Dioxo Complexes

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The Groves–Spiro Dioxomanganese(V) Story

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bonding · manganese · porphyrin · reactivity · stability

The introduction in the seminal 1962 Ballhausen–Gray paper that provided the first molecular orbital description of metal–oxygen multiple bonds (Figure 1) concluded with the following statement: "*It also might be hoped that an understanding of the principal features of the bonding in* VO^{2+} *will be a helpful guide in attempts to develop a general theory of the electronic structures of* MO^{n+} *and* $MO_2{}^{n+}$ *complexes.*"[1] The last sentences in that paper (published in the first issue of *Inorg. Chem.*) read as follows: "*Indeed, it is clear that any complete discussion of the electronic structures of the oxycations of the transition and actinium series must allow for substantial oxygen to metal π-bonding. Furthermore, it can be qualitatively understood why ions of this type in the first transition series usually have the formula* MO^{n+} *(*TiO^{2+}*,* VO^{2+} CrO^{3+}*), while similar ions in the actinium series are invariably* $MO_2{}^{n+}$ *(*$UO_2{}^{2+}$*,* $NpO_2{}^{2+}$*). The two* $2p_\pi$ *orbitals on oxygen can satisfy the π-bonding capacities of the two* $3d_\pi$ *orbitals of a first transition series metal ion, but it takes at least two oxygens to satisfy the combined π-bonding capacities offered by the 5f and 6d orbitals of the metal ions in the actinium series.*"

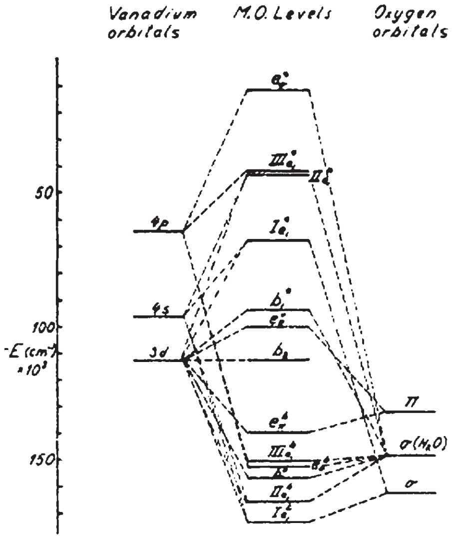

Figure 1. The original MO description of a metal–oxygen multiple bond (for $[VO(H_2O)_6]^{2+}$), in the Ballhausen and Gray 1962 publication. Reproduced from ref. [1].

The enormous importance of metal–oxygen multiple bonds in reaction chemistry was recognized many years later, when the central role of key oxo–metal intermediates in biological processes was uncovered. The research group of J. T. Groves pioneered the *isolation* of synthetic complexes with terminal oxo–metal bonds, including porphyrin-chelated $\{Cr(O)\}^{2+}$, $\{Mn(O)\}^{3+}$, $\{Fe(O)\}^{2+}$, and $\{Ru(O)_2\}^{2+}$ complexes; and T. G. Spiro's group played a leading role in the characterization of both natural and synthetic oxo–metal porphyrins by vibrational spectroscopy.[2] The work of Groves and Spiro not only had an impact on heme and porphyrin chemistry, but also influenced both related (corrole-chelated $\{Cr(O)\}^{3+}$ and $\{Mn(O)\}^{3+}$ complexes, for example)[3] and quite different (non-heme complexes of $\{Fe(O)\}^{2+}$and $\{Fe(O)\}^{3+}$, for example)[4] systems. The Ballhausen–Gray predictions were right on the mark until most recently, as dioxo metal complexes were limited to the second and third transition-metal series, and, although the analysis did not rule out the possible existence of $MO_2{}^{n+}$ species for 3d metal ions, there was only indirect evidence for their involvement in certain cases. This situation has now taken a dramatic new turn, with the most recent publication by Groves, Spiro, and co-workers.[5]

The isolation of (oxo)manganese(V) porphyrins appears to have been much more difficult than that of (oxo)chromium(V) and (oxo)iron(V) porphyrins, the famous Compound I analogue that is nowadays accepted to have an (oxo)iron(IV) porphyrin radical structure.[6] Recall that it took 20 years from the time (oxo)manganese(V) was first proposed as a key intermediate in catalysis until such a complex was unambiguously characterized by Jin and Groves.[7] The diamagnetism of that (and related) species is entirely consistent with the original Ballhausen–Gray MO analysis, as the d^2 low-spin state (paired electrons in the d_{xy} orbital, with the manganese–oxo bonds along the z axis) is obtained only because the d_{xz} and d_{yz} metal orbitals are at relatively high energy, as these orbitals are the antibonding components of the very strong oxygen p_x and p_y π-bonding orbitals. One difference between that research and most other attempted isolations of such complexes was that the experiments were performed in aqueous solution, on a water-soluble manganese porphyrin. Later investigations demonstrated that these complexes display an extraordinary five-order-of-magnitude range of reactivity for the oxo transfer to

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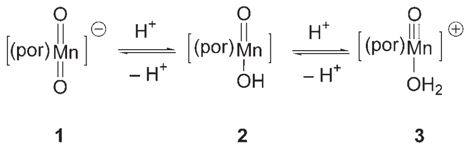
substrate as a function of pH value. This phenomenon was analyzed in terms of prototropic equilibria involving the axial ligand (Scheme 1).[8] Progressive deprotonation of oxo–aqua (**3**) to oxo–hydroxo (**2**) to dioxomanganese(V) porphyrin (**1**) was proposed, with **3** being dominant at low pH values and very reactive and **1** present at high pH values and relatively inert. Experimental data that would provide information about the manganese–oxo bond strength only existed for oxo–aqua species, such as **3**, and it was consistent with the expected triple bond between manganese and oxygen (a bond order of 3).[8]



Scheme 1. The progressive deprotonation of oxo–aqua to oxo–hydroxo to dioxomanganese(V) porphyrins; por = porphyrin.

The uniqueness of the most recent contribution by Groves, Spiro, and co-workers is that they have now obtained physical (spectroscopic) data for species **1** (Scheme 1) and demonstrated the relationship of the structural and electronic features with chemical reactivity.[5] In doing so, they turned their attention to the manganese complexes of the non water-soluble 5,10,15,20-tetramesitylporphyrinato dianion (TMP), and worked in acetonitrile/water solutions. This approach allowed for selective labeling of the oxygen atoms involved in binding to the two available axial coordination sites of the metal ion. Symmetry-based analysis of the ^{1}H NMR spectrum was used to confirm that the two axial positions are identical under basic conditions, as required for the proposed *trans*-dioxomanganese(V) porphyrin structure **1**. This conclusion was corroborated by the vibrational spectra (Raman and IR) of the complex: the isotopic shift (of 44 cm^{-1}) upon $^{16}O/^{18}O$ substitution is much closer to the calculated value for a triatomic O-Mn-O model (42 cm^{-1}) than to that of a terminal metal–oxo unit (33 cm^{-1}). What is more, they even succeeded in obtaining the half-labeled compound and showed that the isotopic shift of that compound is also consistent with the *trans*-dioxomanganese(V) porphyrin structure.

One important outcome of the unambiguous assignment of the stretching frequencies is that it resolves the apparent conflict in a recent report by Nam et al. of a terminal d^2 low-spin oxomanganese(V) porphyrin that has a bond length corresponding to a double rather than a triple bond (determined by extended X-ray absorption fine structure spectroscopy (EXAFS)).[9] Adding the new Raman/IR data from Groves, Spiro, and co-workers to a plot that features an excellent correlation between oxygen–manganese force constants (F_{Mn-O}) and bond lengths (obtained from eight relevant manganese complexes) clearly suggests that the EXAFS data reported by Nam et al have been obtained for a *trans*-dioxomanganese(V) porphyrin, which has a metal–oxo bond order of 2. Reasons for the exceptionally low reactivity of *trans*-dioxomanganese(V) porphyrins were also provided: the negative charge on the complex, and the need to protonate one of the oxo ligands in order to transfer the other one to a substrate.

What has not been explicitly discussed to date is a full description of the bonding in *trans*-dioxomanganese(V) porphyrins (**1** in Scheme 1) in MO terminology; this has been done for 4d and 5d *trans*-dioxo metal complexes.[10] The four bonding orbitals may safely be assumed to be π_{xz}, π_{yz}, σ_2 (p_z(O)–d_{z^2}(Mn)–p_z(O)) and σ_1 (p_z(O)–p_z(Mn)–p_z(O)), thus providing a bond order of 2 for each Mn–O bond. But it is much harder to predict the relative energy levels of the higher occupied orbitals (σ_{nb}, doubly degenerate π_{nb}, and d_{xy}; nb = nonbonding) and their contribution to the magnetic properties of the complex and its stability. Another issue that can be addressed by computational methods is the thermodynamic driving force for conversion of species **2** into **3** by protonation of the hydroxo moiety (Scheme 1) rather than into bishydroxomanganese(V) by protonation of the oxo group. This aspect is very relevant to the oxo–hydroxo tautomerism that is extensively used for explaining many results obtained in oxygenation catalysis by metal complexes.[11]

In summary, Groves and Spiro and their co-workers have greatly enhanced our understanding of the structural and electronic properties of metal–oxo complexes. Their findings demonstrate that a fundamental understanding of chemical bonding paves the way for rigorous analyses of stability and reactivity. One take-home lesson within the family of metal–oxo-containing compounds is that metal–oxygen bond order, bond length, and stretching frequency are not necessarily related to the potency of transferring the oxygen atom to oxidizable substrates, and for that reason, the analysis in the Groves and Spiro paper will aid significantly in reaching a better understanding of oxygen-atom-transfer reactions in both biology and chemistry. It also is likely that accurate calculations and in-depth analysis of the electronic structures of *trans*-dioxomanganese(V) porphyrins will be able to account for both the physical and chemical properties of these intriguing molecules.

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