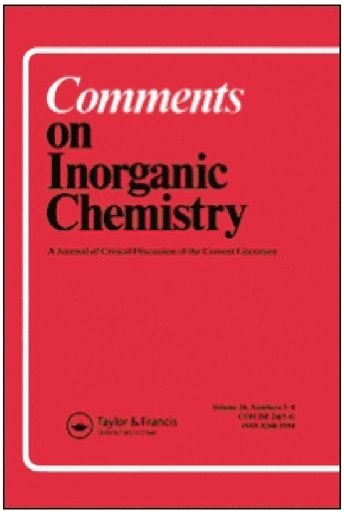

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Why Are There No Terminal Oxo Complexes of the Late Transition Metals? or The Importance of Metal-Ligand π Antibonding Interactions

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Why Are There No Terminal Oxo Complexes of the Late Transition Metals? or The Importance of Metal–Ligand π Antibonding Interactions

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π antibonding interactions result from the overlap of a filled π symmetry ligand orbital with a filled metal d orbital. This antibonding plays an important role in the chemistry of π donor ligands such as oxo and alkoxide. It is in large part responsible for the lack of late transition metal complexes with terminal oxo ligands, and can explain some of the unusual chemistry of late metal alkoxide complexes.

Key Words: *oxo, oxide, alkoxide, π bonding, antibonding*

I. π ANTIBONDING

A number of ligands—for instance oxo (O^{2-}), imido (NR^{2-}), alkoxide (OR^-), and amide (NR_2^-) groups[1-4]—not only form σ bonds to a metal center but also have additional lone pairs that can be involved in bonding. The additional lone pairs are of π symmetry, so these ligands are termed π donors. π bonding will be important when the ligand lone pairs both overlap well and have a good energy match with the metal orbitals of π symmetry (d_π orbitals). Productive π bonding, in other words π interactions

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that stabilize the metal–ligand bond, requires that the metal d_π orbital(s) be empty. If the metal d_π orbitals are filled, however, destabilizing π antibonding interactions result. Ligand-to-metal π donation has received a great deal of attention in recent years (cf. Chisholm and Clark in this journal[4]). It is the aim of this Comment to illustrate that π antibonding can also play a critical role in the chemistry of π donor ligands.

In a molecular orbital picture, overlap of two orbitals generates both bonding and antibonding orbitals, our focus being π and π^* orbitals. The determination of a simple bond order assumes that the destabilization of π^* is equal to the stailization of π. But even at the simplest level of molecular orbital theory the antibonding interaction is greater than the bonding: for the overlap of two identical orbitals, π is stabilized by an energy $\beta/(1 + S)$ while π^* is destabilized by $\beta/(1 - S)$, where S is the overlap integral.[5,6]

The theory reinforces our qualitative understanding that the overlap of two filled orbitals is an unfavorable interaction. In a more general sense, π antibonding can be viewed as a repulsive filled–filled interaction between orbitals not involved in σ bonding.

A frequently cited example of π antibonding or filled–filled interactions is the unusually weak bond in F_2 (Table I). The F–F bond "should be" 80–100 kcal/mole[8] based on the bond strengths in Cl_2 and Br_2 and the normal periodic trend as illustrated for H–X bond strengths. The observed low bond energy for F_2 is usually explained by invoking repulsion between the fluorine lone pairs,[8] in other words π antibonding. The effect of π antibonding is directly seen by comparing the bond strengths of N_2, O_2, and F_2, since these molecules have, respectively, 0, 2, and 4 electrons in π^* orbitals. While the formal bond order changes from 3 in N_2 to 1 in F_2, the bond strength decreases by a factor of 6. Similar

TABLE I

Comparison of diatomic bond strengths[a]

N_2, 225	O_2, 118	F_2, 37	HF, 135
		Cl_2, 57	HCl, 102
		Br_2, 45	HBr, 87

[a] Data in kcal/mole, taken from Ref. 7.

arguments can be used to explain the weakness of O–O and N–N single bonds, for instance in H_2O_2 and N_2H_4 (34, 40 kcal/mole[7]). Since the second row elements carbon through fluorine are known to engage in strong productive π bonding, it is not surprising that π antibonding interactions can be important as well.

Metal–ligand π bonding is discussed in every introductory course on transition metal chemisty[9]. For instance, it is needed to explain the spectrochemical series, that π donors such as fluoride and hydroxide give rise to small ligand field splittings while π acceptors (CO, CN^-) are strong field ligands. However, the substantial effect of π antibonding interactions on the stability and reactivity of π donor ligands has not been widely appreciated. This lack of appreciation is due in part to filled–filled interactions being only a subtle and uncommon effect in organic chemisty. For instance, in the methoxide ion, there are no orbitals on the carbon that have good overlap and energy match with the oxygen lone pairs. In contrast, in transition metal complexes there is almost always a metal d orbital of π symmetry to interact with a ligand lone pair.

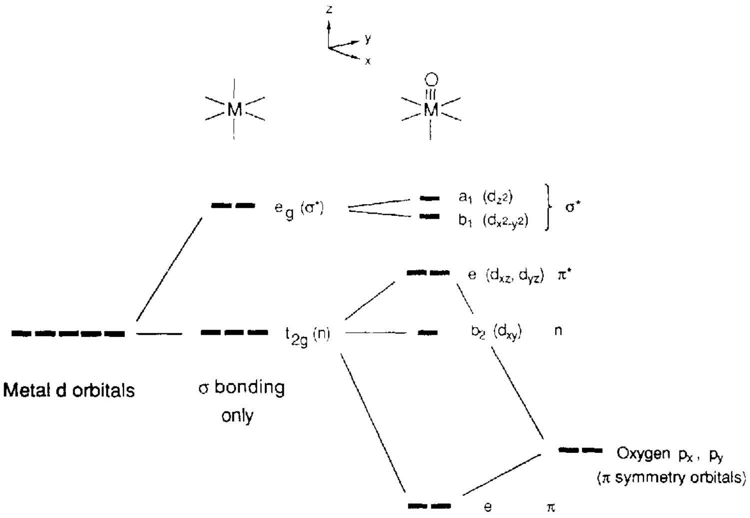
In the succeeding sections we discuss the effects of π antibonding on the chemistry of particular ligands. We begin with the terminal oxo ligand, then take up alkoxides, and conclude with a brief discussion of organometallic ligands such as acetylene and acetylide groups.

II. TERMINAL OXO COMPLEXES

Terminal oxo ligands are ubiquitous in the chemistry of the higher oxidation states of metals from vanadium to osmium.[1,3] Yet there are no examples of stable terminal oxo complexes in the cobalt, nickel, or copper triads.[10] The oxo ligand in the stable oxides and oxo complexes of the late transition metals always bridges two or more metal centers. This is because in most late-metal terminal oxo complexes, as described below, metal–oxygen antibonding orbitals would have to be occupied.

Terminal oxo complexes in general have strong multiple metal–oxygen bonds.[1,3] The strength of the bonding is indicated by short M–O distances,[11] high M–O stretching frequencies (900–1000 cm^{-1}),[12] and the limited thermochemical data available. For example, gaseous tungsten trioxide has an average W–O bond strength of 151 kcal/mole, and the W–O bond in W(O)Cl$_4$ has been estimated (based on heats of formation) to be 195 kcal/mole.[13] Since π bonding involving oxo ligands can be strong, it is to be expected that π antibonding will be an important interaction.

The molecular orbital description of octahedral mono-oxo (and imido and nitrido) complexes (Scheme I) is well established from spectroscopic, theoretical, and chemical studies.[14–16] This picture dates from a 1962 study of the d^1 vanadyl ion (VO^{2+}) by Ballhausen and Gray.[14] The ligand field splitting resembles the octahedral "two above three" pattern except that two of the "t$_{2g}$" orbitals (d$_{xz}$,d$_{yz}$) are involved in π bonding with the oxo—they are the π antibonding components of the M–O bond. Note that the two π bonds are degenerate in C_{4v} symmetry and therefore the M–O bond should be described as a triple bond. The splitting between the nonbonding d$_{xy}$ and the π^* d$_{xz}$,d$_{yz}$ is substantial: roughly 14.000 cm^{-1} in d^1 M(O)Cl$_5^{n-}$ complexes based on their optical spectra.[17] The splitting is large enough that all known d^2 mono-oxo complexes are diamagnetic, with the electrons paired in the d$_{xy}$ orbital.



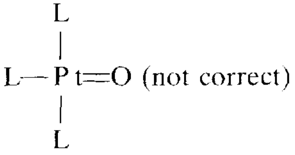
SCHEME I

In this picture up to two d electrons can be accommodated without population of π^* levels. This explains why the vast majority of terminal oxo complexes have d^0, d^1, or d^2 configurations. We have been studying a series of d^4 rhenium–oxo complexes of the form $Re(O)X(RC{\equiv}CR)_2$ which appear to violate this rule.[15,18–21] In fact, these compounds adopt an unusual tetrahedral structure in order to accommodate the four d electrons in roughly nonbonding orbitals.[15] The chemistry of the Re–O bond in these molecules is typical of higher valent rhenium species: the Re–O bond distances are ~1.70 Å, the stretching frequencies in the range 930–980 cm^{-1}, and the oxo group is readily removed by PMe_3 but not by PPh_3. The high electron count does not affect the rhenium–oxo bond because Re–O antibonding orbitals are not populated. We have isolated a trigonal bipyramidal complex, $[Re(O)bipy \cdot (MeC{\equiv}CMe)_2]^+$, which does not undergo Berry pseudorotation presumably because the square pyramidal intermediate would have to populate Re–O π^* levels.[18]

Meyer and more recently Che and others have been studying octahedral d^4 ruthenium–oxo complexes which, in contrast to the tetrahedral rhenium–oxo species, have two electrons in the two Ru–O π^* orbitals.[22] Predictably, these compounds exhibit low metal–oxygen stretching frequencies (roughly 800 cm^{-1}),[12,22] have long Ru–O bond lengths,[11] and are often very reactive. Exceptionally reactive d^4 iron–oxo complexes have been studied as models for the active sites of cytochrome P-450 and peroxidase enzymes.[23] These species also show low stretching frequencies [$\nu(Fe{-}O)$ = 800–850 cm^{-1}][24] and long Fe–O distances.[11] Low metal–oxo stretching frequencies are also observed for excited states of metal oxo complexes in which π^* orbitals are populated. For instance, the molybdenum–oxygen stretch in $Mo(O)Cl_4^-$ is reduced from 1008 cm^{-1} in the ground state to 900 cm^{-1} in the ^2E excited state.[17a] These examples illustrate the strongly antibonding character of the π^* levels.

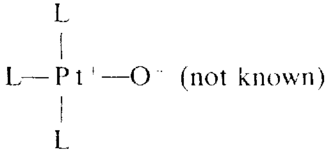
The d^4 iron–oxo complexes are stable only when very bulky ancillary ligands (e.g., tetramesitylporphyrin) are used to prevent dimerization to μ-oxo species. The conversion of terminal oxo ligands to bridging groups is a common way to decrease π antibonding. The π-symmetry lone pair(s) on a bridging oxygen are less available for bonding and metal–oxygen overlap is less at the longer distances found for μ-oxo species. Another example of the conversion of terminal to bridging oxo groups is the reduction of the permanganate ion in aprotic media yielding MnO_2,[25] an insoluble material with triply bridging oxo groups.[26] In the presence of protons, reduction of permanganate yields lower valent complexes with water or hydroxide ligands.

The late transition metals—the cobalt, nickel, and copper triads—cannot easily reach the high oxidation states needed to have empty d_π orbitals.[10] Metal–oxygen multiple bonding is often not possible. Structures such as the hypothetical platinum(II) complex **A**, even though it obeys the eighteen electron rule, are not correct because there is no empty d orbital of π symmetry on the metal.



$L-\overset{\overset{L}{|}}{\underset{\underset{L}{|}}{Pt}}=O$ (not correct)

A



$L-\overset{\overset{L}{|}}{\underset{\underset{L}{|}}{Pt^{+}}}-O^{-}$ (not known)

B

One can speculate on the possible existence of metal–oxo complexes with M–O single bonds, such as **B**, which are formally analogs of amine oxides or alkoxide ions. But the analogy is a poor one: π interactions are not important in R_3NO and R_3CO while metals have filled d_π orbitals that destabilize the M–O bond. In a metal complex such as **B**, the formal negative charge at oxygen and the destabilization of the oxygen lone pairs by filled–filled interactions lead to a very basic oxygen, therefore favoring μ-oxo complexes.

These arguments apply not only to late transition metal complexes but also to any compound in which the d_π orbitals are filled. This includes low-spin octahedral d^6 complexes and essentially all d^8 compounds. An interesting situation obtains when the metal d_π orbitals are partially filled. The only examples of these species are the very reactive iron and ruthenium d^4 octahedral species discussed above in which each metal–oxo π^* orbital is half filled. In addition to utilizing chelating and often bulky ligands to prevent the formation of μ-oxo species, the isolated materials are almost invariably cationic, which reduces the nucleophilicity of the oxo group. Using these approaches, it may be possible to prepare a terminal oxo complex of a metal in the cobalt triad.[27]

III. ALKOXIDE COMPLEXES

Alkoxide ligands are also known to engage in strong π donor interactions with the early transition metals (albeit not as strongly as oxo groups).[4] Therefore we can anticipate that π antibonding interactions will have an effect on the chemistry of alkoxide ligands.[28]

Terminal alkoxide complexes of metal centers with filled d_π orbitals are quite reactive and in general have not been easy species to prepare. In many cases bridged structures such as $(CuO^tBu)_4$[29] predominate. The octahedral d^6 complex $W(OR)(CO)_5^-$ decomposes readily[30] to $W_4(CO)_{12}(\mu_3\text{-}OR)_4^{4-}$. Alkoxide ligands bound to late metals frequently undergo β-hydrogen elimination.[31] Heterolytic cleavage of late transition metal–alkoxide bonds is often quite facile. For instance, treatment of $Ir(OR)(CO)(PPh_3)_2$ with CO yields the salt $[Ir(CO)_3(PPh_3)_2]^+OR^-$,[32] and hydroxide is easily displaced from $Pt(OH)H(P^iPr_3)_2$ by pyridine.[33] Hydroxide complexes can act as very strong bases: platinum hydroxides have been observed to deprotonate acetone and nitromethane.[34] An exceptionally strong hydrogen bond has been observed between $Rh(OC_6H_4Me)(PMe_3)_3$ and HOC_6H_4Me.[35]

In general, late transition metal–oxygen bonds are readily cleaved in a heterolytic fashion and the alkoxide ligands have a tendency to bridge metal centers. These properties are similar to those expected for late metal–oxo bonds as discussed above, and can therefore be understood in terms of related π antibonding effects. The examples above also illustrate that late metal–alkoxide bonds are quite polar[35]—in fact more polar than analogous bonds of early transition metals. It is surprising that the most polar metal–oxygen bonds should occur for the least electropositive metals. This contradiction of simple electronegativity arguments is also apparently due to π antibonding which destabilizes the oxygen lone pairs. Early transition metal–oxygen bonds are less polar because oxygen can act as a π donor. Similar arguments can be used to explain the unusually high basicity observed for some μ-oxo ligands, for instance, oxygen adatoms on copper, silver, and gold surfaces,[36] and the bridging oxo in $Rh_2(\mu\text{-}O)(CO)_2(dppm)_2$ which strongly coordinates Li^+ and BF_3.[37]

Often π bonding and antibonding effects work in concert. It is well known, for instance, that copper and nickel ions prefer to bind nitrogen ligands over oxygen donors, while the reverse is true for chromium and high-spin iron. The late metals prefer ligands which do not π donate to avoid antibonding interactions while the early transition metals with empty or partially filled d_π orbitals have net π bonding with oxygen ligands. We have suggested that d^2 oxo complexes prefer to bind soft, π acceptor ligands *cis* to the oxo and hard π donors in the *trans* position, both to maximize π bonding and to avoid π antibonding.[38] In the solid state structure of the rhenium–oxo–phenoxide complex $Re(O)OPh(MeC{\equiv}CMe)_2$, we have found that the phenoxide is in a sterically unfavorable position in order to have productive Re–OPh π bonding.[20] In addition, an unusually acute Re–O–C angle of 125(1)° is adopted in order to direct an oxygen lone pair away from the rhenium center and minimize π antibonding.

IV. OTHER LIGANDS

The importance of π antibonding is, of course, not limited to oxygen ligands. Very similar arguments can be made for sulfido, imido, and phosphinidine ligands that are isoelectronic with oxo, and for phosphido and amide groups that are related to alkoxides. The many attempts to prepare terminal phosphinidine complexes (M=PR) and the only successful synthesis indicate the importance of these considerations.[39]

π antibonding also is undoubtedly involved in the chemistry of unsaturated organic ligands such as acetylene and acetylide groups. Templeton and co-workers have shown that acetylenes can act not only as σ donor/π acceptor ligands but in addition may behave as strong π donors to metal centers.[40] They have also discussed acetylene–metal π antibonding interactions, particularly with respect to the stability of acetylene complexes of octahedral d^6 tungsten centers and their rearrangement to vinylidene complexes ($HC{\equiv}CR \rightarrow {=}C{=}CHR$).[41] π antibonding is quite important for dialkylacetylene ligands, which are good π donors: late metal dialkylacetylene complexes seem to be somewhat more reactive than early metal analogues, for instance, more easily protonated and more likely to undergo oligomerization to metallacyclopentadienes or arenes. In contrast, π antibonding is not important for acetylenes that behave as π acid ligands, such as dimethylacetylene dicarboxylate.

As one last example, the remarkable carbon basicity of acetylide ligand of $Cp(PMe_3)_2Ru-C{\equiv}C-R$[42] must be due, at least in part, to π antibonding interactions between the filled ruthenium d_π orbitals and the carbon–carbon π orbitals.

CONCLUSIONS

The chemistry of π donor ligands such as oxo and alkoxide depends to a large extent on the nature of the metal–ligand π interaction. Productive π bonding requires empty metal d orbitals, but if the metal d_π orbitals are filled an antibonding interaction results. This antibonding destabilizes terminal oxo complexes of the late transition metals, so that μ-oxo compounds are favored. Terminal alkoxide ligands are also destabilized, with the result that late metal–oxygen bonds are quite polar and readily dissociate OR^-.

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27. An additional difficulty in the formation of late transition metal terminal oxo compounds is that these metals seem less prone to form multiple bonds of any sort (metal–ligand or metal–metal), even when π antibonding is not important. For instance, terminal alkylidene ligands are common for the early transition metals while bridged structures predominate for the late metals. See Ref. 3, Chapters 2 and 5.
28. It should be noted, however, that π antibonding is not the mirror image of π bonding, since antibonding leads to longer metal–ligand distances for which π bonding is less important. In addition, ligands such as alkoxides and amides can distort to move a lone pair farther from the metal center.
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