An Experimental and Theoretical Study of a Heptacoordinated Tungsten(VI) Complex of a Noninnocent Phenylenediamine Bis(Phenolate) Ligand

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Abstract

[W(N_2O_2)(HN_2O_2)] (H_4N_2O_2 = N,N'-bis(3,5-di-tert-butyl-2-hydroxyphenyl)-1,2-phenylenediamine) with a noninnocent ligand was formed by reaction of the alkoxide precursor [W(eg)_3] (eg = the 1,2-ethanediolate dianion) with two equivalents of ligand. The phenol groups on one of the ligands are completely deprotonated and the ligand coordinates in a tetradentate fashion, whereas the other ligand is tridentate with one phenol having an intact OH group. The molecular structure, magnetic measurements, EPR spectroscopy, and density functional theory calculations indicate that the complex is a stable radical with the odd electron situated on the tridentate amidophenoxide ligand. The formal oxidation state of the metal center is W(VI), with the paramagnetic properties being due to the unpaired electron on the ligand.

Graphical abstract

Tungsten(VI) forms a heptacoordinated complex with a tetradentate, redox-noninnocent ligand. The paramagnetic complex is a stable radical with the unpaired electron being located on the ligand.
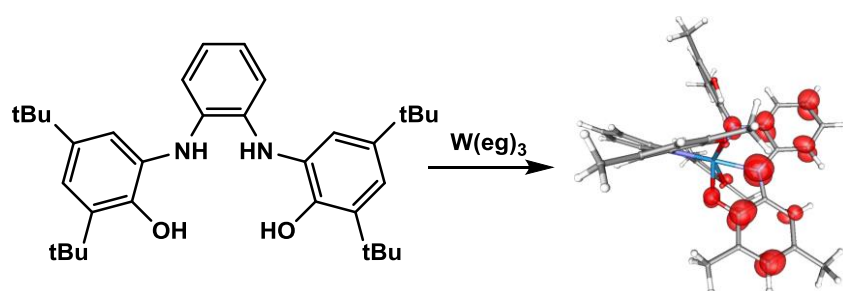

Keywords

Tungsten; oxidation states; noninnocent ligand; amidophenoxide radical, DFT calculations, electronic structure

Catechols and related *ortho*-aminophenols are interesting as redox-active non-innocent ligands that can form metal complexes where the oxidation state of the metal is ambiguous.[1-5] A well-known example of such a ligand is N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine ($H_4N_2O_2$) that may be viewed as a derivative of two bidentate *ortho*-aminophenols.[6] This potentially tetradentate ligand has a versatile electrochemical behavior as it can present five different oxidation states that are interrelated by one-electron transfer steps (see

Chart **1**). Once partially or fully deprotonated, $H_4N_2O_2$ can act as a multidentate ligand to form complexes with the early transition metals Ti, Zr and Hf [7-9] as well as the late transition metals Cu and Zn [6] in a 1:1 metal-to-ligand ratio whereas 1:2 complexes are formed with Mo [10], Mn [11] and Sn [12]. In some cases, coordination to the metal center is associated with an intramolecular reaction leading to the formation of a new noninnocent phenoxazinylate/phenoxylate ligand.[11]
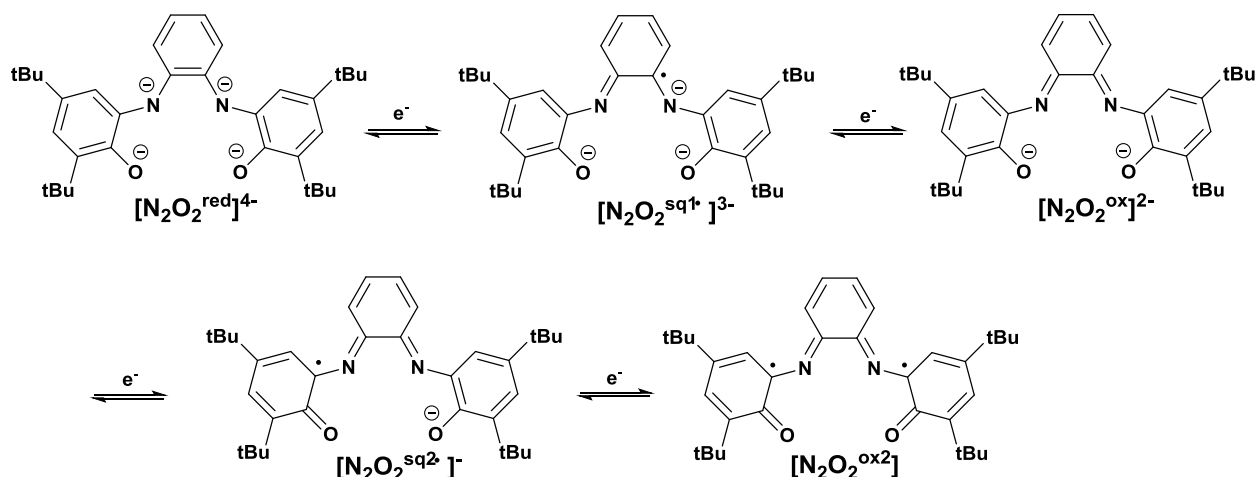
**Chart 1**. Different oxidation states of the deprotonated ligand N_2O_2. Adapted from reference [6].

Relativistic effects are significant in the chemistry of row 5 and 6 d-block metals, being much more important for the heavier (row 6) elements. A relativistic contraction of the core orbitals increases bond dissociation energies, while destabilization of the metal-centered d-orbitals decreases associated redox potentials. There are also some differences in atomic ground state, *i.e.* there are Mo $4d^5 5s^1$ but W $5d^4 6s^2$ ground states.[13] In general, W compounds have lower redox potentials and higher bond strengths than isostructural Mo complexes. Therefore, we might expect some differences in the bonding parameters as well as in the magnetic and electrochemical properties of isostructural Mo and W complexes with the non-innocent ligand $H_4N_2O_2$. $H_4N_2O_2$ is known to react with $[MoO_2(acac)_2]$ to form a heptacoordinated, paramagnetic complex $[Mo(N_2O_2)(HN_2O_2)]$, where the Mo ion has a formal oxidation state of +VI and the non-innocent ligand displays both tetradentate and tridentate coordination modes, with the latter one containing an unpaired electron. [10]

The reaction of the tungsten alkoxide precursor [W(eg)$_3$] (eg = the 1,2-ethanediolate dianion) [14] with $H_4N_2O_2$ in MeOH led to the formation of a dark solution, from which dark, shiny crystals deposited during a few days.[1] The product is soluble in common organic solvents but the NMR spectra were very poor, most likely due to the paramagnetism of the compound (see below). The molecular structure was finally verified by X-ray studies, which revealed that the product [W(N$_2$O$_2$)(HN$_2$O$_2$)] **1** is isostructural with its Mo counterpart.[2] The asymmetric unit consists of two crystallographically independent molecules with very similar structural parameters. One of the two ligands is completely deprotonated and coordinates in a tetradentate fashion, whereas the other ligand is tridentate and has one intact OH group (Figure 1). The coordination geometry can be described as being based on a 4:3 piano stool with the rectangular face defined by donors O1, N1, N4 and N3.

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[1] Tungsten trisdiolate [W(eg)$_3$] (eg = 1,2-ethanediolate dianion) [14] (200 mg, 0.549 mmol) and $H_4N_2O_2$ (284 mg, 0.549 mmol) were mixed in MeOH (10 mL) under ambient atmosphere and the reaction mixture was allowed to stand for five days at room temperature to yield complex **1** as dark, shiny crystals (532 mg, 80 % yield based on the ligand).

[2] CCDC 1822503 contains the supplementary crystallographic data for **1.**

$W(eg)_3 + 2 H_4N_2O_2 \xrightarrow{MeOH}$
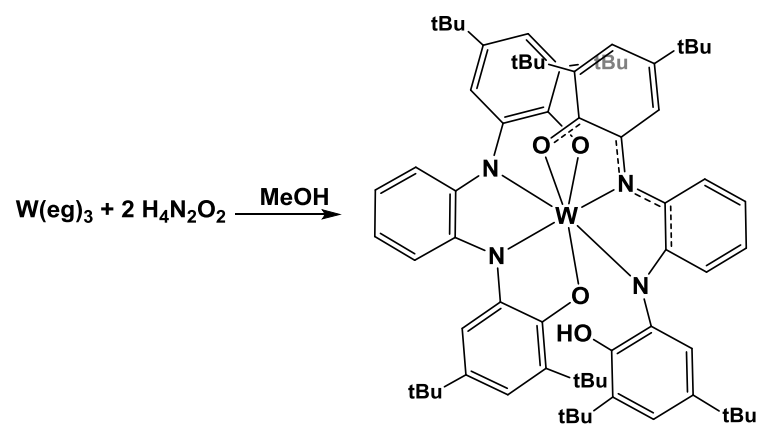
Scheme 1. The formation of **1**.
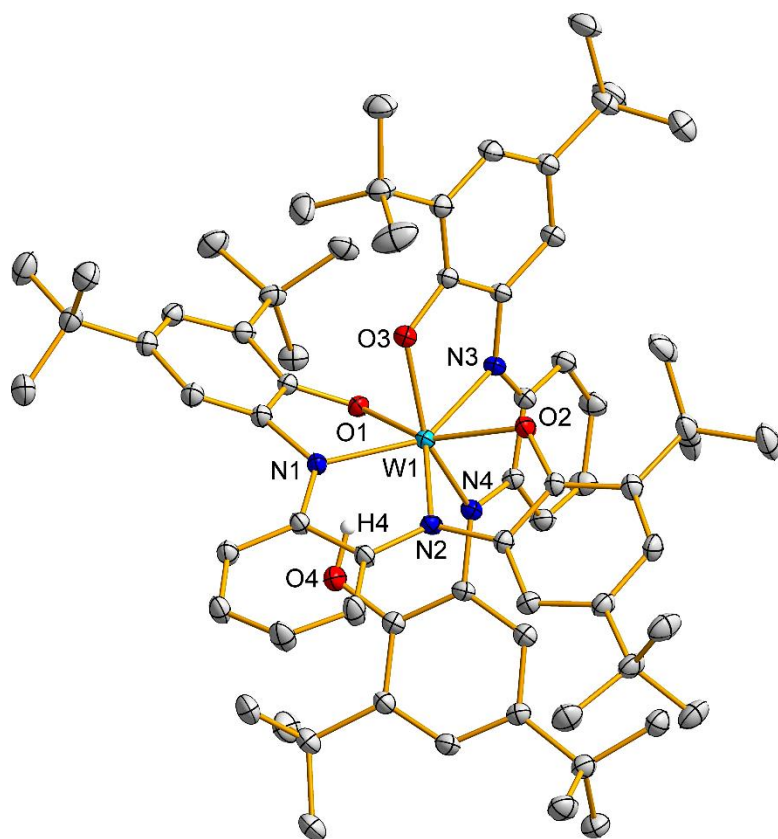
Fig. 1. Crystal structure of **1** showing one of two crystallographically independent molecules in the asymmetric unit. The C–H hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

The protonation states of the ligands were verified by electrospray mass spectrometry as the mass expected for the empirical formula (see Supplementary material for more details). The oxidation state of W is calculated from the estimated oxidation levels of the ligands, *i.e.* the tetradentate ligand is fully deprotonated $[N_2O_2{}^{red}]^{4-}$, whereas the tridentate ligand looks triply deprotonated $[HN_2O_2{}^{sq1\cdot}]^{2-}$ (see Chart 1). As a result, the formal oxidation state of the metal center is W(VI). The unpaired electron in the ligand was observed by electron paramagnetic resonance (EPR) spectroscopy on **1** in dichloromethane and toluene solutions at 77 K. The EPR spectrum shows a signal (S=½) g_{iso} = 1.986 with minor asymmetry. The relatively small *g* anisotropy as well as the narrow spectrum (width of ~ 14 mT) are indicative of an organic radical type signal.[15,16] The g-values of metal centred radicals frequently differ significantly from the free electron value of g = 2.0023, whereas ligand radical complexes often have a much smaller g-anisotropy.[15] For example, the experimental g-values reported for W(V) ions in tungsten enzymes are typically in the range 1.99–1.83 [17], whereas the g-value is even lower for isolated mononuclear sulfido-tungsten(V) model compounds.[18] For **1**, the calculated spin density (see below) indicates that the unpaired electron density is delocalized over the ligand. However, the low experimental g-value indicates some spin density on the central W atom. For comparison, the corresponding molybdenum compound $[Mo(N_2O_2)(HN_2O_2)]$ with a ligand radical shows a rather similar spectrum with g_{iso} = 2.0087.[10] In solid state, complex **1** is paramagnetic with susceptibility χ_{mol} = 1.7·10⁻⁶ m³/mol at 2 K (χ_{mol} = M·χ_v/ρ, where ρ is the density, M is molar mass and χ_v is volume magnetic susceptibility), as measured by a SQUID magnetometer. The temperature dependence of the susceptibility was also measured and the data fitted to the Curie law of localized moments, χ_{mol} = C/(T-ϑ_p). Figure S6 shows the plots of χ_{mol} *vs. T* and *1/χ_{mol} vs. T*. The calculated magnetic moment (μ_{eff}) is 1.43 B.M. As the spin = 1/2 value for an unpaired electron is 1.73 B.M., the magnetic moment indicates the presence of an unpaired electron, even if the value is lower than expected. Although the sample was purified by column chromatography

and subsequently crystallized, we cannot completely exclude the possibility of a mixture of diamagnetic and paramagnetic species with otherwise very similar physical properties including a similar solubility due to the similar overall molecular structure.

The cyclic voltammogram of **1** was measured in acetonitrile in the potential range from +1.4 to -2.0 V vs. Fc$^+$/Fc. Four distinct one-electron oxidation waves (+0.17, +0.40, +0.77 and +1.00 V) and two one-electron reduction waves (-0.08 and -0.51 V) are seen (see Supporting Information). For comparison, the Mo analogue has three distinct one-electron oxidation waves (0.41, 0.83 and 1.23 V) and three one-electron reduction waves (-0.01, -0.63 and -1.26 V) within the acetonitrile solvent window.

In order to probe the electron distribution within the complex, computational modelling of the complex was made. The geometry of the simplified model complex **1'** (aromatic *tert*-butyl groups substituted with methyl groups) was optimized using the PBE1PBE [19] functional and def2-TZVP [20-23] basis set with def2-ECP effective core potential for tungsten atom. For **1'**, the most plausible spin states are a doublet (S = 1/2) with one unpaired electron and a quartet state (S = 3/2) with three unpaired electrons. The doublet state was calculated to be approximately 28 kcal/mol lower in energy than the quartet state, strongly indicating that this is the electronic ground state of the complex. The geometrical parameters (Table S1) obtained from the structural optimization of the doublet state of **1'** are in good agreement with the X-ray structure. The calculated spin density (Figure 2) indicates that the unpaired electron density is delocalized over the HN$_2$O$_2$ ligand, which is not fully supported by the EPR results (see above).
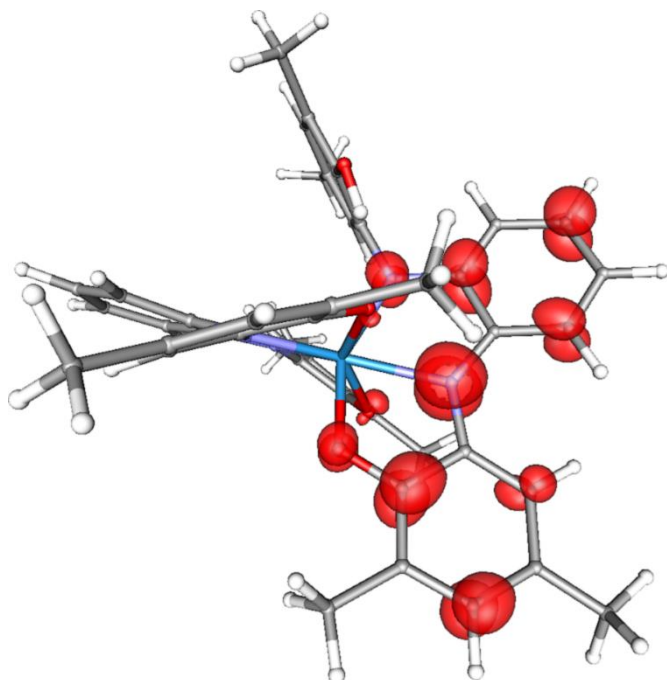
Fig. 2. Spin density of complex **1'**.

In conclusion, the reaction of tungsten(VI) precursor [W(eg)$_3$] (eg = 1,2-ethanediolate dianion) with two equivalents of a redox-active ligand N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine (H$_4$N$_2$O$_2$) leads to the formation of paramagnetic complex [W(N$_2$O$_2$)(HN$_2$O$_2$)] **1**. In this complex unit, one of two ligands is fully deprotonated and tetradentate, whereas the other ligand is tridentate and has one intact OH group. The formal oxidation state of the metal center is W(VI), while the paramagnetic properties are due to the unpaired electron in the ligand. The geometrical parameters of the ligands in complex **1** suggest some change in the oxidation state of the tridentate ligand upon coordination, which is also evident from the odd number of electrons. The doublet state with one unpaired electron is the most probable electronic spin state for the complex. To the best of our knowledge, this is the first example of a stable high-valent tungsten-amidophenoxide radical complex.

Acknowledgements

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