms, which were then positioned so as to complete regular tetrahedra with C-H = 1.0 \AA ; they were then included in the refinements (with isotropic B 's). Full-matrix minimization of $\sum w(F_o^2 - F_c^2)^2$ was based on 338 parameters, including an isotropic extinction parameter g^{2a} final value

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