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5d Early-Transition-Metal Corroles: a Trioxo-Bridged Binuclear Tungsten(VI) Derivative

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Supporting Information

ABSTRACT: The synthesis and full characterization of the first tungsten corrole reveal that it is a binuclear trioxo-bridged complex of tungsten(VI), a coordination motif without precedence for tungsten chelated by other ligands.

In sharp contrast with the exceedingly large research activity on other metal chelates of corroles,[1] very little is currently known about the corresponding third-row (5d) transition-metal complexes. This is limited to an accidentally obtained (oxo)rhenium(V) corrole,[2] the six-coordinated iridium(III) complexes with interesting photophysical properties,[3] and most recent reports about gold chelates of fully brominated corroles.[4] While the most pronounced and unique feature of the tetradentate and trianionic corrolato ligands is stabilization of 3d transition metals in high oxidation states,[5] no extraordinarily high-valent 5d metallocorroles have been reported yet. One-electron oxidation of iridium(III) corroles leads to complexes with partial iridium(IV) and corrole radical character,[6] but the reaction with bleach and ammonia [the most established route to (nitrido)metal(V) and (nitrido)metal(VI) complexes] resulted in N-atom insertion into the macrocycle without a change in the iridium oxidation state.[7] The present knowledge about early-transition-metal corroles is confined to (oxo)titanium(IV),[8] (oxo)vanadium(IV),[8] and (oxo)molybdenum(V) complexes,[9] and only chromium corroles were reported in a large variety of oxidation states: (dipyridinyl)chromium(III),[10−12] (oxo)chromium(IV),[10,13] (oxo)chromium(V),[14,15] and (nitrido)chromium(V/VI).[16] Different from the other rows of the periodic table, only tungsten may be considered as a 5d early-transition-metal element. Its accessible oxidation states range from 2+ to 6+, which has a tremendous impact on the use of tungsten complexes in catalysis such as the activation of small molecules via multielectron redox processes.[17]

Because metalloporphyrins are excellent redox catalysts, the chemistry of tungsten porphyrins has been extensively studied. Tungsten(V) complexes are most common and may be prepared by the reaction of the free-base porphyrin in high-boiling-point solvents with WF_5, H_2WO_4, $K_3W_2Cl_6$, or $W(CO)_6$.[18,19] The complexes obtained under aerobic workup are pseudooctahedral, with the two axial positions occupied by a terminal oxo and anionic ligands trans to it. The treatment of these complexes with water or base affords the μ-oxo-bridged dinuclear species. Tungsten(V) porphyrins undergo slow demetallation, attributed to unfavorable coordination of the small W^{VI} ion (ionic radius = 0.58 Å) formed via aerobic oxidation.[20] The only fully characterized tungsten(VI) porphyrin is W(TPP)(O)(O_2) (TPP = tetraphenylporphyrinato), with an unusually large 1.49 Å displacement of the $[W(O)(O_2)]^{2+}$ moiety from the N_4 plane and a cisoid arrangement of the oxo and peroxo groups.[21] A completely analogous motif, albeit with only a 1.00 Å out-of-plane displacement, was found for a molybdenum(VI) porphyrin many years later.[22] The above introduction accounts for the motivation of the current investigations, which focused on the development of a synthetic strategy toward tungsten complexes of corroles. The results revealed that the air-stable complex is a novel trioxo-bridged binuclear tungsten(VI) corrole, a structure with no precedence for tungsten chelated by any other ligands.

The initial approach for preparation of the target complex relied on the metal carbonyl method.[23] Using the most stable free-base corrole H_3(tpfc),[24] both the reaction time and temperature were revealed to play an important role in its reaction with hexacarbonyltungsten. Very gentle heating and close followup of changes in color (from purple to red) and thin-layer chromatography are required because when the temperature was too high or too low, the product decomposed or much starting material was recovered, respectively. The yields using $W(CO)_6$ varied between 8 and 20%, but utilization of WCl_6 did not suffer from the above invariability and the chemical yield from many syntheses averaged to 35%.[25]

On the basis of the other analogues in the same group of the periodic table, the expected product was (oxo)tungsten(V) corrole. The initial mass spectrometry (MS; MALDI$^-$) examinations displayed an isotopic pattern consistent with the addition of one W and two O atoms relative to the free-base corrole, information that could be in harmony with the structures drawn in Scheme 1.

Another important piece of information is that the product was EPR-silent and NMR-active, hence indicating a diamagnetic complex. The paramagnetic compound C of Scheme 1 may, hence, be ruled out, unless it contains a π-oxidized ligand (corrole radical) that is strongly coupled in an antiferromagnetic fashion to the d^1 W^V. Some rather broad resonances in the room temperature (RT) ^{19}F NMR spectrum of this compound could support the last possibility, but the low-temperature (T) spectra are more in line with dynamic processes (restricted *meso*-C_6F_5 ring rotation?) on the NMR time scale (Figure 1). Resonances that are relatively sharp at RT become broader at low T (i.e., transition from fast to slow processes), while those

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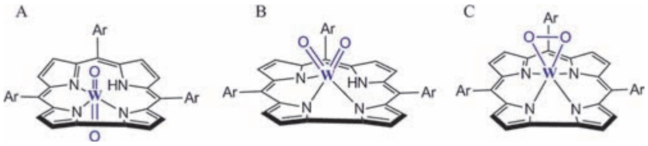
Scheme 1. Possible Structures of (tpfc)WO$_2$: (A) *trans*-Dioxotungsten(VI) Corrole, (B) *cis*-Dioxotungsten(VI) Corrole, and (C) Peroxotungsten(V) Corrole[a]



[a] Note that the oxidation state of tungsten is 6+ in A and B but 5+ in C and that both A and B may also be drawn as anionic complexes with coordination of all four N atoms of the corrole.

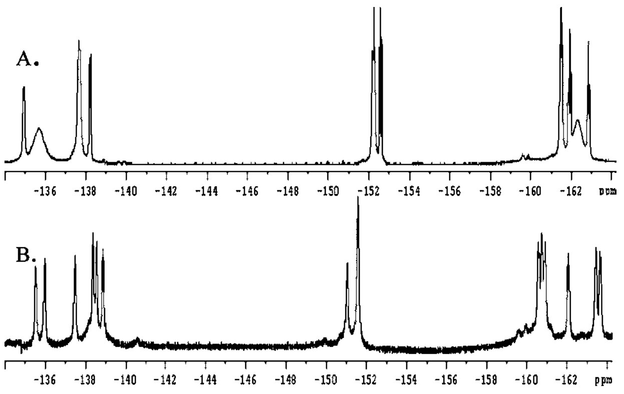


Figure 1. ^{19}F NMR spectra of [W(tpfc)]$_2$O$_3$ at room temperature (A) and at −60 °C (B).

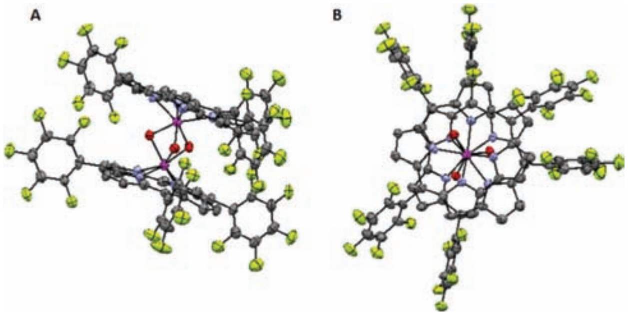


Figure 2. Projection of [W(tpfc)]$_2$O$_3$: (A) side view; (B) top view.

that are broad at RT split into widely separated signals at low *T* (i.e., transition from slow to frozen processes).

The low-*T* spectrum revealed three unique C_6F_5 groups, which all display two different kinds of *o*-F (−135 to −140 ppm) and *m*-F (−161 to −165 ppm) atoms, inconsistent with all possible structures drawn in Scheme 1. The *o*-F and *o*-F′, as well as the *m*-F and *m*-F′ atoms on the C_6F_5 rings, display up to 4 ppm differences in chemical shifts, much larger than those recorded in all pyramidal metal complexes of the same ligand (tpfc^{3-}).[26,27] In fact, Δδ(*o*-F − *o*-F′) values of >2 ppm are confined to binuclear complexes that contain either directly bound ruthenium(III) or *μ*-oxo-bridged iron(IV) corroles.[28,29] These resonances are widely separated because one of them is heavily affected by the *π*-aromatic system of both corrole rings.

On the basis of the above analysis, the MS examinations where repeated with much less ionization power in order to reveal if the previously obtained mass represents the molecular weight of the complex or a fragment of it. This experiment was highly informative indeed: the obtained spectrum was consistent with a dinuclear tungsten complex chelated by two corrolato trianions, three O atoms, and one water molecule. The electron count leads to d^0 W^{VI}, in line with the apparent diamagnetism, and the binuclear structure is in harmony with ^{19}F NMR analysis. These spectroscopy-based conclusions were substantiated by X-ray crystallography performed on high-quality crystals obtained from CH_2Cl_2 and heptane solutions (Figure 2), which provided other highly valuable information.

The analysis revealed a dinuclear complex in which each of the two W^{VI} ions resides well outside the mean plane of the adjacent corrole core to accommodate the high (7) coordination number manifested by the W ion in the present case. Their distances from the mean plane of the four pyrrole N atoms in the corresponding corrole rings are 0.961(4) and 0.970(4) Å. The corrole complexes are characterized by domed conformations, with all four pyrrole rings turning upward with their N-atom sites directed at the perching metal ions. The two roughly parallel tpfc moieties are partly staggered with respect to one another to avoid collision between the peripheral pentafluorophenyl substituents. The compound is further characterized by two approximate prismatic environments about each of the W centers, with the three equally spaced (at ~2.45 Å) bridging O atoms forming one, common, three-sided face. The latter reside on a median plane between, and at an equal distance from, the two corrole components. The four N atoms of the corrole ring comprise the other four-sided face on both sides. The observed coordination distances are within W−N = 2.058(7)−2.124(7) Å and W−O = 1.804(6)−2.217(6) Å, while the W−W distance in the dimeric structure is 2.7980(6) Å, in good agreement with earlier literature.[30,31]

Comparable double-decker-type structures involving tetraphenylporphyrin (instead of tpfc) and oxo-bridged metal ions (e.g., Nb,[32,33] Yb,[34] Zr,[35,36] and Hf[37−39]) are known.[40] In all these examples, the metal ions deviate significantly (about 1 Å, Table 1) from the porphyrin plane, coordinating simultaneously to the pyrrole N atoms and either three or four oxo-bridging ensembles placed at the median plane of the double-decker structure. A particularly relevant example involves the tris(*μ*-oxo)bis(tetraphenylporphyrinatoniobium) compound,[32,33] the overall structure of which reveals a remarkable resemblance to our tungsten corrole (Figure 2). The other examples are slightly different, including cases of four rather

Table 1. Interatomic Distances (Å) of Different *μ*-Oxo-Bridged Complexes

	[W(tpfc)]$_2$(*μ*-O)$_3$	[Hf(TPP)]$_2$(*μ*-O)(*μ*-OH)$_2$	[Zr(TPP)]$_2$(*μ*-O)(*μ*-OH)$_2$	[Nb(TPP)]$_2$(*μ*-O)$_3$
M−OH	n/a	2.167 (14)−2.206(14)	2.176(6)−2.181(6)	n/a
M−O	1.804(6)−2.217(6)	1.977(13)	1.981(5)	1.81(2)−1.89(2)
M−M′	2.7980(6)	3.071(1)	3.064(1)	2.751(4)
M−N$_{avg}$	2.058(7)−2.124(7)	2.27(3)	2.290(22)	2.250(7)
M out-of-plane	0.961(4)−0.970(4)	1.048	1.057	1.000
ionic radius	0.67	0.76	0.78	0.70

than three bridging O atoms and variability in their protonation.

We have introduced tungsten corroles via full characterization of a new complex that appears to be novel by virtue of presenting (a) the first 5d early-transition-metal metallocorrole and (b) the first binuclear tungsten complex with a trioxo bridge.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for $[W(tpfc)]_2O_3$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Synthesis of $[(tpfc)W]_2O_3$. A solution of $H_3(tpfc)$ (50 mg, 0.125 mmol) and WCl_6 (50 mg, 0.126 mmol) in 20 mL of decalin was heated to 170−180 °C under nitrogen. After 40 min, the color of the mixture changed from deep purple (reactant) to blood red (product). Purification by flash chromatography (silica; 1:2 CH_2Cl_2/hexanes), followed by crystallization from a CH_2Cl_2/heptane mixture, 45 mg (35%) of dark-red X-ray-quality crystals. ^{19}F NMR (376 MHz, $CDCl_3$): δ −134.91 (br s, 2F), −135.62 (br s, 4F), −137.66 (br s, 2F), −138.20 (d, J = 24.8 Hz, 2F), −152.23 (t, J = 20.8 Hz, 4F), −152.57 (t, J = 22 Hz, 2F), −161.52 (m, 4F), −161.92 (td, J = 24.4 and 8.8 Hz, 2F), −162.35 (m, 4F), −162.85 (td, J = 25.6 and 8.8 Hz, 2F). MS (MALDI-TOF-LD; %): m/z 2019 ($[M + H_2O]^-$, 100%). UV/vis (CH_2Cl_2): λ_{max}, nm (log ε, M^{-1} cm^{-1}) 409 (3.20), 486 (1.75), 538 (2.30), 562 (2.41).

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