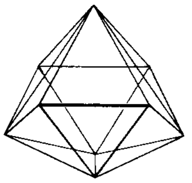
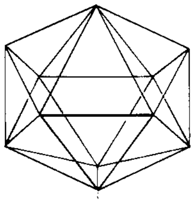
logical transformation for generating polar deltahedra with *n* skeletal electron pairs. The symmetry restrictions arising from the definition of polar deltahedra with a unique atom on the principle axis limits them to clusters with $3p + 1$ atoms belonging to the C_{3v} and T_d point groups. The tetrahedron ($p = 1$) and capped octahedron ($p = 2$) represent other examples of polar deltahedral clusters with *n* bonding skeletal electron pairs. Fowler[14] has identified polyhedra with 16, 19, and 22 atoms that belong to the C_{3v} and T_d point groups and have *n* skeletal electron pairs. For deltahedra with C_{2v} symmetry, e.g. **6** and **7** the degeneracy of the L^π/L^π nonbonding set is no longer dictated by the symmetry and whether they have *n* or $n + 1$ skeletal electron pairs is influenced by the extent to which the degeneracy is removed. In $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$ the degeneracy is removed sufficiently for $n + 1$ skeletal electron pairs to be accommodated. For $B_{13}H_{13}$ Fowler's calculations suggest that the degeneracy is retained sufficiently for the *n* electron pair situation to be preferred.[14] The introduction of a metal fragment on the principal axis in **6** and **7** could, however, lead to a stabilization of the *n* electron pair situation. Baker[5] has cited some examples of such compounds in his paper.



6

e.g. $[IrH(PMe_3)_2(B_8H_7Cl)]$



7

e.g. $[B_{11}H_{11}]^{2-}$

Acknowledgment. The SERC is thanked for financial support, and M. Walters is thanked for developing a graphics program for representing the polyhedral structures.

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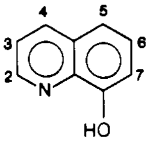
Tungsten(IV/V) Eight-Coordinate Mixed-Ligand-Chelate Electrochemistry

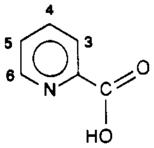
Robert J. Nowak[1a] and Ronald D. Archer*[1b]

Received July 1, 1985

Quantitative cyclic voltammetric measurements on the complete series of eight-coordinate tungsten chelates of the general formula $ML_nL'_{4-n}$ where $n = 0$–4 indicate a smooth change in $E^{\circ\prime}$ from 0.404 to 0.275 V for L = 5,7-dichloroquinolinolato and L′ = 5-methylpicolinato in tetrahydrofuran vs. a sodium-saturated calomel electrode. The change parallels the MLCT spectral transition change although the magnitude of the redox change is a little lower than that of the charge-transfer transition. Together these two series of values provide information as to the relative energies of the HOMO and LUMO levels of such eight-coordinate systems.



1



2

Inert, completely chelated eight-coordinate complexes of tungsten can be prepared through the reaction of excess 8-quinolinol (Hq, **1**) and picolinic acid (Hpic, **2**) derivatives with a variety of tungsten compounds at elevated temperatures,[2] even though the chemistry of tungsten with classical Werner type ligands is dominated by oxo species such as $WO_2(q)_2$.[3] The very stable d^2 tungsten(IV) $W(q)_4$ and $W(pic)_4$ type species are 18-electron complexes. Even so, they can be oxidized to the analogous tungsten(V) 17-electron $W(q)_4^+$ and $W(pic)_4^+$ type species, also thought to be 8-coordinate.[4] Oxidation occurs spontaneously at elevated temperatures in the presence of excess ligand or at room temperature with chlorine, bromine, or perchloric acid. The tungsten(V) chelates disproportionate in strong base, such as alcoholic KOH, to give $W(q)_4$ and $WO_2(q)_2$ type complexes, or they undergo reduction cleanly to $W(q)_4$ with copper metal.[4] However, no quantitative electrochemical data have been available to correlate the relative oxidation–reduction tendencies of the quinolinato and picolinato chelates. The lack of electrochemical data is not surprising given the extremely low solubility of $W(q)_4$ in all practical electrochemical solvents. However, the availability of an entire series of $W(dcq)_n(mpic)_{4-n}$ chelates (where $n = 0$–4, Hdcq = 5,7-dichloro-8-quinolinol, and Hmpic = 5-methylpicolinic acid),[5] which have better solubility, makes such a study feasible and is the subject of this paper.

Cyano and dithio type ligands, such as dithio acids, dithiocarbamates, and dithioxanthates, also stabilize tungsten in these two oxidation states via eight-coordination. The electrochemical data available on these other systems show a wide variation in the relative stability of the two oxidation states.[6]

The stability and inertness of the eight-coordinate tungsten(IV) and -(V) chelates has been explained in terms of π-overlap in several of the papers noted above by using an extension of the original suggestion of Orgel.[7] Ligand exchange is very slow, and even isomer rearrangements have high activation parameters.[5] Proof of eight-coordination with a geometry consistent with Orgel's rule has been obtained through a crystal structure of one of the tungsten(IV) chelates.[8] The electronic spectra of all of the tungsten(IV) quinolinolates and picolinates have low energy (ca. 14000–17000 cm^{-1}) metal-to-ligand charge-transfer transitions[2,5] and the analogous tungsten(V) ions exhibit ligand-to-metal charge-transfer bands in the visible region.[4] The determination of electrochemical properties of these species allows further elucidation of these inert chelates.

Experimental Section

Syntheses. The tungsten chelates were synthesized by using procedures reported previously: $W(dcq)_4$ and $W(mpic)_4$ were prepared from $W(CO)_6$ and excess ligand at elevated temperature.[2] The mixed-ligand species $W(dcq)_3(mpic)$, $W(dcq)_2(mpic)_2$, and $W(dcq)(mpic)_3$ were prepared similarly by using ligand mixtures and were purified by chromatography on silica gel.[5] Purity was ascertained by elemental analysis and proton NMR and electronic spectra; cf. ref 5.

Electrochemical Measurements. The lithium perchlorate (Eastman) electrolyte was stored in a vacuum oven at 50 °C for several weeks before use. The solvent, tetrahydrofuran (Burdick and Jackson UV grade), was heated under reflux conditions over calcium hydride and then distilled under an inert atmosphere. Platinum electrodes (Bioanalytical Systems, W. Lafayette, IN) were polished on a Buehler high-speed polishing wheel. Metadi diamond paste (0.25 μm) was used for the final polishing. Electrodes were sonicated in ASTM type I or better water followed by THF to remove traces of polishing compound. An electrochemical cell

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[1] (a) Naval Research Laboratory. (b) University of Massachusetts.

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Table I. $W(dcq)_n(mpic)_{4-n}$ Electrochemical and Spectroscopic Values

compd	$E^{\circ\prime}$, V vs. SSCE[a]	i_{pa}/i_{pc}[a]	MLCT,[b] eV
$W(mpic)_4$	0.404 ± 0.003	1.2 ± 0.1	2.07 ± 0.02[c]
$W(dcq)(mpic)_3$	0.38 ± 0.02	1.1 ± 0.1	1.98 ± 0.02
$W(dcq)_2(mpic)_2$	0.342 ± 0.003	0.9 ± 0.1	1.89 ± 0.02[d]
$W(dcq)_3(mpic)$	0.30 ± 0.01	1.1 ± 0.1	1.84 ± 0.02
$W(dcq)_4$	0.275 ± 0.007	1.1 ± 0.1	1.76 ± 0.02[e]

[a] Averages based on duplicate cyclic voltammograms at six sweep rates from 0.010 to 0.500 V/s. [b] Mixed-ligand-complex values calculated from information in ref 5. [c] Calculated from data in ref 2a. [d] Average of values for the two isomers. [e] Calculated from data in ref 2c.

of conventional design was used in all experiments. A sodium-saturated calomel electrode (SSCE) and a platinum coil were used as reference and auxilliary electrodes, respectively. A PARC Model 173 potentiostat/galvanostat with a PARC Model 179 digital coulometer, a PARC Model 175 universal programmer, and an IBM Model 7424 MT X-Y recorder were used in all electrochemical experiments.

Results and Discussion

Electrochemical Results. Cyclic voltammetric data for the IV–V oxidation for the five tungsten complexes are summarized in Table I. The entries represent average values obtained from duplicate determinations at six voltage sweep rates (0.010, 0.020, 0.050, 0.100, 0.200, and 0.500 V/s). The cyclic voltammograms for these compounds are normal pseudoreversible CVs. Additional one-electron-oxidation peaks (V → VI) were observed for the $W(dcq)_4$ and $W(mpic)_4$ compounds, and irreversible reduction peaks presumed to be ligand reductions were also observed. These features were not studied thoroughly as such a study was beyond the scope of this investigation.

A thin-layer spectroelectrochemical experiment[9] using the $W(dcq)_3(mpic)$ compound confirmed that the oxidation is a one-electron process ($n = 1.03 \pm 0.05$).

$E^{\circ\prime}$ Trend. The linear increase in $E^{\circ\prime}$ as dichloroquinolinolato ligands are replaced by methylpicolinato ligands (Table I) is undoubtedly a composite of electronic and steric effects. The tungsten(IV) d^2 state is more favored relative to the tungsten(V) d^2 state by the methylpicolinato ligand. The more favorable reduction observed as the number of methylpicolinato ligands increases is consistent with the lower basicity of carboxylic oxygen donor atoms relative to phenolic oxygen atoms. Reduction requires the addition of an electron into a coordination sphere that is rather crowded in the tetrakis(quinolinolato) complexes (the oxygen atoms being much closer than their normal van der Waals radii would cause one to predict).[8] Thus, less basic oxygen atoms should relax the coordination sphere relative to the quinolinolates and ease the reduction, as is observed.

The values observed for this tungsten series lie within the range of values observed for analogous tungsten sulfur donor species.[6] Specifically, the $E^{\circ\prime}$ values for the dithiocarbamate complexes range from about −0.7 V vs. SCE for aliphatic carbamates and −0.5 for the aromatic ones on one extreme to 0.6 V for aromatic dithioacids. The quinolinolate and picolinate donors in this study lie closer to the dithio acids for which the d^2 form is more stable under normal solution conditions. The well-known octacyanotungstates have an analogous peak between 0.0 and 0.4 V vs. H_2, depending on solvent,[10] or about 0.25–0.65 V vs. SSCE.

If all of the electronic effects of a dichloroquinolinolato ligand of a tungsten chelate are summed together as σ_1 and the analogous effects of an methylpicolinato ligand are summed together as σ_2, a linear correlation for the $W(dcq)_n(mpic)_{4-n}$ chelates yields

$$\sigma_{total} = n\sigma_1 + (4 - n)\sigma_2$$

The $E^{\circ\prime}$ values correlate with this relationship in a reasonably liner fashion as noted in Figure 1, where the $n{:}(4 - n)$ ligand ratios correspond to $n\sigma_1$ and $(4 - n)\sigma_2$ units. The lack of any sharp break at either end of the series is consistent with a smoothly changing electronic environment at the metal center. The use of substituent constants such as the Taft σ^* constants would undoubtedly lead to a similar correlation if they were available for such diverse ligands; *cf.* the $W(alkyldithio\ acid)_4$ correlation in ref 6.

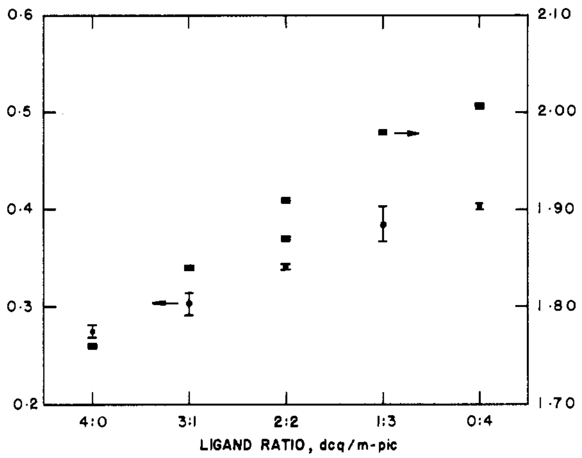

Figure 1. $E^{\circ\prime}$ (●) and MLCT (■) values vs. the ratio of dcq/mpic ligands for the $W(dcq)_n(mpic)_{4-n}$ species. The two MLCT values for the 2:2 ratio represents values for the freshly separated isomers; cf. ref 5.

$E^{\circ\prime}$ Correlation with the Low-Energy MLCT Band. The linear increase in $E^{\circ\prime}$ as dichloroquinolinolato ligands are replaced by methylpicolinato ligands is paralleled by an increase in the energy of the lowest energy charge-transfer transition as noted in Table I and Figure 1. This parallel trend is consistent with the metal-to-ligand charge-transfer (MLCT) designation suggested previously.[2] That is, the relatively greater ease of oxidation for the tungsten complexes with more dichloroquinolinolato ligands means the highest occupied molecular orbital (HOMO) is closer to ionization in the complexes with more dichloroquinolinolato ligands—other factors being equal. The HOMO is thought to be a metal orbital of π-symmetry [b_1 in the D_{2d} point group found for the analogous tetrakis(5-bromo-8-quinolinolato)tungsten(IV) species[8]]. The HOMO is completely filled in the d^2 tungsten(IV) species and half-filled in the tungsten(V) species. The LUMO is thought to be a π^*-ligand orbital. These metal-to-ligand bands are analogous to the ruthenium(II) tris-2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) chelates, which have a filled π-symmetry metal level (a_1 in the D_3 point group) as HOMO and an empty π^*-orbital (a_2 in D_3) as LUMO and intense metal-to-ligand charge-transfer bands at low energies.[11]

The energy changes for the charge-transfer transition of this series are about double the energy changes in the $E^{\circ\prime}$ values. This fact provides some information about the LUMO energy levels. That is, if the $E^{\circ\prime}$ values are considered to be a measure of the HOMO energy level, cf. Smith and Schultz,[12] and the charge-transfer transition is considered to be a measure of the energy between the HOMO and the LUMO (the ligand π^* level in these complexes), then the steeper slope for the MLCT provides an indication that the LUMO is less favorable as more methylpicolinate ligands are involved, as anticipated for the single-ring mpic ligand. Naturally, such factors as electron correlation would be necessary for a fully quantitative evaluation.[12] Although the ligand reduction potential should provide a measure of the LUMO energy directly, we find that the ligand reductions are irreversible in the present system and provide no further enlightenment as to the energy levels. On the basis of the tungsten (V → IV) $E^{\circ\prime}$ values and the MLCT transition energies, we anticipate an energy level sequence similar to that shown in Figure 2. The $^4/_3$ D electron correlation correction for low-spin d^2 systems could vary slightly in the series, but the energy trends are as anticipated. That is, even though the d orbital that is filled in the d^2 tungsten(IV) chelates is of lower energy in the chelates containing more me-

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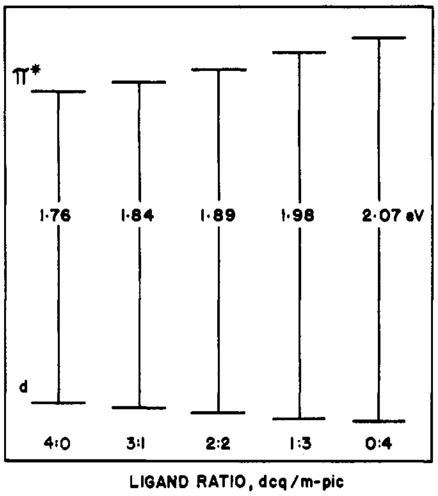

Figure 2. HOMO and LUMO levels for the $W(dcq)_n(mpic)_{4-n}$ series.

thylpicolinate ligands, the ligand π^* levels are high enough in energy that the MLCT transition energy values vary more than the $E^{\circ\prime}$ values. Smith and Schultz[12] had found only a small variation in the charge-transfer transitions of their S-donor complexes relative to the electrochemical potentials. However, their systems possess charge-transfer levels of the ligand-to-metal type rather than the metal-to-ligand variety; thus the LUMO and HOMO level changes appear to parallel each other in the S-donor species, unlike the present ones in which they move apart.

Acknowledgment. Partial support of this research by the Office of Naval Research is gratefully acknowledged. The help of Drs. Debra Rolison, David Venezky, and Marian Stankovich during various aspects of this study are also acknowledged with grateful appreciation.

Registry No. $W(mpic)_4$, 61805-72-9; $W(dcq)(mpic)_3$, 61805-73-0; $W(dcq)_2(mpic)_2$, 103301-97-9; $W(dcq)_3(mpic)$, 61880-51-1; $W(dcq)_4$, 33752-56-6; $W(mpic)_4^+$, 103202-97-7; $W(dcq)(mpic)_3^+$, 103202-98-8; $W(dcq)_2(mpic)_2^+$, 103202-99-9; $W(dcq)_3(mpic)^+$, 103203-00-5; $W(dcq)_4^+$, 47884-67-3.

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An Oxotungsten(V) Dimer with Unusual Stereochemistry: Synthesis and Structure of *anti*-Bis(μ-2-methyl-1-propanethiolato)bis[oxodichloro(triphenylphosphine oxide)tungsten(V)]

Joanne M. Ball, P. Michael Boorman,* and John F. Richardson

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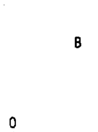
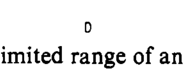
In contrast to the large variety of well-characterized oxomolybdenum(V) and -(VI) species of the types shown here (A–E),

A

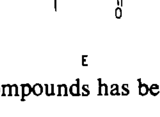


B

C



D



E

a more limited range of analogous compounds has been reported for tungsten.[1] Recent reports by Wieghardt and co-workers[2,3] described the first examples of compounds containing an anti M_2O_4 core (M = Mo, W), of type E. There are theoretical reasons[3] for speculating that the syn isomers of M_2O_4 systems, and those of related species such as M_2S_4, are more stable than the anti isomers. We are thus prompted to report the unexpected isolation and characterization of the title compound *anti*-$Cl_2O(Ph_3PO)W(\mu\text{-S-}i\text{-Bu})_2W(Ph_3PO)Cl_2O$ (**1**). This compound appears to be the first reported tungsten compound that contains the anti $OW(\mu\text{-X})_2WO$ moiety.

Table I. Crystallographic Parameters

formula	$C_{44}H_{48}Cl_4O_4P_2S_2W\cdot1.6CH_2Cl_2$
fw	1412.4
space group	$P2_1/n$ (alt $P2_1/c$, No. 14)
a, Å	11.303 (3)
b, Å	14.229 (2)
c, Å	16.952 (4)
β, deg	98.67 (1)
vol, Å^3	2695 (1)
Z	2
D_c, g cm^{-3}	1.95
cryst descn	red, irregular blocks
cryst dimens, mm	0.24 × 0.35 × 0.40
radiation	Mo Kα (λ = 0.71069 Å, graphite monochromator)
temp, °C	21 (1)
scan range ($\Delta\omega$), deg	1.5(0.80 + 0.347 tan θ)
scan speed, deg min^{-1}	3.4–0.7
max Θ, deg	25
octants collected	$+h,-k,\pm l$
no. of unique data collected	4734
no. of obsd data ($I > 3\sigma(I)$)	3556
μ(Mo Kα), cm^{-1}	50.8
min, max abs cor	0.67, 1.37
no. of variables in final cycle	285
GOF	1.17
weighting formula	$[\sigma^2(F_o) + 0.00001(F_o^2)]^{-1}$
isotropic ext parameter	1.4 (4) × 10^{-5}
R, R_w[a]	0.048, 0.051

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Experimental Section

Synthesis. In an attempt to prepare a heterobimetallic μ-thiolato complex containing a $W^{IV}(\mu\text{-SR})_2Cu^I$ moiety, a stirred solution of $WCl_4(Me_2S)_2$ (1 g) in CH_2Cl_2 (30 mL) was reacted with 2 molar equiv of $Pb(S\text{-}i\text{-Bu})_2$ under an atmosphere of dry nitrogen. After the heterogeneous mixture was stirred for 15 min, 1 molar equiv of Cu(I) was added, in the form of the complex $[CuCl(Ph_3P)]_4$. After the $PbCl_2$ (produced in the initial metathesis reaction between $WCl_4(Me_2S)_2$ and $Pb(S\text{-}i\text{-Bu})_2$) was filtered off, the solution was reduced in volume to ~10 mL and allowed to stand at room temperature for 48 h. Red crystals were formed that appeared from the infrared spectrum to contain terminal oxo groups, W–Cl bonds, and probably Ph_3P. In view of the small quantities of the product and the inferred incorporation of Cu–PPh_3 entities, we undertook an X-ray crystal structure determination which showed that the crystals were, in fact, the unexpected compound **1**, rather than a compound containing the target moiety, $W(\mu\text{-S-}i\text{-Bu})_2Cu$.

IR spectrum of **1** (Nujol mull between CsI plates) (cm^{-1}): 1590 (w), 1270 (m), 1245 (w), 1160 (w), 1120 (s) (ν(P=O)), 1100 (sh), 1060 (s), 1030 (w), 1000 (w), 970 (s) (ν(W=O)), 940 (sh), 750 (s), 730 (s), 690 (s), 535 (s), 520 (m, sh), 450 (w), 405 (w), 330 (w) [308 (m), 290 (sh), 280 (m) (ν(W–Cl))].

X-ray Analysis. The crystal data and experimental details are given in Table I. The crystal chosen for data collection was an irregular block cut from a larger sample and sealed in a glass capillary under nitrogen. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered reflections (15 < θ < 19°). The choice of space group $P2_1/n$ is unam-

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