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Rhenium(V)-oxo corrolazines: isolating redox-active ligand reactivity[†]

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Abstract

The synthesis of the first example of a third-row metallocorrolazine characterized by single crystal X-ray diffraction is reported. This Re^V(O) porphyrinoid complex shows an exclusively ligand-based reactivity with strong acids and oxidizing agents. The one-electron oxidized π -cation-radical complex is capable of H-atom abstraction.

The synthesis of rhenium complexes is of interest due to their potential use as catalysts for oxygen-transfer,¹ X–H (X = Si, B, P and H) bond activations,² and in CO₂ photoreduction reactions.³ In addition, certain isotopes of rhenium are used in medical imaging, diagnostics, and therapeutics.⁴ Although not found in natural heme systems, a few examples of rhenium porphyrins have been synthesized, including Buchler's first report of high-valent Re^V(O)(X) porphyrins.⁵ A decade later, the ring-contracted high-valent metal-oxo Re^V(O)(TCF₃C) (TCF₃C = 5,10,15-tris(trifluoromethyl)corrole) was serendipitously prepared in an attempted porphyrin metallation reaction, providing the only example of a rhenium corrole.⁶

High-valent metal-oxo porphyrinoid complexes are of significant interest because of their role in synthetic and biological oxidation catalysis.⁷ Our group recently described the characterization of high-valent Mn^V(O) and Cr^V(O) corrolazine (Cz) complexes by single crystal X-ray diffraction (XRD), and showed that these complexes exhibited dramatically different abilities to abstract hydrogen atoms from X–H (X = O, C) bonds.⁸ In earlier efforts, it was also shown that the Mn^V(O)(Cz) complex could be chemically oxidized to give Mn^V(O)(Cz⁺), the first example of an Mn^V(O) π -radical cation complex. The latter complex showed greatly enhanced O-atom transfer (OAT) reactivity compared to its neutral precursor.⁹ Lewis/Brønsted acids (LA) were also shown to have a profound influence on Mn^V(O)(Cz), stabilizing the valence tautomer Mn^{IV}(O)(Cz⁺)(LA) and providing a rare example of a chemically driven, reversible valence tautomerization. The reactivity of Mn^{IV}(O)(Cz⁺)(LA) was significantly different from Mn^V(O)(Cz), with the metal-oxo unit and redox-active Cz ligand functioning together to carry out H-atom transfer (HAT) and OAT reactions.¹⁰ Recently, much attention has been given to redox-active ligands and how they operate in conjunction with a metal ion to mediate various chemical transformations.¹¹

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Herein we report the synthesis and characterization by XRD of an $\text{Re}^{\text{V}}(\text{O})(\text{Cz})$ complex, the first metallocorrolazine containing a third-row metal ion, and a rare example of a structurally characterized rhenium porphyrinoid complex. This complex was prepared as an isoelectronic analog of $\text{Mn}^{\text{V}}(\text{O})(\text{Cz})$. Addition of strong Brønsted acids does not lead to stabilization of a valence tautomer in this case, but rather the reversible protonation of a remote site on the ligand. It is shown that the redox-active Cz ring can participate in electron-transfer and H-atom transfer reactions without the involvement of the metal-oxo unit. The H-atom transfer reactivity for the one-electron-oxidized $\text{Re}^{\text{V}}(\text{O})(\text{Cz}^{+\bullet})$ is also shown to be strongly dependent on the nature of the external one-electron oxidant through a surprising observation of “zero-order” kinetics.

The synthesis of the $\text{Re}^{\text{V}}(\text{O})$ corrolazine complex was accomplished by metallation of TBP_8CzH_3 (**1**) with excess ReCl_5 in refluxing decalin (Scheme 1). The product was purified by chromatography and gave $\text{Re}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ (**2**) as a dark green solid (99% yield). The UV-vis spectrum of **2** exhibits a Soret band at 460 nm, which is the most red-shifted for any metallocorrolazine, and a Q-band at 670 nm. The ^1H NMR spectrum of this complex is diamagnetic, consistent with a low-spin Re^{V} ion. Eight doublets appear between 8.44 – 7.26 ppm, which can be assigned to the peripheral *para*-substituted phenyl substituents (Fig. S1[†]). An LDI-TOF mass spectrum gives $M^+ = 1557.38$ *m/z*, in good agreement with the $\text{Re}(\text{O})(\text{TBP}_8\text{Cz})$ formulation.

Confirmation of the structure of **2** comes from single crystal X-ray crystallography. Single crystals of **2** were obtained by vapor diffusion of acetonitrile in toluene. The molecular structure is shown in Fig. 1, revealing a 5-coordinate Re center, with a terminal oxo ligand at a Re–O distance of 1.682(5) Å. This distance is consistent with an Re–O triple bond.^{1e,12} The Re ion is displaced by *ca.* 0.74 Å from the plane defined by the four $\text{N}_{\text{pyrrole}}$ atoms. For comparison, $\text{Re}^{\text{V}}(\text{O})(\text{TCF}_3\text{C})$ exhibits an Re–O bond length of 1.662(2) Å and an out-of-plane distance of 0.701 Å.⁶ The Re–O distance in **2** is significantly elongated compared to $\text{Mn}^{\text{V}}(\text{O})$ (1.5455(18) Å) and $\text{Cr}^{\text{V}}(\text{O})$ (1.553(2) Å) corrolazines,^{8a} as expected for a third-row metal ion. The Re ion is also much further out of plane, by at least 0.2 Å, compared to either Mn^{V} or Cr^{V} complexes.

We previously found that $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ reacts with Lewis and Brønsted acids at 23 °C to give $\text{Mn}^{\text{IV}}(\text{O})(\text{TBP}_8\text{Cz}^{+\bullet})(\text{LA})$ ($\text{LA} = \text{H}^+$, Zn^{II} , $\text{B}(\text{C}_6\text{F}_5)_3$), in which the paramagnetic Mn^{IV} valence tautomer is stabilized over the diamagnetic, low-spin Mn^{V} species through a proposed weakening of the Mn–O π -bonding from coordination of LA to the terminal oxo group.¹⁰ In contrast, the addition of the Brønsted acid $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (HBArF) to $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ at low temperature (–60 °C) led to protonation of a remote *meso*-nitrogen atom on the Cz ring and retention of the low-spin Mn^{V} configuration. Protonation of the *meso*-N atoms in Mn^{III} corrolazines was also definitively confirmed by XRD.¹³ To determine the reactivity of the isoelectronic $\text{Re}^{\text{V}}(\text{O})$ analog toward Brønsted acids, the reaction of **2** with HBArF was examined. Addition of one equiv of HBArF to **2** in CH_2Cl_2 causes clear shifts in the UV-vis spectrum (Fig. 2a), although these changes are not

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consistent with formation of a Cz π -radical-cation. The final spectrum is more typical of protonation at the remote site on the Cz ligand.¹³ Spectral titration with HBarF supports a 1:1 binding stoichiometry (inset, Fig. 2a) to form $[\text{Re}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})(\text{H})]^+$ (**3**).

Characterization of the monoprotonated complex **3** was performed by 1D (Fig. 2B) and 2D (Fig. S3–4[†]) NMR spectroscopy. The ^1H NMR spectrum of **3** is diamagnetic, confirming that the paramagnetic valence tautomer $\text{Re}^{\text{IV}}(\text{O})(\text{Cz}^{+\bullet})$ is not observed. Spectra for **2** and **3** are shown in Fig. 2b (see Fig. S2[†]). A new peak is observed at 13.45 ppm for the protonated complex, and integrates to 1H. This peak can be assigned to protonation of a *meso*-N of the corrolazine ring, shifted downfield by the ring current effect. For comparison, the *meso* C–H proton of Zn octaethylporphyrin appears at *ca.* 10 ppm.¹⁴ The aromatic pattern is complex, consistent with addition of H^+ to one of the *meso*-N atoms that does not lie on the mirror plane bisecting the pyrrole-pyrrole linkage. The NMR spectrum for **2** at 23 °C is similar to what was observed for protonation of $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ at –60 °C.¹³

The IR spectrum of **2** shows an intense peak at 997 cm^{-1} (Fig. 3a), in the region expected for the stretching frequency of an $\text{Re}^{\text{V}}\text{--O}$ triple bond. However, an intense peak at $\sim 997\text{ cm}^{-1}$ has also been observed in several other metallocorrolazines, and may arise from Cz vibrational modes.¹⁵ To conclusively identify the Re–O stretch, we synthesized the isotopically labeled $\text{Re}^{\text{V}}(^{18}\text{O})(\text{TBP}_8\text{Cz})$ (**2- ^{18}O**) by addition of excess H_2^{18}O (80 equiv) to the Re metallation reaction involving TBP_8CzH_3 (**1**) and ReCl_5 in decalin. This method yielded the $\text{Re}^{\text{V}}(\text{O})$ complex with >99% ^{18}O isotopic incorporation as seen by LDI-MS (Fig. S5[†]), and indicates a mechanism of oxygen incorporation that involves hydrolysis of an $\text{Re}^{\text{V}}(\text{Cl})_2(\text{TBP}_8\text{Cz})$ precursor.⁵ The appearance of a new band upon ^{18}O substitution at 945 cm^{-1} is accompanied by a slight decrease in intensity of the band at 997 cm^{-1} (Fig. 3). These spectral changes are consistent with the $\nu(\text{Re}^{16}\text{O})$ mode overlapping with the intense peak at 997 cm^{-1} . The predicted isotopic shift for ^{18}O substitution in an isolated Re–O diatomic oscillator is 52 cm^{-1} , in excellent agreement with the predicted value of $\nu(\text{Re}^{16}\text{O}) = 997\text{ cm}^{-1}$. The Re–O stretch is close to that observed for $\text{Re}^{\text{V}}(\text{O})$ corrole (994 cm^{-1}),⁶ but higher than most $\text{Re}^{\text{V}}(\text{O})$ porphyrins, phthalocyanines^{5,12b} or N-confused porphyrin.^{12a}

The effect of protonation on the Re–O bond can be probed by IR spectroscopy (Fig. 3b). Upon protonation of **2** with HBarF, a sharp peak at 3280 cm^{-1} appears, consistent with the N–H stretch of a *meso*-NH group (Fig. S6[†]). At the same time, the $\nu(\text{Re}^{18}\text{O})$ peak at 945 cm^{-1} disappears, and only a broad band associated with BARF^- is present at 975 cm^{-1} without any clear evidence for a new Re– ^{18}O stretch. However, replacing HBarF with HOTf causes the broad peak at 975 cm^{-1} to disappear, revealing a new peak for $\nu(\text{Re}^{18}\text{O}) = 956\text{ cm}^{-1}$ (Fig. 3b). These data indicate that an 11 cm^{-1} blue shift occurs for the metal-oxo stretch, implicating a strengthening of the metal–oxo bond upon protonation of a remote site on the ligand.

Density functional theory (DFT) calculations were performed on complexes **2** and **3** to support structural and spectroscopic assignments. Geometry optimizations were performed at the PBE0/LANL2TZ/6-31G** level of theory, beginning with the crystal structure coordinates for **2**. The peripheral aryl substituents were replaced by H atoms to facilitate the calculations. The optimized geometry for **2** matched well with the experimentally

determined crystal structure. Geometry optimizations for protonated **2** were performed with the H⁺ attached at either the *meso*-N or the terminal oxo ligand. These calculations showed that the O–H tautomer is +29 kcal/mol higher in energy than the N–H tautomer **3** (Fig. S7[†], Table S2[†]), and indicate that the *meso*-N is the preferred site of protonation. Frequency calculations give $\nu(\text{Re–O}) = 1055\text{ cm}^{-1}$ for **2** and 1064 cm^{-1} for **3**, which are both higher than the corresponding experimental values. DFT is known to overestimate vibrational frequencies due to systematic errors.¹⁶ However, the difference between the calculated $\nu(\text{Re–O})$ values for **2** and **3** ($\nu(\text{ReO}) = 9\text{ cm}^{-1}$) is in excellent agreement with experiment (11 cm^{-1}).

The $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ complex reacts rapidly with phosphine derivatives through an O-atom transfer mechanism.^{10c} Attempts to react **2** with the phosphine derivatives PPh_3 , PMe_3 , or PEt_3 in CH_2Cl_2 at 23°C showed no reaction even over prolonged reaction times (5 d). Similarly, H-atom donors such as TEMPOH or 2,4-di-*tert*-butylphenol were unreactive toward **2**, although the isoelectronic $\text{Mn}^{\text{V}}(\text{O})$ complex readily abstracts H-atoms from both of these substrates.^{8b} Reduction of **2** with strong one-electron donors such as cobaltocene ($E_{\text{red}} = -1.33\text{ V vs SCE}$)¹⁷ was also unsuccessful. We speculated that **3**, with an additional full unit of positive charge, might show enhanced oxidative reactivity compared to **2**, but reactions with PR_3 or ArOH substrates led only to deprotonation and recovery of **2**. Both the neutral and monoprotonated $\text{Re}^{\text{V}}(\text{O})$ complexes appear inert to either H-atom or O-atom transfer reactions, suggesting a greatly enhanced stability for $\text{Re}^{\text{V}}(\text{O})$ compared to $\text{Mn}^{\text{V}}(\text{O})$ in the corrolazine environment.

To gain further insights into the reactivity of **2** and **3**, cyclic voltammetric measurements were performed (Fig. 4). Complex **2** exhibits a single reversible wave at 1.04 V vs SCE, which is close to an assigned Cz ring oxidation for $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$,⁹ as well as other metallocorrolazines.^{15a} However, there are no other redox events observed for **2**, in contrast to the $\text{Mn}^{\text{V}}(\text{O})$ complex, which exhibits an $\text{Mn}^{\text{V}}/\text{Mn}^{\text{IV}}$ couple near -0.05 V .¹⁵ Upon protonation of **2**, the ring oxidation wave disappears, leaving only an irreversible reduction at -0.17 V as seen in the CV for **3**. Thus for **2** and **3** there are no clearly accessible metal-based redox couples, consistent with a lack of HAT and OAT reactivity. However, the reversible oxidation seen for **2** at 1.04 V suggested that a one-electron oxidized $\text{Re}^{\text{V}}(\text{O})$ ($\text{Cz}^{+\bullet}$) π -cation-radical complex might be accessible by chemical oxidation.^{9,18}

Reaction of $\text{Re}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ with $[\text{Ar}'_3\text{N}^{+\bullet}][\text{SbCl}_6^-]$ ($\text{Ar}' = 4\text{-BrC}_6\text{H}_4$, $E_{\text{red}} = 1.16\text{ V vs SCE}$)¹⁷ resulted in isosbestic conversion to a new species with a broadened Soret peak at 445 nm and a relatively weak, red-shifted band at 760 nm (Figure 4b). These features are characteristic of a corrole,¹⁹ porphyrazine,²⁰ and corrolazine π -radical.^{9–10,18} Spectral titration showed one equiv of oxidant was required for complete formation of the π -radical cation complex (Fig. S8[†]). EPR spectroscopy revealed a sharp singlet at $g = 2.00$, similar to $\text{Mn}^{\text{V}}(\text{O})$ and $\text{Mn}^{\text{V}}(\text{imido})\text{Cz-}\pi$ -radical cation species.^{9,18} Quantitation of the EPR signal showed a 94% yield of the oxidized product. Attempts to isolate this product as a solid were unsuccessful, but taken together the data show that **2** can be oxidized in situ by $\text{Ar}'_3\text{N}^{+\bullet}$ to give the monocationic complex $\text{Re}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz}^{+\bullet})$ (**4**).

In earlier work, dramatic enhancements in OAT reactivity were seen for $\text{Mn}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz}^{+\bullet})$ compared to its neutral precursor,⁹ but the Re^{V} analog **4** remained unreactive to OAT. Addition of phosphine derivatives to **4** in CH_2Cl_2 led only to 1-e^- reduction, restoring **2** with no evidence of oxo-transfer. However, addition of the H-atom donor 9,10-dihydroanthracene (DHA) to **4** resulted in quantitative conversion to monoprotonated **3**. Analysis by GC-FID showed anthracene was produced in 90% yield, confirming that formal HAT occurs via the net reaction in Scheme 2. Although these observations implied that **4** was abstracting an H-atom from DHA, UV-vis time course experiments under pseudo-first-order conditions (excess DHA) showed a surprising *linear dependence* for the decay of **4** and production of **3** (Fig. S10[†]). These data were indicative of a reaction *zero-order* in **4**. The zero-order kinetics can be explained by a mechanism involving back electron-transfer between $\text{Ar}'_3\text{N}$ and **4**, establishing the equilibrium shown in Eq 1. The redox potentials for **2** and $[\text{Ar}'_3\text{N}^{+\bullet}][\text{SbCl}_6^-]$ indicate a relatively small $K_{\text{ET}} = 107$. The minor $\text{Ar}'_3\text{N}^{+\bullet}$ species can then oxidize DHA to give anthracene and $\text{Ar}'_3\text{N}$ in the rate-determining step (Eq 2), while the released H^+ binds to **2** in preference to $\text{Ar}'_3\text{N}$ ($\text{pK}_\text{a} \approx -4$).^{21a} Independent experiments confirm that $[\text{Ar}'_3\text{N}^{+\bullet}][\text{SbCl}_6^-]$ oxidizes DHA to anthracene (98%) relatively rapidly in a second-order process ($k = 0.126 \text{ M}^{-1} \text{ s}^{-1}$) (Fig. S11[†]).

Replacement of $[\text{Ar}'_3\text{N}^{+\bullet}][\text{SbCl}_6^-]$ with the more powerful oxidant $\text{Ce}^{\text{IV}}(\text{NH}_4)_2(\text{NO}_3)_6$ (CAN, $E_{\text{red}} = +1.33 \text{ V}$)¹⁷ led to a distinct change in mechanism. Oxidation of **2** with CAN in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (100:1 v/v) gives a UV-vis spectrum similar to **4**, and addition of excess DHA results in an *exponential decay* of **4** with the concomitant formation of **2** (Eq 3) (Fig. S12[†]). These data are consistent with a pseudo-first-order process. The use of the stronger oxidant CAN greatly disfavors back electron-transfer. In this case, the rate-determining step involves the direct reaction of **4** with DHA, and variation of $[\text{DHA}]$ leads to a $k_2 = 6.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. This reaction likely occurs through an HAT mechanism between DHA and **4** to give **3**, which is then rapidly deprotonated by the NO_3^- counterion^{21b} to give **2**. Control experiments show that **3** is rapidly deprotonated by $\text{Bu}_4\text{N}^+\text{NO}_3^-$ (Fig. S14[†]).

We have reported the synthesis and XRD characterization of the first third-row metallocorrolazine. This $\text{Re}^{\text{V}}(\text{O})$ complex is strikingly inert to both H-atom and O-atom transfer reactions, in contrast to its isoelectronic $\text{Mn}^{\text{V}}(\text{O})$ analog. Protonation of **2** gives a cationic $\text{Re}^{\text{V}}(\text{O})$ complex and no evidence of valence tautomerism, supporting the conclusion that protonation occurs exclusively on the *meso*-N atom and not on the oxo

ligand. Taking advantage of the inertness of the Re–O group, we have provided the first insights into the reactivity of a porphyrinoid π -radical-cation completely decoupled from its high-valent metal-oxo core. This Cz π -radical-cation, which contains a weakly basic *meso*-N site, appears to be competent to abstract H-atoms from relatively weak C–H substrates. These observations suggest that porphyrin π -radical cations, including those found in heme enzyme metal-oxo intermediates, may have as yet unidentified roles to play in oxidative reactivity.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.

Displacement ellipsoid plot (30% probability level) of Re^V(O)(TBP₈Cz) (**2**). Selected bond distances (Å): Re–O, 1.682(5), Re–N_{ave}, 1.976, Re–N_{plane}, 0.739. a) Top view; b) side view (peripheral aryl groups were omitted). In both cases, the disorder and H-atoms were removed for clarity.

Fig. 2.

a) UV-vis spectral changes upon addition of HBArF (0–2 equiv) to **2** in CH₂Cl₂. Inset: spectral titration at 723 nm showing maximal formation of product at 1 equiv HBArF. b) Comparison of ¹H NMR spectra (400 MHz) near the aryl region of **2** (black) and **3** (red) in CD₂Cl₂ at 23 °C.

Fig. 3. ATR-IR spectra ($800 - 1200 \text{ cm}^{-1}$) of a) $2\text{-}^{16}\text{O}$ (black) and $2\text{-}^{18}\text{O}$ (red), b) $2\text{-}^{18}\text{O}$ (red), $(3\text{-}^{18}\text{O})(\text{BArF}^-)$ (blue), and $(3\text{-}^{18}\text{O})(\text{OTf}^-)$ (green). Asterisk (*) = peaks associated with OTf^- or BArF^- counterions.

Fig. 4.

a) Cyclic voltammograms of **2** (black line) and **3** (red line) in CH_2Cl_2 , with 0.1 M TBAPF_6 supporting electrolyte, 150 mV/s. b) UV-vis spectral changes of **2** observed upon addition of $[\text{Ar}'_3\text{N}^+][\text{SbCl}_6^-]$ (0–1 equiv) in CH_2Cl_2 . Inset: X-band EPR of $\text{Re}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})^{*+}$ (**4**) (3 mM) at 298 K in CH_2Cl_2 .

Scheme 1.
Synthesis of $\text{Re}^{\text{V}}(\text{O})(\text{TBP}_8\text{Cz})$ (**2**).

Scheme 2.

Reaction of **4** with 9,10-DHA to form **3** and anthracene.