

Metal–dioxygen and metal–dinitrogen complexes: where are the electrons?

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Transition-metal complexes of O₂ and N₂ play an important role in the environment, chemical industry, and metalloenzymes. This Perspective compares and contrasts the binding modes, reduction levels, and electronic influences on the nature of the bound O₂ or N₂ group in these complexes. The charge distribution between the metal and the diatomic ligand is variable, and different models for describing the adducts have evolved. In some cases, single resonance structures (e.g. M–superoxide = M–O₂⁻) are accurate descriptions of the adducts. Recent studies have shown that the magnetic coupling in certain N₂²⁻ complexes differs between resonance forms, and can be used to distinguish experimentally between resonance structures. On the other hand, many O₂ and N₂ complexes cannot be described well with a simple valence-bond model. Defining the situations where ambiguities occur is a fertile area for continued study.

Introduction: binding of O₂ and N₂ to transition metals

The diatomic molecules N₂ and O₂ are the primary constituents of the atmosphere, and each is important for life as we know it. Reduction of N₂ gives ammonia, the precursor to nitrogen-containing biomolecules like nucleic acids and proteins, while reduction of O₂ provides energy. Both N₂ and O₂ have also become important raw materials in large-scale industrial chemistry because of their simplicity and abundance. For both gases, transition metals are commonly used to bring about their chemical manipulation and functionalization. As a result, there has been intense research activity focusing on the mechanisms and elementary steps involved in the multielectron reductions of these diatomic molecules by transition metal complexes. This Perspective compares and contrasts complexes of O₂ and N₂ in the literature with respect to their charge distributions, geometries,

and binding modes. Because of the large volume of existing research and excellent reviews on complexes of dioxygen¹ and dinitrogen,² this review is not comprehensive: rather, it focuses on models through which chemists assign the location of electrons in the metal complexes of these two diatomic molecules. Examples of structurally characterized molecules will be given to illustrate key points, and recent developments will be a main focus.

Binding modes

Diatomic molecules can bind to metals in several ways, outlined in Fig. 1. The interaction with each metal is classified as “end-on” or “side-on” to indicate the hapticity as η¹ (one atom bound to the metal) or η² (two atoms bound to the metal).

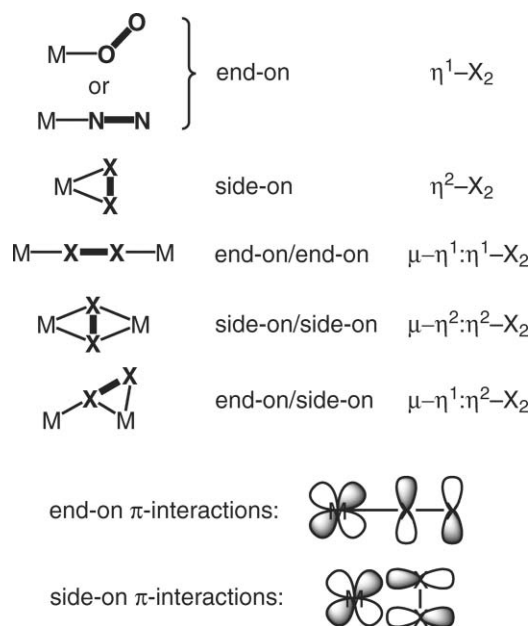
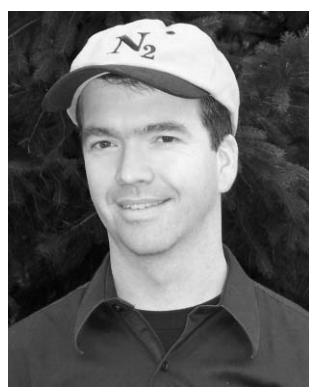


Fig. 1 Binding modes for diatomic ligands. The bond order is not indicated, because it can vary depending on the metal and spectator ligands.

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Patrick Holland was born in Pennsylvania, and grew up in Ohio and Florida. He received an A.B. degree from Princeton in 1993, and a Ph.D. from Berkeley in 1997 under the guidance of Robert Bergman and Richard Andersen. In an NIH postdoctoral fellowship at Minnesota with William Tolman, he worked with biologically inspired complexes of O₂. In 2000, he started his independent academic career at the University of Rochester by

exploring the bioinorganic chemistry of N₂. He has been the recipient of an NSF CAREER award and a Sloan Fellowship, and currently holds the rank of Associate Professor.

End-on N_2 complexes are always linear at the proximal nitrogen atom, allowing a π -backbonding interaction from metal d orbitals into the π^* orbitals of N_2 (bottom of Fig. 1). The extent of backbonding in the N_2 complexes is variable, depending on the energy of the d orbitals with the correct symmetry to engage in this interaction. In general, backbonding is greatest with low-valent, relatively electropositive metals (e.g. Zr, Hf, Ta), and least with relatively electronegative metals (e.g. Fe, Ru, Co, Rh, Ni). End-on O_2 complexes always have a bent geometry at the proximal oxygen atom, and in this geometry the π -interactions between the metal and the diatomic are lessened. The predominance of the linear MNN binding in N_2 complexes contrasts with the predominance of bent MOO binding in O_2 complexes, and is one of the major differences between complexes of the two diatomic molecules.

In the side-on geometry, a π^* orbital of the diatomic species can interact with a d orbital in a different manner (bottom of Fig. 1), akin to the backbonding interaction between a metal and an alkene.³ Side-on bound O_2 is found in a number of mononuclear complexes (see Fig. 3 below). In N_2 chemistry, on the other hand, there are no stable examples of the side-on binding mode for mononuclear complexes. The paucity of side-on N_2 relative to side-on O_2 is probably related to the stronger π bonds in free N_2 , which cannot be easily disrupted. In an osmium system, it has been possible to generate a *metastable* side-on mononuclear Os– N_2 complex by irradiating ($\lambda \sim 400$ nm) the complex $[Os(NH_3)_5(N_2)]^{2+}$.⁴ This species has been characterized during irradiation in the solid state by X-ray diffraction and vibrational spectroscopy.

Side-on bound dioxygen often bridges to an additional metal through a second side-on interaction, and the resulting binding mode is described as μ - η^2 : η^2 or “side-on/side-on” binding (Fig. 1). The most intense characterization of this binding mode for O_2 complexes has come in μ - η^2 : η^2 -peroxodicopper(II) complexes, because they are synthetic analogues for copper-based O_2 carriers (oxyhemocyanin) and enzymatic intermediates (oxytyrosinase, oxy-catechol oxidase).⁵ Even though mononuclear side-on N_2 complexes are not stable as noted above, the μ - η^2 : η^2 binding mode has been observed in a number of N_2 complexes.⁶ Most examples of μ - η^2 : η^2 - N_2 binding come from complexes of early (group 5 and lower) transition metals and lanthanides.^{7–11} (The structurally characterized exceptions are a recent dichromium complex,¹² and a nickel–sodium–lithium cluster.^{13,14}) In both O_2 and N_2 complexes, the preference for end-on vs. side-on bridging is determined by several factors, including the availability of metal d orbitals^{7c} and steric hindrance from the spectator ligands.¹⁰

An especially interesting binding mode is “end-on/side-on” or μ - η^1 : η^2 binding (Fig. 1). A number of μ - η^1 : η^2 - O_2 complexes have been characterized crystallographically, with metals from groups 5 and 6.¹⁵ This binding mode has been observed more recently in dinuclear O_2 complexes of cobalt and rhodium.¹⁶ Palladium complexes of this type have also been characterized.¹⁷ In bioinorganic chemistry, μ - η^1 : η^2 - O_2 has been observed in a bimetallic iron-copper complex of relevance to cytochrome *c* oxidase,¹⁸ and in dicopper complexes with asymmetric binucleating ligands.¹⁹ In N_2 complexes, there are relatively few examples of μ - η^1 : η^2 binding, but they are some of the most exciting N_2 complexes because they react with weak electrophiles. The best-studied is a ditantalum complex that undergoes stoichiometric N_2 functionalization reactions (see below).²⁰ Cooperative end-on and side-on binding of N_2 have

also been seen in a Ti_3 complex,²¹ and in complexes with end-on late transition metals and side-on alkali metal cations.²² In the late-metal complexes, the side-on binding of the alkali metal has been shown to enhance backbonding by stabilizing negatively charged N_2 .²³

There are also some examples of O_2 binding between more than two transition metals, including tetracopper²⁴ and tetrairon²⁵ complexes and a hexanickel complex.²⁶ There are fewer examples of a single molecule of N_2 binding to more than two transition metals, but one especially notable one is a hydrazine-derived Au_6 complex.²⁷ There are also examples of end-on binding of N_2 to transition metals concomitant with side-on binding to alkali metals.^{13,22,23}

Models for the charge distribution

The binding and reduction of dioxygen have been studied in greater detail than binding and reduction of dinitrogen, and will be discussed first. As shown at the left of Fig. 2, O_2 can be reduced by one electron to give the superoxide radical anion, O_2^- , or by two electrons to give the peroxide dianion, O_2^{2-} . Metal-free or protonated O_2 , O_2^- , and O_2^{2-} are straightforward to distinguish, because they have distinctly different O–O bond lengths, spin states, and vibrational frequencies.²⁸ However, when these fragments are attached to a metal, determining the reduction level becomes more problematic because the reduction level of O_2 is inextricably linked to the oxidation state of the metal ion. For example, the O_2 adduct of deoxyhemoglobin (a Fe^{2+} metalloprotein) could in principle be described through the resonance structures $Fe^{2+}-O_2$, $Fe^{3+}-O_2^-$, or $Fe^{4+}-O_2^{2-}$, which differ only in the location of a few electrons.

	$S = 0$	$N \equiv N$	1.10 Å, 2359 cm^{-1}		
		$S = 1/2$	$[N \equiv \overset{\cdot\cdot}{N}]^-$		
$S = 1$	$O = O$	1.21 Å, 1580 cm^{-1}	$S = 1$	$[N = N]^{2-}$	1.25 Å, 1583/1529 cm^{-1}
$S = 1/2$	$[O \cdots O]^-$	1.33 Å, 1098 cm^{-1}	$S = 1/2$	$[N \cdots N]^{3-}$	
$S = 0$	$[O - O]^{2-}$	1.49 Å, 877 cm^{-1}	$S = 0$	$[N - N]^{4-}$	1.45 Å, 885 cm^{-1}

Fig. 2 Equilibrium spin states, bond distances, and stretching frequencies for O_2 and N_2 fragments. For anions, the given bond distances and frequencies are for the protonated analogues, because these are known in solution and are more directly analogous to metal complexes.

Inorganic chemists typically seek to assign the “best” resonance structure based upon spectroscopic and/or structural data.¹ (There may be no single structure that is an adequate description; this issue will be addressed later in this Perspective.) The most common strategy in metal–dioxygen complexes is to focus on the O_2 -derived ligand. The frequency of the O–O vibration and the length of the O–O bond each report on the O–O bond order, and these two measures correlate with one another in complexes of O_2 , using Badger’s rule (Fig. 3).^{29,30} Typically, the vibrational frequency is the preferred measure, because librational motions of the diatomic ligand can give systematic errors in the O–O distance from X-ray crystallography.^{31,32} Once the charge on the O_2 -derived ligand has been established, the oxidation state of the metal can be inferred. For example, in the O_2 adduct of hemoglobin, the ν_{OO} value of 1106 cm^{-1} is close to the value for

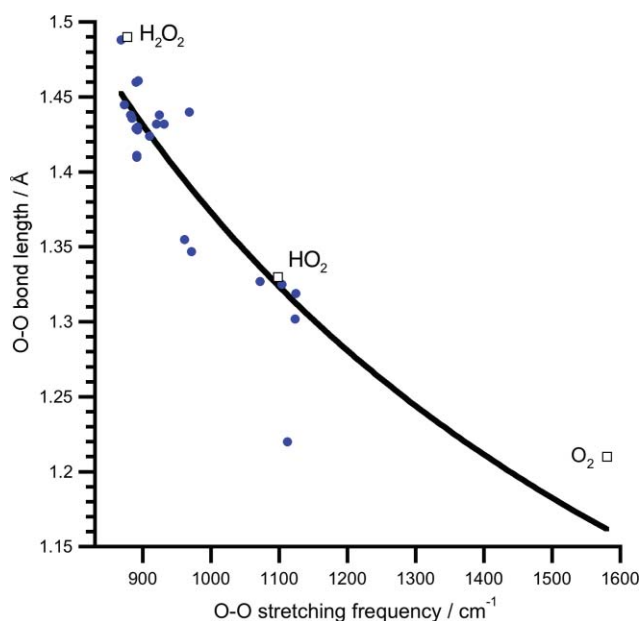


Fig. 3 Correlation of O–O bond length with O–O stretching frequency in mononuclear O₂ complexes with high-quality low-temperature crystal structures (solid circles). Bond lengths are from the Cambridge Structural Database, which cites the papers in which the vibrational spectra may be found. In cases with Fermi or other splitting of the O–O stretching band, the average frequency is used. Open squares show the values for protonated reference compounds. The curve is a best-fit line to the expected dependence based on Badger's rule, $d_{\text{NN}} \propto C\nu^{-2/3} + \delta$. Note that Badger's rule does not predict a linear relationship between d and ν .

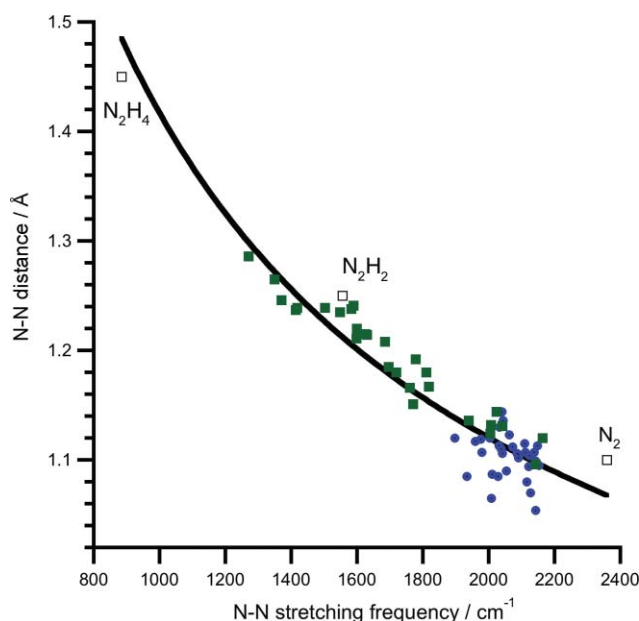


Fig. 4 Correlation of N–N bond length with N–N stretching frequency in N₂ complexes with high-quality low-temperature crystal structures (solid circles = mononuclear; solid squares = dinuclear). Bond lengths are from the Cambridge Structural Database, which cites the papers in which the vibrational spectra may be found. Open squares show the values for protonated reference compounds. The curve is a best-fit line to the expected dependence based on Badger's rule, $d_{\text{NN}} \propto C\nu^{-2/3} + \delta$. Note that Badger's rule does not predict a linear relationship between d and ν .

HO₂ (1098 cm⁻¹), and defining the ligand as O₂⁻ implies that the iron ion is in the +3 oxidation state.³³ In an alternative strategy for oxidation state assignment, X-ray absorption, Mössbauer, magnetic susceptibility, or other spectroscopic data can define the metal's oxidation state, which in turn implies the number of electrons on the diatomic ligand. In the same example used above, the Mössbauer parameters of oxyhemoglobin ($\delta = 0.20$ mm s⁻¹) are much more similar to those for Fe(III) methemoglobins ($\delta = 0.15$ – 0.20 mm s⁻¹) than Fe(II) deoxyhemoglobin ($\delta = 0.90$ mm s⁻¹).³⁴ Likewise, the XANES spectrum of oxyhemoglobin shows that the core electrons of Fe are about 5 eV deeper in energy than those in deoxyhemoglobin, suggesting oxidation of the iron atom.³⁵ Thus, Fe³⁺–O₂⁻ is a spectroscopically accurate description of oxyhemoglobin, from the perspective of the metal *and* from the perspective of the O₂ fragment.

The corresponding partially reduced forms of N₂ are shown at the right of Fig. 2. Because N₂ has a triple bond, and because cleavage of N₂ requires more electrons than that of O₂, there are more potential redox levels of N₂. When comparing N–N distances in complexes to those in metal-free species, common reference molecules are diazene (HN=NH) for N=N double bonds and a formal assignment as N₂²⁻, and hydrazine (H₂N–NH₂) for N–N single bonds and a formal assignment as N₂⁴⁺. In analogy to the strategy described above for O₂, the N–N stretching frequency and N–N distance are tools for defining the redox level and bond order of the ligand, and thus the corresponding oxidation state of the metal. The correlation between known N–N stretching frequencies and bond lengths based on Badger's rule is given in Fig. 4.³⁶

The above discussion treats charge distributions as having each electron localized either on the metal or on the ligand. However, Fig. 3 and 4 contain numerous points that do not clearly correspond with a single redox state of O₂ or N₂. Interestingly, these situations are described in different ways for the two diatomic ligands. Though chemists usually quantize the oxidation level of O₂ through the use of descriptors such as “superoxide” or “peroxide,” the charge distribution in other diatomics like CO and N₂ is viewed in a more circumspect manner. In the case of CO, the conventional description is that the diatomic is *formally* neutral, but that there is a variable contribution from resonance structures in which the metal transfers electrons to the ligand (Fig. 5). Using this resonance structure model, the charge transfer is continuous rather than quantized. N₂ is treated in an analogous fashion.

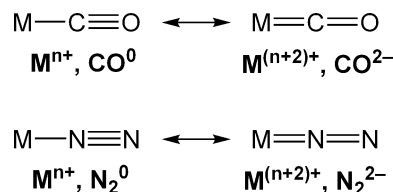


Fig. 5 Resonance structures of metal–CO and metal–N₂ complexes, demonstrating the movement of electrons from the metal to the ligand with backbonding.

It is interesting that different strategies are used for accounting for the location of electrons in metal complexes of such similar diatomic molecules. In the author's view, the model used with metal complexes of CO and N₂ (neutral ligand with variable

backbonding) has arisen in response to a desire for accurate electron bookkeeping regardless of the actual oxidation level of the metal (hence the term “*formal* oxidation states”), while the use of electron-specific resonance-structure descriptors for O₂ has arisen in response to the more widespread use of spectroscopic tools for M–O₂ complexes that specify the oxidation level of the metal. In most cases, the two strategies are equally effective, as long as sufficient compromises are made: one can set aside a formal oxidation state model in favor of “oxidation levels” or “spectroscopic oxidation states,”³⁷ or using a crystal-field model, variable amounts of “covalency” are taken into account.³⁸ In contrast, computational investigations typically give *molecular* orbitals that may be delocalized over much of the complex, and the intuitive simplicity of resonance structures is sometimes difficult to extract.³⁹ Despite the clear signs (discussed in more detail below) that descriptors based on single resonance structures are oversimplifications, these labels serve an important role in categorizing complexes, and these categories will be used in the following sections of this Perspective. After proceeding through these categories, we shall return to the issue of determining the best model for describing the electronic structure, highlighting some special systems in which descriptive models make *different* predictions.

Binding “without reduction,” and with “one-electron reduction.”

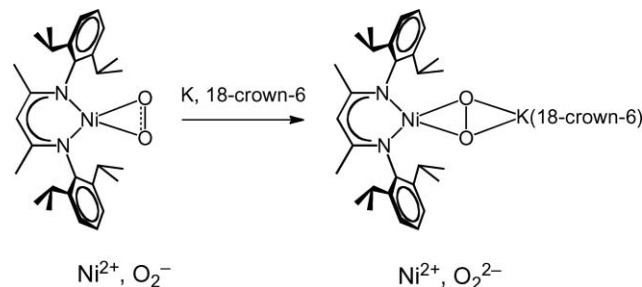
Dioxygen typically binds concomitantly with one-electron reduction to the superoxide oxidation level. The O–O bond is always reduced upon binding, which is clear from the lack of complexes near the right of Fig. 3. In contrast, binding of the N₂ molecule to a transition metal often causes little reduction of the N₂ group, which is evident from the bunching of many points at the right of Fig. 4. The assignment of N₂ as a neutral ligand in these complexes is supported by N–N stretching frequencies in the range of 1900–2200 cm⁻¹, and N–N distances of 1.15 Å or less. The relative ease of electron transfer to O₂ compared to N₂ is consistent with the higher electron affinity of O₂ relative to N₂.⁴⁰

Early in the study of the binding of O₂ to metals, there was significant controversy about whether the O₂ unit is reduced in the metal–O₂ complexes. In all transition-metal dioxygen complexes, the O–O bond weakens as judged by the O–O bond length and stretching frequency, and thus the predominant view is that electrons are transferred from the metal to O₂ π* orbitals upon binding, forming superoxide (O₂⁻) or peroxide (O₂²⁻). However, some models described bound O₂ as derived from an excited singlet state of O₂ that has a weaker O–O bond than the ground-state triplet.⁴¹ Interestingly, some recent results have reopened this question. In the recent study, some bis(*N*-heterocyclic carbene)Rh(I) species bind O₂ to give side-on complexes with $d_{\text{OO}} = 1.27\text{--}1.32$ Å and $\nu_{\text{OO}} = 1010$ cm⁻¹.⁴² While these characteristics would typically suggest an O₂⁻ ligand and thus rhodium(II), analysis of L-edge XANES (X-ray absorption near-edge spectra) were more consistent with a d⁸ ligand field, implying Rh(I) and neutral singlet O₂. In the future, X-ray absorption techniques coupled with computations should be applied to a wider range of complexes, in order to understand the scope and applicability of XANES to bound diatomics, and to develop our understanding of whether doublet O₂⁻ or singlet O₂ is a better descriptor in O₂ complexes.

These recent results notwithstanding, the evidence supporting superoxide descriptions in many complexes is overwhelming.

Formation of a superoxide complex is especially clear when the metal can only transfer a single electron to O₂; for example, the complex Tp*₂SmO₂ has $d_{\text{OO}} = 1.319$ Å and $\nu_{\text{OO}} = 1124$ cm⁻¹ for its side-on superoxide ligand.⁴³ In this case, binding of O₂ cannot form a mononuclear peroxo complex without oxidizing the metal to the unprecedented oxidation state of samarium(IV). In other cases, the use of weakly donating ligands prevents the metal from reducing the O₂ to peroxide by destabilizing the doubly oxidized metal that would be produced. Examples include tris(pyrazolyl)borate complexes of chromium and copper that give side-on O₂,^{31,44} and a tris(guanidine) complex of copper.⁴⁵ EPR, vibrational, and structural evidence also supports a side-on O₂⁻ ligand on nickel(II) complexes supported by diketiminate⁴⁶ and tris(thioether)⁴⁷ ligands.

Superoxide complexes are widely postulated as intermediate species on the way to further reduced O₂ in multimetallic peroxo or oxo complexes. Note that the distal oxygen of the superoxide complex has radical character, and is prone to react with another reducing metal. In a stepwise example, a crystallographically characterized nickel(II) superoxide complex has been reported to react with potassium metal to give a nickel(II)-potassium(I) complex with a μ-η²:η²-peroxo ligand (Scheme 1).⁴⁸



Scheme 1

Reversibility of O₂ and N₂ binding

Binding of O₂ and N₂ may be reversible despite structural and spectroscopic evidence for electronic shifts from the metal to the diatomic upon binding. For example, superoxide complexes are often susceptible to loss of O₂ with reduction of the metal, either upon addition of a stronger ligand or with vacuum.¹ Thus O₂ binding may be reversible even though the binding of the O₂ molecule formally reduces O₂ to superoxide or peroxide. This is the case in numerous N₂ complexes as well, because even complexes with ligands best described as N₂²⁻ (described below) can lose N₂.² In general, it is not advisable to use the ground-state parameters of the diatomic ligand in the complex to predict the binding constant or binding kinetics.⁴⁹

Reversible binding of both N₂ and O₂ has been used productively. For example, many sources of natural gas are unusable because they contain significant amount of contaminating N₂. Reversible binding of N₂ could be used to purify the natural gas, and water-soluble iron–N₂ complexes are promising “scrubbers” for this task.⁵⁰ For O₂, an important motivation for studying reversible binding is the relationship to hemoglobin, myoglobin, and other biological O₂ carriers.^{1d} A significant amount of research has been devoted to developing “artificial blood” that carries O₂.⁵¹ In metal-based O₂ carriers, a research challenge is to understand how to make O₂ loss proceed cleanly, because if the metal loses the

superoxide anion instead, the metal remains in an one-electron oxidized state. This oxidized “met” form cannot bind O₂. On the other hand, the reverse of this undesirable one-electron O₂ reduction is useful in the context of removing potentially harmful superoxide from biological systems—the superoxide dismutase (SOD) enzymes function by oxidizing superoxide to dioxygen, and the electron that is obtained goes to another molecule of superoxide to generate peroxide.⁵²

Binding with “two-electron reduction.”

It is common for coordinatively unsaturated metal species to bind O₂ and N₂ with reduction of the diatomic to a two-electron reduced form. Because the reduction of O₂ is relatively easy, weakly reducing metals such as Fe²⁺, Co⁺, Ni⁰, Ni⁺ and Cu⁺ are often found to interact with O₂ to give peroxide complexes, concomitant with two-electron oxidation of the metal. Peroxide complexes can also be accessed by addition of H₂O₂ or simple peroxide salts to transition metals, which involves no redox at the metal. Because of the high negative charge on the peroxide group, peroxide complexes typically have two M–O bonds, either in a side-on (η^2) interaction with a single metal or bridging two or more metals. An example is a series of thoroughly characterized L₂Pd(O₂) complexes, of special interest because of the relevance to Pd–O₂ binding during oxidation catalysis.⁵³ With metals having weak ligand fields, however, side-on binding can give a superoxide species as noted above. An early example was Tp^{tBu,iPr}Cu(O₂),⁴⁴ which has $\nu_{\text{OO}} = 1112 \text{ cm}^{-1}$, and recently a (diketiminate)Ni(O₂) complex has been shown to have a superoxo ligand by X-ray, vibrational, and EPR techniques.⁴⁶ In the recent nickel complex, the reason for the limited charge transfer to O₂ may be the stability of a square-planar d⁸ configuration at nickel(II), as the analogous (diketiminate)Cu(O₂) complex achieves a d⁸ configuration by reducing O₂ to peroxide in a square-planar copper(III) peroxo complex.⁵⁴ There are also complexes with ligands that are likely to be intermediate between peroxide and superoxide, and these will be discussed in a later section.

Even within the set of complexes clearly identifiable as peroxide, the strength of the O–O bond can vary depending on the binding mode and/or the spin state of the metal. For example, there is a significant difference between the O–O stretching frequencies in peroxodicopper(II) species with an end-on/end-on O₂²⁻ bridge (803–847 cm⁻¹) compared to those with a side-on/side-on O₂²⁻ bridge (713–765 cm⁻¹).^{5a} This difference has been attributed to backbonding of metal d orbitals into the O₂²⁻ σ^* orbital.^{55,56}

The two-electron reduction of N₂ is more difficult than that of O₂, and requires more strongly reducing metals. One category of such metals is the lanthanides and actinides, which are exceptionally strong reducing agents in low oxidation states. Significant work has gone into the study of reduced N₂ complexes of metallocenes, and complexes with π -donor ligands.⁹ A reasonable model for many of these complexes is complete electron transfer from the metal d orbitals to the N₂ ligand, resulting in an anionic form of N₂ bound to a d⁰ metal center. These complexes often contain side-on/side-on (μ - η^2 : η^2) bridging N₂, presumably because the metals are devoid of valence d electrons and cannot backbond in a linear end-on geometry.

Another class of compounds with N₂²⁻ ligands uses metals in groups 5–6 of the periodic table. The reduced precursors to these

complexes have high-energy d electrons in a d² to d⁴ electronic configuration. The predominant binding mode is end-on, either a linear MNN unit on a single metal or a linear MNNM unit that bridges two metals end-on/end-on. These were some of the first N₂ complexes identified in the literature in the 1960's and 1970's, and in some cases the N–N bonds are significantly weakened. These complexes have been extensively reviewed.⁵⁷

More recently, it has become clear that the more electronegative metals in groups 8 and 9 can reduce N₂ to the N₂²⁻ level, but only if they have the appropriate metal environment induced by an unusual ligand field. The bulky β -diketiminate ligands shown in Fig. 6 drive up the energies of a singly-occupied d orbital in a way that makes these d orbitals exceptionally good at donating electrons to the π^* orbital of N₂,⁵⁸ and N–N distances in the range 1.18–1.24 Å have been observed for iron and cobalt complexes.²³ In some complexes, the presence of alkali metal cations near the bound N₂ weakens the N–N bond more, because the positive charge increases the driving force for charge transfer from the metal to N₂. This conclusion was supported by electronic structure calculations that compare the species with and without alkali metals.²³

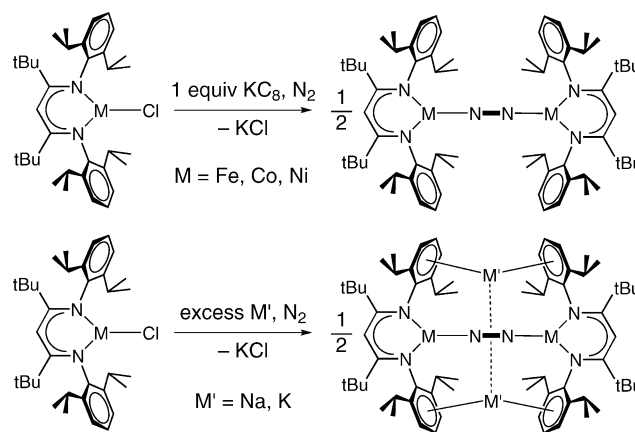


Fig. 6 β -Diketiminate complexes that show exceptional weakening of N–N bonds. The N–N bond order varies by metal and oxidation state, and to generalize the N–N bond is shown as a heavy line. In the formally monovalent, neutral complexes, the N–N bond lengths are 1.19 (Fe), 1.14 (Co), and 1.12 (Ni) Å. In the formally zero-valent, dianionic complexes at the bottom, the N–N bond lengths are 1.21 (Fe, Na), 1.24 (Fe, K), 1.21 (Co, Na), 1.22 (Co, K), and 1.18 (Ni, K) Å.

Binding with “three-electron reduction” and “four-electron reduction.”

Three-electron reduction of O₂ has not been observed, because the resultant O₂³⁻ species would have an O–O bond order of only 0.5. (Evidence was recently presented for the first example of an S₂³⁻ complex,⁵⁹ but in the O₂ analogue of this complex the dioxygen is completely reduced to two O²⁻ ligands.⁶⁰) However, N₂³⁻ has a bond order of 1.5, and can be isolated in the appropriate metal environment. A recent synthetic–spectroscopic–computational study has described the first definitive examples of N₂³⁻ complexes, using dysprosium and yttrium (Fig. 7).⁶¹ These μ - η^2 : η^2 bridging dinitrogen ligands have N–N bond distances near 1.40 Å. The assignment of N₂³⁻ is supported by EPR studies on the Y compounds that show hyperfine splitting consistent with an

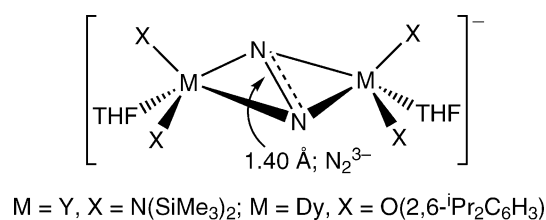


Fig. 7 Complexes of N_2^{3-} . The formulation as trianionic N_2^{3-} has been demonstrated with crystallography, electron paramagnetic resonance (EPR), and DFT computations.

N_2 -based radical, and DFT studies that reproduce the N–N bond distance and stretching frequency. The N_2^{3-} complexes can also be oxidized by one electron to give the N_2^{2-} congeners.

There are many complexes in the literature with ligands that are assigned as bridging N_2^{4-} , with an N–N single bond. A number of these complexes have two group 4–6 metals and linear MNNM bridges.⁶² In addition, there are an increasing number of side-on/side-on complexes having this oxidation level.⁶ One of the first $\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2^{4-}$ complexes was a dizirconium complex of a chelating PNP ligand,^{7a} and others have been identified with other strongly donating ligands and early transition metals.^{7,8,10,11} In these complexes, the N–N distance varies significantly, from 1.38 Å to 1.63 Å. In the $\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2^{4-}$ complexes, the N_2 cannot be displaced because the significant reduction makes it very strongly bound. The $\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2^{4-}$ complexes have been observed to react with cleavage of the N–N bond in a number of cases,^{11,63–65} and some form ammonia^{10c} or new C–N bonds.^{7f,66} Some $\mu\text{-}\eta^1\text{:}\eta^1\text{-N}_2^{4-}$ complexes can perform similar N–N bond cleavage and N–Si bond formation, suggesting that the different N_2^{4-} isomers may interconvert.^{10,11,67}

Another interesting binding mode for an N_2^{4-} ligand is $\mu\text{-}\eta^1\text{:}\eta^2$, the “end-on/side-on” binding mode described briefly above. This binding mode can be described through the limiting resonance structures shown at the top of Fig. 8. The presence of additional bridging ligands (enforcing a short M–M distance) appears to be essential for stabilizing the $\mu\text{-}\eta^1\text{:}\eta^2$ binding mode, because no examples are known without additional bridges.²⁰ Tantalum complexes of the strongly donating NPN ligands have $d_{\text{NN}} = 1.32\text{--}1.34$ Å and $\nu_{\text{NN}} = 1165$ cm^{-1} , indicating an N–N bond order between 1 and 2, somewhat stronger than those in $\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2^{4-}$ complexes.^{20b} These complexes react with boranes, acetylenes, and silanes to form new B–N, C–N, and Si–N bonds (Fig. 8

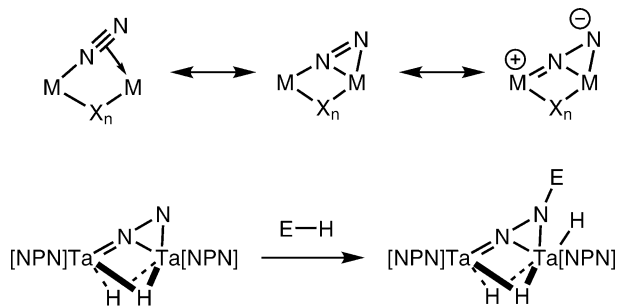


Fig. 8 Resonance structures for end-on side-on ($\mu\text{-}\eta^1\text{:}\eta^2$) bound N_2 . Tantalum compounds are best described with the right resonance structure, while zirconium complexes are better described with the center resonance structure.

bottom).^{20b} A recent report describes (indenyl)(cyclopentadienyl)-zirconium complexes that have $\mu\text{-}\eta^1\text{:}\eta^2$ binding but stronger N–N bonds with $d_{\text{NN}} = 1.20\text{--}1.22$ Å and $\nu_{\text{NN}} = 1583$ cm^{-1} that indicate an $[\text{N}=\text{N}]^{2-}$ ligand with less reduction of the N_2 unit.⁶⁸

Trends by metal, spin state, and spectator ligand

The sections above described the differences between early transition metals, late transition metals, and lanthanide/actinide metals in their abilities to transfer charge to O_2 and N_2 . In this section, some trends are noted, with a special focus on N_2 complexes. Fig. 9 illustrates the general periodic trends in N_2 weakening and reactivity. The amount of charge transfer from the metal to the diatomic ligand is dependent on the energy of the metal d orbitals (as well as the geometry; see below). Higher-energy d orbitals are more apt to transfer electron density into the diatomic ligand. The d-orbital energies decrease from the left to the right of the transition series, and accordingly the complexes of metals further to the right in the periodic table typically have less reduced ligands with higher O–O or N–N stretching frequencies and with shorter O–O or N–N bond lengths. In some cases, it has been possible to examine complexes with different metals and the same supporting ligand, isolating the influence of the particular metal as a contributor. For example, direct comparison of Ti and Zr analogues in $\mu\text{-}\eta^2\text{:}\eta^2$ complexes has shown that the Zr complexes are more reactive at N_2 .^{10b} A N_2P_2 ligand has been used to create N_2 complexes of Ti, Mn, and Fe, showing that the more electronegative metals give less N–N bond weakening.⁸ Likewise, comparison of directly analogous β -diketiminato complexes of Fe, Co, and Ni show that the metals further to the right of the periodic table give less N–N weakening.^{23b}

	1	2	3	4	5	6	7	8	9	10	11	12
H												
Li	Be											
Na	Mg	----- transition metals -----										
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	
Fr	Ra	Ac										

binds N_2 without weakening
 binds N_2 with weakening
 binds and activates N_2 toward reactions

Fig. 9 The metal dependence of N_2 binding and weakening. Complexes of all of the colored elements have been observed to bind N_2 . The blue elements have complexes that have been observed to weaken the N–N bond in N_2 in some complexes. The dark teal elements have complexes that have been observed to break the N–N bond completely through well-characterized reactions.

The type of species formed is also dependent on the oxidation level of the metal: for example, iron(II) porphyrins bind O_2 to give iron(III)-superoxide species, but iron(I) porphyrins bind O_2 to give iron(III)-peroxide species with greater reduction of the O_2 unit.^{1c}

The same trend is often seen in N_2 complexes, where the rationale for seeing more reduction by metals in a lower oxidation state is that more electrons (and higher orbital energies) in reduced metals leads to stronger π -backbonding.^{2,23b,69} An interesting exception to this trend has been seen in a series of end-on/end-on MoNNMo complexes, for which *oxidation* of the core in one-electron steps gives *weakening* of the N–N bond.⁶⁴ This trend was explained on the basis of a molecular-orbital model in which oxidation removes electrons from orbitals with N–N bonding character, rather than the more common situation where oxidation removes electrons from N_2 π^* orbitals.

Many recent studies demonstrate that the spectator ligands on the metal play an extremely important role in determining the binding mode and reduction level of the diatomic ligand as well. For example, complexes with Cp-type supporting ligands have less N_2 weakening than complexes supported by π -donor supporting aryloxo or amido ligands.^{68,70} Likewise, the only late transition metal N_2 complexes with significant N_2^{2-} character have π -donor β -diketiminato²³ or P_2N_2 supporting ligands.⁸ In another example, more electron-donating *trans* ligands in octahedral W dinitrogen complexes give more N–N weakening,⁷¹ and electron-withdrawing carbonyl supporting ligands shorten N–N bonds in end-on N_2 complexes.⁷²

The geometry of the metal center has also emerged as a key factor that influences electron distribution in the complexes. Often, the geometric changes are enforced using bulky supporting ligands. In one type of example, adding methyl groups to cyclopentadienyl ligands influences the extent of N–N activation, usually through changing the binding mode by forcing the two metal atoms apart.^{70,73} In other cases, the changes in orbital energies brought about by the bulky ligands are responsible for changes in N–N bond order. In particular, a series of studies on hindered β -diketiminato complexes has shown that a trigonal-planar geometry at the metal leads to N–N bond weakening in N_2 complexes of iron, cobalt, and nickel,^{23,69} though these metals do not typically have sufficient backbonding ability to reduce N_2 . Similar bond weakening can be accomplished using bulky ligands to enforce a tetrahedral geometry.^{8,74} Crystal-field analysis shows that trigonal-planar and tetrahedral geometries encourage strong π -backbonding.⁵⁸ Therefore, there is promise for continued use of geometric manipulation at the metal to modulate the extent of backbonding and N_2 reduction.

Using magnetic studies and spectroscopy to distinguish between quantized vs. continuous reduction levels of N_2 and O_2

Is there a rationale for a quantized description of $M-N_2$ and $M-O_2$ complexes in integer oxidation levels of the metal and bound diatomic fragment? After all, these are “resonance structures,” implying that the best description of the complex is a weighted average of contributors, with a continuous range of electron distribution. Recent results have shown that paramagnetic complexes provide excellent tools such as magnetic susceptibility, EPR spectroscopy, and X-ray absorption to address this question, in addition to the traditional measures of bond lengths and stretching frequencies.

The O–O bond lengths and vibrational frequencies in superoxide and peroxide complexes cover a range of values, as shown in Fig. 3.²⁹ Interestingly, there is a distinct “bunching” of points in

Fig. 3 near the values expected for superoxide and peroxide. This suggests that a quantized view of the bound O_2 as “superoxide” or “peroxide” is usually a good approximation, and consistent with this idea, techniques that focus on the metal often indicate integer oxidation states for peroxide and superoxide complexes. For example, Mössbauer studies of bridging Fe–O–O–Fe complexes are clearly consistent with a diiron(III) formulation,⁷⁵ and X-ray absorption studies show a distinct difference in the copper edge energy between copper(II) superoxide and copper(III) peroxide complexes.⁷⁶ Likewise, EPR spectra of some $S = 1/2$ metal-superoxo complexes have shown a small spread of g values and small hyperfine coupling to the metal, which shows that the radical is localized on the ligand.⁴⁶ Thus, O_2 binding often gives compounds in which a *single resonance structure* is an adequate description of the molecule. However, this situation is not universal! There are points throughout the range of Fig. 3 that are not well-described by “superoxo” or “peroxo.” In a recent example, computational studies on (β -diketiminato)Cu(η^2-O_2) complexes have shown a smooth transition from copper(II) superoxide to copper(III) peroxide character by varying the electronics of the supporting ligand.^{54c,77} Further studies are needed to establish in which systems these intermediate states are accessible.

The N–N bond lengths and stretching frequencies in N_2 complexes cover the range more smoothly (Fig. 4), suggesting that single resonance structures are less often applicable for N_2 than for O_2 . This makes sense, because the valence orbitals of N_2 are higher in energy and hence overlap better with metal d orbitals than those of O_2 . Compared to O_2 complexes, N_2 complexes have only recently been subjected to a high level of spectroscopic inquiry to experimentally address the charge distribution between the metal and N_2 .

One way to ascertain the suitability of different single-resonance-structure models has recently been proposed in recent studies on compounds for which the NN bond lengths and NN stretching frequencies suggest an N_2^{2-} ligand. An especially interesting facet of N_2^{2-} (using a single-structure formulation) is that it is a ground-state triplet ($S = 1$).⁷⁸ Coupling of this triplet to paramagnetic metal centers in a “three-spin model” (right of Fig. 10) might be expected to influence the magnetic behavior in N_2^{2-} complexes, whereas the neutral singlet N_2 would give different magnetic coupling (left of Fig. 10). Thus this particular oxidation level of N_2 has the potential to experimentally distinguish between $M-N_2$ (with a singlet bridge) and $M^{2+}-N_2^{2-}$ (with a triplet bridge) descriptions of a molecule, or to show

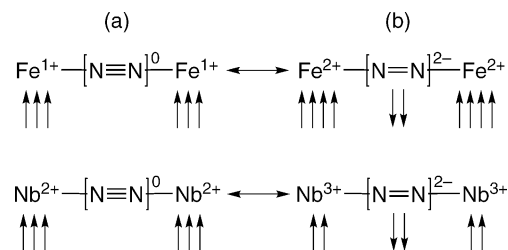


Fig. 10 Comparison of a “two-spin” model with neutral N_2 on the left (a) with a “three-spin” model with N_2^{2-} on the right (b), for compounds that are formally diiron(I) and formally diniobium(II). In each case shown, the three-spin model more easily explains the observed ground spin state ($S = 3$ and $S = 1$, respectively).

whether these simplistic models are faulty and the electrons are delocalized over the entire M–N₂ core.

The “three-spin model” for an N₂²⁻ complex has been described fully in the context of variable-field Mössbauer spectroscopy of the end-on/end-on N₂ complexes LFeNNFeL (L = β-diketimate and tris(phosphino)borate ligands).^{79,80} Using single-resonance-structure models, these compounds can be formulated as (a) diiron(I) complexes with a neutral N₂ bridge, or (b) diiron(II) complexes with a dianionic N₂²⁻ bridge. With each supporting ligand, experimental results show that the ground state is a septet ($S = 3$). A septet ground state admits two resonance-structure interpretations, as shown in the top of Fig. 10. In interpretation (a), ferromagnetic coupling between two spin-3/2 iron(I) sites explains the $S = 3$ ground state. When L = tris(phosphino)borate, EPR and solid-state magnetic susceptibility studies support interpretation (a), with $J = +4 \text{ cm}^{-1}$. The diiron(I) model implies a neutral N₂ bridge, and the short N–N bond of 1.13 Å is consistent with this idea. Interpretation (b) holds that antiferromagnetic coupling of the triplet N₂²⁻ with two high-spin iron(II) sites gives a total spin of $S_{\text{total}} = S_{\text{FeI}} - S_{\text{N}_2} + S_{\text{FeII}} = 2 - 1 + 2 = 3$. When L = β-diketimate, Mössbauer spectroscopy has shown isomer shift, quadrupole splitting, and internal field values similar to those previously seen in the amidoiron(II) complexes (β-diketimate)FeNH(*tert*-butyl),⁸¹ supporting the presence of iron(II). The longer N–N bond distance of 1.18 Å in this compound corroborates the presence of N₂²⁻ and the situation as described in interpretation (b). With each supporting ligand, DFT computations have supported the proposed interpretation with appropriate spin density found on the iron atoms (and on N₂ in the β-diketimate compound). Therefore, the tris(phosphino)borate supporting ligand gives Fe^I–N₂–Fe^I with a neutral N₂ bridge and the β-diketimate supporting ligand gives Fe²⁺–N₂²⁻–Fe²⁺ with a triplet N₂²⁻ bridge. The different “resonance forms” can be distinguished experimentally!

The three-spin model with triplet N₂²⁻ can also explain (or reinterpret) some magnetic susceptibility data for end-on/end-on N₂ complexes in the literature. For example: (i) (mesityl)₃VNNV(mesityl)₃ has been shown to be a ground-state singlet ($S = 0$),⁸² (ii) (N₂P₂)NbNNNb(P₂N₂) has been established to be a ground-state triplet,⁸³ and (iii) (amido)₃MoNNMo(amido)₃ is also a triplet.⁶⁴ These ground states are difficult to understand using neutral N₂ (which would imply d² V³⁺, d³ Nb²⁺, and d³ Mo³⁺, respectively). However, considering the bridge as triplet N₂²⁻, the total spins are easily rationalized as $S_{\text{total}} = \frac{1}{2} - 1 + \frac{1}{2} = 0$ for a V⁴⁺–N₂²⁻–V⁴⁺ compound, $S_{\text{total}} = 1 - 1 + 1 = 1$ for a Nb³⁺–N₂²⁻–Nb³⁺ compound, and $S_{\text{total}} = 1 - 1 + 1 = 1$ for a Mo⁴⁺–N₂²⁻–Mo⁴⁺ compound. Fig. 10 shows a “three-spin” coupling scheme for the niobium compound as an example. In the latter two compounds, an N₂²⁻ formulation is also consistent with the observed N–N bond distances of 1.272(5) and 1.214(5) Å.

However, some systems do not clearly agree with either a N₂ or a N₂²⁻ localized-electron model. In a recent report, both (β-diketimate)CoNNCo(β-diketimate) and its dianion have been characterized by crystallography and variable-temperature SQUID magnetometry.^{23b} The former (formally Co^I) has an $S = 2$ ground state and the latter (formally Co⁰) has an $S = 1$ ground state. Using the three-spin model, these ground states can be rationalized as $S_{\text{total}} = 3/2 - 1 + 3/2 = 2$ for Co²⁺–N₂²⁻–Co²⁺ and $S_{\text{total}} = 1 - 1 + 1 = 1$ for Co^I–N₂²⁻–Co^I. Thus the spin

states support an N₂²⁻ model. However, only the latter compound has an N–N bond distance indicative of N₂²⁻, while the short N–N bond distance of 1.139(2) Å in (β-diketimate)CoNNCo(β-diketimate) indicates neutral N₂. In the latter compound, a model with neutral N₂ bound to Co^I ions is inconsistent with the variable-temperature magnetic susceptibility, which would require surprisingly strong ferromagnetic coupling. Therefore, in this system a model with delocalized electrons is best for explaining the data, and a delocalized DFT model indeed predicted the observed $S = 2$ ground state.^{23b}

It is not yet understood when one should expect delocalized models or localized models to be more consistent with magnetic data. The three-spin N₂²⁻ model and delocalized-core models can be distinguished if the antiferromagnetic coupling between the metals and N₂²⁻ is weak, but in the limit of strong coupling ($-J > 300\text{--}400 \text{ cm}^{-1}$) both the three-spin and delocalized models predict a similar temperature dependence of the magnetic susceptibility. In this case, compounds should be evaluated using all possible techniques, including X-ray absorption spectroscopy. Computations are also essential, with the caveat that the results may be dependent on the method used. For example, in the neutral β-diketimate-iron–N₂²⁻ compounds described above, multiconfigurational self-consistent field (MCSCF) *ab initio* calculations showed six unpaired electrons in delocalized orbitals,^{23a} while time-dependent density functional theory (TD-DFT) calculations supported a three-spin model.⁷⁹ The two sets of computations show different signs of the spin density on the N₂ ligand. Clearly, the study of more complexes is warranted, in order to provide experimental and computational evidence to resolve these questions.

Biological relevance

There is a vast literature describing biological O₂ complexes in enzymes and oxygen carriers.^{1,5,84} Because O₂ is used as a terminal oxidant for respiration as well as numerous biosynthetic processes, this area has been studied in great detail. Several protein crystal structures have characterized metalloproteins with O₂ bound to the active site.⁸⁵ However, even the highest-resolution X-ray crystal structures of metalloproteins rarely give bond distances of sufficient accuracy to reliably assign a reduction level of a diatomic ligand. Alternatively, EXAFS (Extended X-ray Absorption Fine Structure) techniques can give metal–ligand distances with a reliability of ~0.02 Å, but can be hampered by the results of radiation damage or the presence of other species.⁸⁶ Therefore, bioinorganic chemists often use spectroscopic techniques in comparison to synthetic metal–O₂ complexes with some structural similarity to the biological site.^{1,29,32}

Biological N₂ chemistry is much less developed. So far, no N₂ adduct has been detected in a metalloenzyme using vibrational spectroscopy or crystallography. However, recent electron-nuclear double resonance (ENDOR) studies have detected $S = 1/2$ species derived from N₂ binding to the iron–molybdenum cofactor of molybdenum nitrogenase.⁸⁷ Interestingly, the ENDOR spectra show the presence of only one type of ^{14/15}N with magnetic coupling to the metal cluster, suggesting that only the N atom nearest to the cluster bears spin density and that the electrons from the paramagnetic cofactor are not delocalized onto the N₂ unit (alternatively, the N–N bond might have been broken). One hopes that further data on these presumptive intermediates will give

insight into this first example of an N₂ complex in a biological system.

The synthetic transition metal-N₂ complexes described above are expected to inform our understanding of the biological N₂ complexes. For example, the correlations between N–N bond length and stretching frequency could be of use if vibrational data from nuclear resonance vibrational spectroscopy (NRVS) can be compared to nitrogenase–N₂ intermediates.⁸⁸ ENDOR studies of paramagnetic synthetic complexes could be useful if the ENDOR coupling parameters seen in the nitrogenase–N₂ species can be correlated with binding mode and reduction level.⁸⁹ Finally, the recently proposed “electron inventory” that describes the location of electrons in different intermediates in the nitrogenase system⁹⁰ implicitly assumes a valence-bond model. However, the recent studies on M–N₂ complexes suggest that delocalized models should also be evaluated.

Conclusions and outlook

This Perspective has shown that, although metal–dioxygen and metal–dinitrogen complexes are often treated using different bonding models in the literature, there are similarities that can be enlightening. Similar binding modes are observed for the two. Both can be reduced through binding to transition metals, leading to interesting reactivity. Both suffer from ambiguity of the location of electrons in the metal–O₂ or metal–N₂ complex, and resolving these trends is crucial for identifying key species in metalloenzymes. Recent studies on metal–dioxygen and metal–dinitrogen complexes have shown that simplistic pictures of localized electrons on metal and ligand are sometimes accurate descriptions, but in other systems there remain ambiguities that warrant a more nuanced view. There is a need for the synthesis of complexes with many supporting ligands and metals, and for further development of physical techniques that accurately report the location of electrons. These will allow systematically varied complexes to be evaluated with spectroscopy. In concert with these experimental investigations, computational work is essential for a full understanding of the electronic structure. By combining these methods, chemists will continue to develop our understanding of the metal complexes of the essential diatomic molecules N₂ and O₂.

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References

- 1 Representative reviews: (a) L. Vaska, *Acc. Chem. Res.*, 1976, **9**, 175; (b) J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235; (c) M. Momenteau and C. A. Reed, *Chem. Rev.*, 1994, **94**, 659; (d) R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
- 2 (a) M. P. Shaver and M. D. Fryzuk, *Adv. Synth. Catal.*, 2003, **345**, 1061; (b) M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115; (c) T. A. Bazhenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69; (d) F. Tuczek and N. Lehnert, *Angew. Chem., Int. Ed.*, 1998, **37**, 2636; (e) M. D. Fryzuk and S. A. Johnson, *Coord. Chem. Rev.*, 2000, **200–202**, 379; (f) B. A. MacKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385; (g) S. Gambarotta and J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 5298; (h) P. L. Holland, “Nitrogen Fixation,” in *Comprehensive Coordination Chemistry II*, ed. J. McCleverty and T. J. Meyer, Elsevier, Oxford, 2004, p. 569; (i) J. C. Peters and M. P. Mehn, “Bio-organometallic approaches to nitrogen fixation chemistry,” in *Activation of Small Molecules*, ed. W. B. Tolman, Wiley, New York, 2006, p. 81.
- 3 R. Mason, *Nature*, 1968, **217**, 543.
- 4 (a) D. V. Fomitchev, K. A. Bagley and P. Coppens, *J. Am. Chem. Soc.*, 2000, **122**, 532; (b) D. Schaniel, T. Woike, B. Delley, C. Boskovic and H.-U. Güdel, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5531.
- 5 (a) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, 1992, **114**, 1277; (b) E. I. Solomon, F. Tuczek, D. E. Root and C. A. Brown, *Chem. Rev.*, 1994, **94**, 827; (c) A. G. Blackman and W. B. Tolman, *Struct. Bonding*, 2000, **97**, 179; (d) L. M. Mirica, X. Ottenwaelder and T. D. P. Stack, *Chem. Rev.*, 2004, **104**, 1013; (e) E. A. Lewis and W. B. Tolman, *Chem. Rev.*, 2004, **104**, 1047.
- 6 E. A. MacLachlan and M. D. Fryzuk, *Organometallics*, 2006, **25**, 1530.
- 7 (a) M. D. Fryzuk, T. S. Haddad and S. J. Rettig, *J. Am. Chem. Soc.*, 1990, **112**, 8185; (b) M. D. Fryzuk, T. S. Haddad, M. Mylvaganam, D. H. McConville and S. J. Rettig, *J. Am. Chem. Soc.*, 1993, **115**, 2782; (c) J. D. Cohen, M. D. Fryzuk, T. M. Loehr, M. Mylvaganam and S. J. Rettig, *Inorg. Chem.*, 1998, **37**, 112; (d) E. A. MacLachlan, F. M. Hess, B. O. Patrick and M. D. Fryzuk, *J. Am. Chem. Soc.*, 2007, **129**, 10895; (e) L. Morello, M. Joao Ferreira, B. O. Patrick and M. D. Fryzuk, *Inorg. Chem.*, 2008, **47**, 1319; (f) M. Hirotsu, P. P. Fontaine, P. Y. Zavalij and L. R. Sita, *J. Am. Chem. Soc.*, 2007, **129**, 12690.
- 8 W. A. Chomitz and J. Arnold, *Chem. Commun.*, 2007, 4797.
- 9 (a) R. Duchateau, S. Gambarotta, N. Beydoun and C. Bensimon, *J. Am. Chem. Soc.*, 1991, **113**, 8986; (b) W. J. Evans, G. Zucchi and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 10; (c) W. J. Evans, D. S. Lee, C. Lie and J. W. Ziller, *Angew. Chem., Int. Ed.*, 2004, **43**, 5517; (d) W. J. Evans, D. S. Lee and J. W. Ziller, *J. Am. Chem. Soc.*, 2004, **126**, 454; (e) W. J. Evans, D. S. Lee, D. B. Rego, J. M. Perotti, S. A. Kozimor, E. K. Moore and J. W. Ziller, *J. Am. Chem. Soc.*, 2004, **126**, 14574; (f) W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435.
- 10 (a) P. J. Chirik, L. M. Henling and J. E. Bercaw, *Organometallics*, 2001, **20**, 534; (b) J. A. Pool, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2003, **125**, 2241; (c) J. A. Pool, E. Lobkovsky and P. J. Chirik, *Nature*, 2004, **427**, 527; (d) W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2005, **127**, 14051; (e) W. H. Bernskoetter, A. V. Olmos, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2006, **25**, 1021; (f) T. E. Hanna, W. H. Bernskoetter, M. W. Bouwkamp, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2007, **26**, 2431; (g) T. E. Hanna, I. Keresztes, E. Lobkovsky and P. J. Chirik, *Inorg. Chem.*, 2007, **46**, 1675.
- 11 A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 2000, **122**, 3652.
- 12 W. H. Monillas, G. P. A. Yap, L. A. MacAdams and K. H. Theopold, *J. Am. Chem. Soc.*, 2007, **129**, 8090.
- 13 K. Jonas, *Angew. Chem.*, 1973, **85**, 1050.
- 14 K. Jonas, D. J. Brauer, C. Krueger, P. J. Roberts and Y. H. Tsay, *J. Am. Chem. Soc.*, 1976, **98**, 74.
- 15 A recent example: L. Salles, J.-Y. Piquemal, Y. Mahha, M. Gentil, P. Herson and J.-M. Brégeault, *Polyhedron*, 2007, **26**, 4786.
- 16 (a) C. Tejel, M. A. Ciriano, S. Jiménez, V. Passarelli and J. A. López, *Angew. Chem., Int. Ed.*, 2008, **47**, 2093; (b) M. J. Bennett and P. B. Donaldson, *Inorg. Chem.*, 1977, **16**, 1585; (c) A. L. Gavrilova, C. J. Qin, R. D. Sommer, A. L. Rheingold and B. Bosnich, *J. Am. Chem. Soc.*, 2002, **124**, 1714.
- 17 T. Miyaji, M. Kujime, S. Hikichi, Y. Moro-oka and M. Akita, *Inorg. Chem.*, 2002, **41**, 5286.
- 18 C. Takefumi, S. Yuichi, T. Fumito, T. Yoshimitsu, N. Yoshinori, K. Satoru, H. Shinya and M. Yonezo, *Angew. Chem., Int. Ed.*, 2003, **42**, 2788.
- 19 (a) Y. Tachi, K. Aita, S. Teramae, F. Tani, Y. Naruta, S. Fukuzumi and S. Itoh, *Inorg. Chem.*, 2004, **43**, 4558; (b) Y. Tachi, Y. Matsukawa, J. Teraoka and S. Itoh, *Chem. Lett.*, 2009, **38**, 202.
- 20 (a) M. D. Fryzuk, S. A. Johnson, B. O. Patrick, A. Albinati, S. A. Mason and T. F. Koetzle, *J. Am. Chem. Soc.*, 2001, **123**, 3960; (b) M. D. Fryzuk, *Acc. Chem. Res.*, 2009, **42**, 127.

- 21 G. P. Pez, P. Apgar and R. K. Crissey, *J. Am. Chem. Soc.*, 1982, **104**, 482.
- 22 J. Scott, I. Vidyaratne, I. Korobkov, S. Gambarotta and P. H. M. Budzelaar, *Inorg. Chem.*, 2008, **47**, 896.
- 23 (a) J. M. Smith, A. R. Sadique, T. R. Cundari, K. R. Rodgers, G. Lukat-Rodgers, R. J. Lachicotte, C. J. Flaschenriem, J. Vela and P. L. Holland, *J. Am. Chem. Soc.*, 2006, **128**, 756; (b) K. Ding, A. W. Pierpont, W. W. Brennessel, G. Lukat-Rodgers, K. R. Rodgers, T. R. Cundari, E. Bill and P. L. Holland, *J. Am. Chem. Soc.*, 2009, **131**, 9471.
- 24 (a) J. Reim and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1969; (b) F. Meyer and H. Pritzkow, *Angew. Chem., Int. Ed.*, 2000, **39**, 2112.
- 25 (a) R. Çelenligil-Çetin, R. J. Staples and P. Stavropoulos, *Inorg. Chem.*, 2000, **39**, 5838; (b) W. Micklitz, S. G. Bott, J. G. Bentsen and S. J. Lippard, *J. Am. Chem. Soc.*, 1989, **111**, 372.
- 26 E. J. Brown, A. K. Duhme-Klair, M. I. Elliott, J. E. Thomas-Oates, P. L. Timmins and P. H. Walton, *Angew. Chem., Int. Ed.*, 2005, **44**, 1392.
- 27 H. Shan, Y. Yang, A. J. James and P. R. Sharp, *Science*, 1997, **275**, 1460.
- 28 (a) D. R. Lide, ed., *CRC Handbook of Chemistry & Physics*, Taylor and Francis, 90th Edition, 2009; (b) F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Advanced Inorganic Chemistry*, Wiley, New York, 1999; (c) HO₂ stretching: D. D. Nelson and M. S. Zahniser, *J. Mol. Spectrosc.*, 1991, **150**, 527; (d) H₂O₂ stretching: P. A. Giguere, *J. Chem. Phys.*, 1950, **18**, 88.
- 29 R. M. Badger, *J. Chem. Phys.*, 1934, **2**, 128.
- 30 Badger's rule has been questioned: (a) B. R. Bender, G. J. Kubas, L. H. Jones, B. I. Swanson, J. Eckert, K. B. Capps and C. D. Hoff, *J. Am. Chem. Soc.*, 1997, **119**, 9179; (b) T. Hascall, D. Rabinovich, V. J. Murphy, M. D. Beachy, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 1999, **121**, 11402.
- 31 C. J. Cramer, W. B. Tolman, K. H. Theopold and A. L. Rheingold, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 3635.
- 32 For example, the O–O bond distance in the seminal O₂ compound (Ph₃P)₂IrCl(CO)(O₂) was originally reported to be 1.30(3) Å and thus superoxide, but was recently redetermined to be 1.465(4) Å, in better agreement with a peroxide-like O–O single-bond stretching frequency of 855 ± 1 cm⁻¹. See: H. Lebel, C. Ladjel, F. Bélanger-Garlépy and F. Schaper, *J. Organomet. Chem.*, 2008, **693**, 2645.
- 33 J. C. Maxwell and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, 1974, **60**, 1309.
- 34 G. Lang and W. Marshall, *J. Mol. Biol.*, 1966, **18**, 385.
- 35 S. Pin, B. Alpert, A. Congiu-Castellano, S. Della Longa and A. Bianconi, *Methods Enzymol.*, 1994, **232**, 266.
- 36 Diazene N–N distance: (a) M. Carlotti, J. W. C. Johns and A. Trombetti, *Can. J. Phys.*, 1974, **52**, 340; (b) Diazene N–N stretching: N. C. Craig and I. W. Levin, *J. Chem. Phys.*, 1979, **71**, 400; (c) Hydrazine N–N stretching: A. Braibanti, F. Dallavalle, M. A. Pellinghelli and E. Leporati, *Inorg. Chem.*, 1968, **7**, 1430.
- 37 (a) P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermueller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213; (b) H. Chun, C. N. Verani, P. Chaudhuri, E. Bothe, E. Bill, T. Weyhermueller and K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4157.
- 38 E. I. Solomon, A. B. P. Lever, ed., "Ligand Field Theory," in *Inorganic Electronic Structure and Spectroscopy*, Vol. I, Ch. 1, Wiley, New York, 1999.
- 39 Selected recent reviews: (a) T. R. Cundari, "The Application of Modern Computational Chemistry Methods to Organometallic Systems," in *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, New York, 2007, Vol. 1, pp. 639–669; (b) F. Neese, *Coord. Chem. Rev.*, 2009, **253**, 526.
- 40 The electron affinity of O₂ is 0.45 V, and the electron affinity of N₂ is negative. See ref. 28a.
- 41 R. S. Drago and B. B. Corden, *Acc. Chem. Res.*, 1980, **13**, 353.
- 42 J. M. Praetorius, D. P. Allen, R. Wang, J. D. Webb, F. Grein, P. Kennepohl and C. M. Crudden, *J. Am. Chem. Soc.*, 2008, **130**, 3724.
- 43 X. Zhang, G. R. Loppnow, R. McDonald and J. Takats, *J. Am. Chem. Soc.*, 1995, **117**, 7828.
- 44 K. Fujisawa, M. Tanaka, Y. Moro-oka and N. Kitajima, *J. Am. Chem. Soc.*, 1994, **116**, 12079. The O–O bond length in the room-temperature structure in this paper is likely to be incorrect, and represents the outlier in Fig. 3. For reanalysis of this compound using computations, see ref. 29.
- 45 C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer and S. Schindler, *Angew. Chem., Int. Ed.*, 2006, **45**, 3867.
- 46 S. Yao, E. Bill, C. Milschmann, K. Wieghardt and M. Driess, *Angew. Chem., Int. Ed.*, 2008, **47**, 7110.
- 47 K. Fujita, R. Schenker, W. Gu, T. C. Brunold, S. P. Cramer and C. G. Riordan, *Inorg. Chem.*, 2004, **43**, 3324.
- 48 S. Yao, Y. Xiong, M. Vogt, H. Gruetzmacher, C. Herwig, C. Limberg and M. Driess, *Angew. Chem., Int. Ed.*, 2009, **48**, 8107.
- 49 G. J. Leigh, *Acc. Chem. Res.*, 1992, **25**, 177.
- 50 J. D. Gilbertson, N. K. Szymczak, J. L. Crossland, W. K. Miller, D. K. Lyon, B. M. Foxman, J. Davis and D. R. Tyler, *Inorg. Chem.*, 2007, **46**, 1205.
- 51 J. E. Squires, *Science*, 2002, **295**, 1002.
- 52 A.-F. Miller, *Curr. Opin. Chem. Biol.*, 2004, **8**, 162.
- 53 (a) S. S. Stahl, J. L. Thorman, R. C. Nelson and M. A. Kozee, *J. Am. Chem. Soc.*, 2001, **123**, 7188; (b) B. V. Popp, J. L. Thorman, C. M. Morales, C. R. Landis and S. S. Stahl, *J. Am. Chem. Soc.*, 2004, **126**, 14832; (c) C. R. Landis, C. M. Morales and S. S. Stahl, *J. Am. Chem. Soc.*, 2004, **126**, 16302.
- 54 (a) N. W. Aboelella, S. V. Kryatov, B. F. Gherman, W. W. Brennessel, V. G. Young, Jr., R. Sarangi, E. V. Rybak-Akimova, K. O. Hodgson, B. Hedman, E. I. Solomon, C. J. Cramer and W. B. Tolman, *J. Am. Chem. Soc.*, 2004, **126**, 16896; (b) L. M. R. Hill, B. F. Gherman, N. W. Aboelella, C. J. Cramer and W. B. Tolman, *Dalton Trans.*, 2006, 4944; (c) C. J. Cramer and W. B. Tolman, *Acc. Chem. Res.*, 2007, **40**, 601.
- 55 (a) M. J. Baldwin, D. E. Root, J. E. Pate, K. Fujisawa, N. Kitajima and E. I. Solomon, *J. Am. Chem. Soc.*, 1992, **114**, 10421; (b) E. I. Solomon, R. Sarangi, J. S. Woertink, A. J. Augustine, J. Yoon and S. Ghosh, *Acc. Chem. Res.*, 2007, **40**, 581.
- 56 (a) J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, Jr., L. Que, Jr., A. D. Zuberbuehler and W. B. Tolman, *Science*, 1996, **271**, 1397; (b) J. Cahoy, P. L. Holland and W. B. Tolman, *Inorg. Chem.*, 1999, **38**, 2161; (c) X. Ottenwaelder, D. J. Rudd, M. C. Corbett, K. O. Hodgson, B. Hedman and T. D. P. Stack, *J. Am. Chem. Soc.*, 2006, **128**, 9268.
- 57 J. Chatt, J. R. Dilworth and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.
- 58 P. L. Holland, *Acc. Chem. Res.*, 2008, **41**, 905.
- 59 J. Berry, *Chem.–Eur. J.*, 2010, **16**, 2719.
- 60 D. E. Root, M. J. Henson, T. Machonkin, P. Mukherjee, T. D. P. Stack and E. I. Solomon, *J. Am. Chem. Soc.*, 1998, **120**, 4982.
- 61 (a) W. J. Evans, M. Fang, G. Zucchi, F. Furche, J. W. Ziller, R. M. Hoekstra and J. I. Zink, *J. Am. Chem. Soc.*, 2009, **131**, 11195; (b) W. Kaim and B. Sarkar, *Angew. Chem., Int. Ed.*, 2009, **48**, 9409.
- 62 One of many examples: A. Caselli, E. Solari, R. Scopelliti, C. Floriani, N. Re, C. Rizzoli and A. Chiesi-Villa, *J. Am. Chem. Soc.*, 2000, **122**, 3652.
- 63 (a) C. E. Laplaza, M. J. A. Johnson, J. Peters, A. L. Odom, E. Kim, C. C. Cummins, G. N. George and I. J. Pickering, *J. Am. Chem. Soc.*, 1996, **118**, 8623; (b) J. C. Peters, J.-P. F. Cherry, J. C. Thomas, L. Baraldo, D. J. Mindiola, W. M. Davis and C. C. Cummins, *J. Am. Chem. Soc.*, 1999, **121**, 10053.
- 64 J. J. Curley, T. R. Cook, S. Y. Reece, P. Muller and C. C. Cummins, *J. Am. Chem. Soc.*, 2008, **130**, 9394.
- 65 (a) A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1998, **120**, 437; (b) G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock and F. G. N. Cloke, *J. Am. Chem. Soc.*, 1999, **121**, 10444; (c) G. B. Nikiforov, I. Vidyaratne, S. Gambarotta and I. Korobkov, *Angew. Chem., Int. Ed.*, 2009, **48**, 7415.
- 66 (a) W. H. Bernskoetter, J. A. Pool, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2005, **127**, 7901; (b) W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, *Angew. Chem., Int. Ed.*, 2007, **46**, 2858; (c) D. J. Knobloch, E. Lobkovsky and P. J. Chirik, *Nat. Chem.*, 2010, **2**, 30.
- 67 M. Hirotsu, P. P. Fontaine, A. Epshteyn, P. Y. Zavalij and L. R. Sita, *J. Am. Chem. Soc.*, 2007, **129**, 9284.
- 68 D. Pun, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2008, **130**, 6047.
- 69 S. Pfirrmann, C. Limberg, C. Herwig, R. Stoesser and B. Ziemer, *Angew. Chem., Int. Ed.*, 2009, **48**, 3357.
- 70 J. R. Hagadorn and J. Arnold, *Organometallics*, 1998, **17**, 1355.
- 71 C. M. Habbeck, N. Lehnert, C. Nather and F. Tuczek, *Inorg. Chim. Acta*, 2002, **337**, 11.
- 72 M. D. Butts, J. C. Bryan, X.-L. Luo and G. J. Kubas, *Inorg. Chem.*, 1997, **36**, 3341.
- 73 P. J. Chirik, *Dalton Trans.*, 2007, 16.
- 74 T. A. Betley and J. C. Peters, *J. Am. Chem. Soc.*, 2003, **125**, 10782.
- 75 A representative example: D. D. LeCloux, A. M. Barrios, T. J. Mizoguchi and S. J. Lippard, *J. Am. Chem. Soc.*, 1998, **120**, 9001.
- 76 R. Sarangi, N. Aboelella, K. Fujisawa, W. B. Tolman, B. Hedman, K. O. Hodgson and E. I. Solomon, *J. Am. Chem. Soc.*, 2006, **128**, 8286.

- 77 B. F. Gherman and C. J. Cramer, *Inorg. Chem.*, 2004, **43**, 7281.
- 78 (a) D. Schoemaker and E. Boesman, *Phys. Status Solidi B*, 1963, **3**, 1695; (b) H. Sugimoto, Y. Shiraki and K. F. Komatsubara, *Appl. Phys. Lett.*, 1971, **18**, 461.
- 79 S. A. Stoian, J. Vela, J. M. Smith, A. R. Sadique, P. L. Holland, E. Münck and E. L. Bominaar, *J. Am. Chem. Soc.*, 2006, **128**, 10181.
- 80 M. P. Hendrich, W. Gunderson, R. K. Behan, M. T. Green, M. P. Mehn, T. A. Betley, C. C. Lu and J. C. Peters, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 17107.
- 81 H. Andres, E. Bominaar, J. M. Smith, N. A. Eckert, P. L. Holland and E. Münck, *J. Am. Chem. Soc.*, 2002, **124**, 3012.
- 82 R. Ferguson, E. Solari, C. Floriani, D. Osella, M. Ravera, N. Re, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1997, **119**, 10104.
- 83 M. D. Fryzuk, C. M. Kozak, M. R. Bowdridge, B. O. Patrick and S. J. Rettig, *J. Am. Chem. Soc.*, 2002, **124**, 8389.
- 84 (a) A. L. Feig and S. J. Lippard, *Chem. Rev.*, 1994, **94**, 759; (b) K. D. Karlin and Y. Gultneh, *J. Chem. Educ.*, 1985, **62**, 983; (c) J. P. Klinman, *Chem. Rev.*, 1996, **96**, 2541; (d) E. I. Solomon, U. M. Sundaram and T. E. Machonkin, *Chem. Rev.*, 1996, **96**, 2563; (e) M. Costas, M. P. Mehn, M. P. Jensen and L. Que, Jr., *Chem. Rev.*, 2004, **104**, 939.
- 85 Selected examples: (a) A. Karlsson, J. V. Parales, R. E. Parales, D. T. Gibson, H. Eklund and S. Ramaswamy, *Science*, 2003, **299**, 1039; (b) S. T. Prigge, B. A. Eipper, R. E. Mains and L. M. Amzel, *Science*, 2004, **304**, 864; (c) S. Nagano and T. L. Poulos, *J. Biol. Chem.*, 2005, **280**, 31659; (d) E. G. Kovaleva and J. D. Lipscomb, *Science*, 2007, **316**, 453.
- 86 L. M. Utschig, S. D. Chemerisov, D. M. Tiede and O. G. Poluektov, *Biochemistry*, 2008, **47**, 9251.
- 87 B. M. Barney, T.-C. Yang, R. Y. Igarashi, P. C. Dos Santos, M. Laryukhin, H.-I. Lee, B. M. Hoffman, D. R. Dean and L. C. Seefeldt, *J. Am. Chem. Soc.*, 2005, **127**, 14960.
- 88 Y. Xiao, K. Fisher, M. C. Smith, W. E. Newton, D. A. Case, S. J. George, H. Wang, W. Sturhahn, E. E. Alp, J. Zhao, Y. Yoda and S. P. Cramer, *J. Am. Chem. Soc.*, 2006, **128**, 7608.
- 89 N. S. Lees, R. L. McNaughton, W. V. Gregory, P. L. Holland and B. M. Hoffman, *J. Am. Chem. Soc.*, 2008, **130**, 546.
- 90 B. M. Hoffman, D. R. Dean and L. C. Seefeldt, *Acc. Chem. Res.*, 2009, **42**, 609.