Chemistry of Nitric Oxide Relevant to Biology

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1. Introduction

Nitric oxide (NO) was long thought of as a poisonous, pungent-smelling gas: an unpleasant and dangerous product of the oxidation of ammonia and of incomplete combustion of gasoline in motor vehicle exhausts. However, in the 1980s NO was discovered to be one of the most important physiological regulators,[1] playing a key role in signal transduction and cytotoxicity, possibly one of the biggest surprises in

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biological chemistry in recent times, and certainly one of the most significant in coordination chemistry in that decade. Until that time, the supposition had been that NO, like its analogues CO and CN⁻, bound irreversibly to metal centers and therefore functioned as a poison, particular with respect to respiratory processes. The moral, if there is one to be drawn, is that one can always expect surprises in biology, and that apparently well-established theories which lead almost to prejudices have a habit of unraveling, primarily because no one had been able to find examples of, or characterize, the unexpected.

This review focuses on the coordination chemistry of NO of particular relevance to topical bio-inorganic systems. It does not deal in detail with metallo-biomolecules containing NO, instead concentrating on biomimetic systems which seek to clarify aspects of geometrical and electronic structure, and the biological function of native NO-containing or -activating metallo-bimolecular systems. Consequently, the contents focus extensively on the coordination chemistry of iron, cobalt, and copper with NO. Some

other transition metal species are mentioned when appropriate. This article is not intended to provide a comprehensive survey, the intention being to provide information on and some illumination of current problems, preoccupations, and directions in biomimetic transition metal nitrosyl chemistry. It does not contain a discussion of organometallic nitrosyl species, except where they may be relevant to actual or perceived biomolecular species or processes. For comprehensive accounts of metal nitrosyl chemistry, including details of synthesis, organometallic and cluster chemistry, and the reactivity of coordinated NO, the reader is referred to a selection of reviews.[2]

2. Nitric Oxide: The Molecule

Nitric oxide is a stable free radical, the molecular orbital diagram of NO (Figure 1) showing that the unpaired electron in this molecule resides in a π^* molecular orbital. This electronic configuration explains the high reactivity of the NO molecule, in particular the ease of oxidation to the nitrosonium ion (NO^+), the probability of reduction to the nitroxide ion (NO^-), the facile attack by oxygen leading to formation of NO_2, and reaction with halogens (X_2) affording XNO. NO is isoelectronic with the dioxygen monocation (O_2^+), and NO^+ is isoelectronic with CO and CN^-, while NO^- is isoelectronic with O_2, having a triplet ground state. This last relationship accounts for the continuing interest in the study of certain types of metal nitrosyl complexes which have structural and electronic analogies with biological oxygen activators. NO can be an effective probe of metalloenzyme structure (geometrical and electronic) and function, where a spectroscopic examination of the resting or oxygenated enzyme is difficult or impossible because of instability.

Nitric oxide has an ionization potential of 9.26 eV and an electron affinity of 0.024 eV.[3] The nitrosonium ion has been isolated as a series of stable salts, and is a useful synthetic and oxidizing agent. However, NO^+ in all likelihood has an extremely short independent life in biological media, although metal complexes may function as transport agents. The independent chemistry of reduced nitric oxide (NO^-) is currently minimal, although the anion formally plays a significant role in binding with transition metals, as is reported later.

The nitric oxide molecule is redox-active in solution, a most important property which has a major influence on the chemistry of its transition metal complexes. The redox potential for the reversible process $NO \rightleftharpoons NO^+ + e^-$ is strongly solvent dependent, and in water is also pH-dependent.[4,5] Under strongly basic conditions, NO is reducing, viz. NO_2^- + H_2O + $e^- \rightarrow$ NO + $2OH^-$, $E° = -0.46$ V vs NHE. The standard potential for the reduction of NO^+ to NO has been estimated to be ca. $+1.2$ V vs NHE.[5] The reduction of NO to triplet and singlet NO^- has been quoted as lying between $+0.39$ and -0.35 V vs NHE, but a recent paper has substantially and authoritatively revised these data to -0.8 ± 0.2 V for $^3NO^-$ and -1.7 ± 0.2 V for $^1NO^-$, respectively, indicating that singlet NO^- is inaccessible physiologically.[6]

The bond length of free NO is 1.154 Å, lying between that of a double (1.18 Å) and a triple (1.06 Å) bond. Convention regards this bond length as equivalent to a bond order of 2.5, consistent with the MO diagram in Figure 1 (see also the valence bond
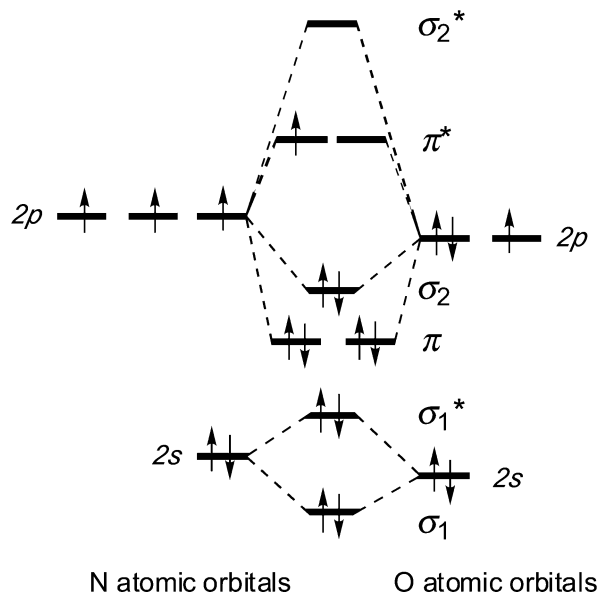

Figure 1. MO diagram of NO.

representations shown in Figure 2a).[7] Oxidation to NO^+ causes the bond distance to contract to 1.06 Å, equivalent to bond order 3. Reduction of NO to NO^- leads, concomitantly, to an increase in bond length (1.26 Å) because of further population of the π^* orbital.[3b,8]

The bond length changes discussed above are reflected in the IR stretching frequencies of these simple diatomic species: ν_{NO} decreasing with increasing charge, from 2377 (NO^+) through 1875 (NO) to 1470 cm^{-1} (NO^-).[9] Electron spin resonance studies indicate that ca. 60% of the spin density is concentrated on the N atom of neutral nitric oxide.[7] The nitrosyl halides, alkanes, and arenes are "bent" molecules, the N=O distance varying from 1.13 to 1.22 Å, and the X–N=O bond angle falling in the range from 101° to 134°, both dimensions depending on substituent.[10] These bond lengths are strongly dependent on the electronegativity of the substituents. Substituent effects also influence ν_{NO}, which occurs between 1621 and 1363 cm^{-1}, broadly equivalent to bond order 2, as shown in Figure 2b.
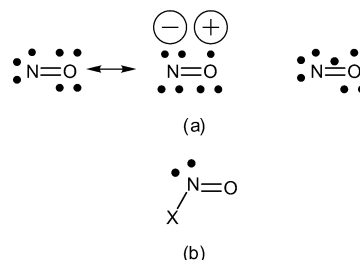

Figure 2. (a) Valence bond and other representations of NO and (b) structure of nitrosyl halides and related species having a "bent" X–N–O bond.

3. Bonding of NO to Transition Metals

3.1. Terminal Metal Nitrosyl Systems

Under normal conditions, bonding of NO to transition metals involves attachment of the N atom to the metal, viz., M−N−O. Other types of bonding occur under special conditions, as is described in section 3.3 below. Generally, in biomimetic systems, metals bind one or two NO groups and the M−N−O bond angles may be essentially linear or bent, up to ca. 120°. It is possible for NO to bridge two or three metal centers, although this is rarely encountered in biomimetic systems. However, examples of doubly and triply bridging NO are encountered in organometallic and cluster chemistry.

Early efforts to rationalize the bonding between NO and transition metal complexes involved attempts to correlate NO stretching frequencies in the IR region with limited structural data.[11] Much of the thinking occurred under the influence of the strongly developing field of transition metal organometallic chemistry, where the so-called 18-electron rule was an extremely useful method of structural and stoichiometry rationalization. Mononitrosyl compounds containing linear M−N−O groups were assumed to contain bound NO$^+$, whereas those having bent M−N−O arrangements were regarded as containing NO$^-$, but this has subsequently been found to be highly misleading.

When applying a *valence bond* approach to a linear M−N−O arrangement, it is convenient to regard the N and O atoms in the NO$^+$ group as being sp hybridized. Resonance forms contributing to linear metal nitrosyl binding are shown in Figure 3. As
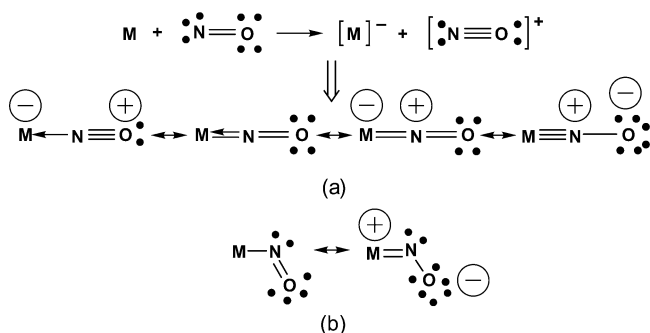

(a)

(b)

Figure 3. Valence bond representation of metal−nitrosyl bonding (a) involving NO$^+$ and (b) involving NO$^-$.

metal carbonyl and organometallic chemistry developed, so too did the parallel chemistry of NO, often in association with C-based ligand systems. These simple bonding ideas proved initially quite useful and also helped in an understanding of the reactivity of coordinated NO. Although this thinking is still prevalent, it effectively ignores the strong covalent nature of the M−N−O bond and cannot meaningfully contribute to the subtleties of the metal−NO interaction. Furthermore, the use of ν_{NO} in diagnosis of M−N−O bond angle is extremely unreliable (see below).

In a *molecular orbital* approach, the bonding of NO to a metal is thought of as having two components. The first involves donation of electron density from

NO to the metal, involving a σ orbital on the N atom (σ_2 in MO scheme, Figure 1) and the second back-donation from metal d_π orbitals to the π^* orbitals of NO. The $d_\pi−\pi^*$ interaction is shown in Figure 4. This

Figure 4. Molecular orbitals involved in $d_\pi−\pi^*$ bonding between metal and NO.

bonding description is very similar to that between CO and metals. However, as NO is more electronegative than CO, it is a better electron acceptor than CO. Furthermore, within the M−N−O group, the metal−nitrogen bond is usually strong, as is well illustrated in the valence bond picture in Figure 3, whereas the N−O bond is relatively weak. This contrasts with the metal carbonyl linkage, where the M−C bond is relatively weak and the C−O bond is strong.

In recognition of the covalent nature of the M−N−O interaction and the difficulty, not to say unreasonableness, of assigning formal oxidation states to the metal and the NO in nitrosyl complexes, Enemark and Feltham proposed a formalism which treated the metal nitrosyl as a single entity.[12] This was represented as $\{M(NO)_x\}^n$, in which n is the total number of electrons associated with the metal d and π^*(NO) orbitals. The number of d electrons is determined by the formal oxidation state of the metal atom, *assuming no charge on the NO group*. Some examples of this notation are given below:

[Mn(CN)$_5$(NO)]$^{3-}$	Mn^{II}	d^5	1 π^* NO e$^-$	{Mn(NO)}^{6}
[Fe(NO)(oep)]	Fe^{II}	d^6	1 π^* NO e$^-$	{Fe(NO)}^{7}
[Fe(NO)$_2$(SR)$_2$]$^-$	Fe^I	d^7	2 × 1 π^* NO e$^-$	{Fe(NO)$_2$}^{9}
[Co(NO)(NH$_3$)$_5$]$^{2+}$	Co^{II}	d^7	1 π^* NO e$^-$	(Co(NO)}^{8}

Notwithstanding this pragmatic scheme, it is still necessary to reflect on the charge distribution between metal and NO, particularly with respect to the electronic and magnetic behavior of complexes, and one can still usefully apportion charges as, for example, $\{M^{z-1}−(NO^+)\}$, $\{M^z−(NO^\bullet)\}$, or $\{M^{n+1}−(NO^-)\}$, as is described later. In this regard, the position of the NO stretching frequency and, occasionally, $^{14/15}$N NMR chemical shifts, can be informative.

3.1.1. Mononitrosyl Complexes

As mentioned above, terminal nitrosyl ligands may adopt either linear or bent M−N−O geometries. Very few complexes have truly linear arrangements, generally being slightly "bent", with deviations from 180° of up to 10°. The precise interpretation of the degree of deviation from expected linearity is still an open question. In some cases, DFT calculations have indicated that such departures from linearity do represent a genuine minimum in the overall energy of particular structural forms. In mononitrosyls, most M−N−O interactions are essentially linear in six-coordinate complexes having the configurations {M(NO)}^{6}, and this can be readily understood from a very simple molecular orbital treatment.[13] The requirements for this simple MO picture are that the M−N−O bond defines the z axis, the other ligands
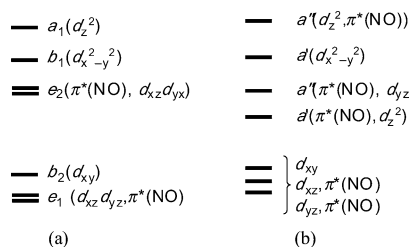
Figure 5. Arrangement of molecular orbitals in six-coordinate $\{M(NO)\}^n$ when M−N−O is (a) 180° and (b) 120°.

adopting positions either trans to the NO or on the other two Cartesian axes. In this scheme, the metal $d_{x^2-y^2}$ and d_{z^2} orbitals interact with the ligand σ orbitals, including that of NO, and the d_{xz} and d_{yz} orbitals interact with the $\pi^*(NO)$ orbitals. The metal d_{xy} orbital is relatively unperturbed in this arrangement. Figure 5 shows the arrangement of molecular orbitals in ascending energies.

For $\{M(NO)\}^6$ the electronic configuration will be $(e_1)^4(b_2)^2(e_2)^0$ (Figure 5a). In such an arrangement, or in any other with fewer metal d electrons (providing six-coordination is maintained), there should be no significant bending of the M−N−O bond. However, for $\{M(NO)\}^7$, the configuration $(e_1)^4(b_2)^2(e_2)^1$ results in occupation of a totally antibonding π-type orbital and bending according to Walsh's rules. This inevitably leads to distortions of the M−N−O bond angle, a change in symmetry, and mixing of the a_1 and the x component of the previously designated e_2 orbital. This is illustrated in Figure 5b. This mixing affords a more bonding a' level, mainly $\pi^*(NO)$ admixed with d_{z^2}, and an equivalent antibonding level which is mainly d_{z^2} in character. There are other smaller alterations in energies and symmetries of the e_1 and b_2 levels, but these are unimportant with respect to the frontier orbitals. Consequent on the bending of the M−N−O bond, the electronic configuration of $\{M(NO)\}^7$ (discounting the six electrons in the former e_1 and b_2 levels) will be $...(a')^1(a'')^0$. This is tantamount to describing the coordinated nitric oxide as NO•. In $\{M(NO)\}^8$, the electronic configuration in this MO system will be $(a')^2(a'')^0$, equivalent to the coordination of singlet NO−.

Of course, the molecular orbital scheme shown in Figure 5 assumes a relatively strong ligand field, in which the separation of the "t_{2g}" and "e_g" levels is significant. In first-row transition metals, this separation could be much reduced, depending on the co-ligands. The energies of the $d_{x^2-y^2}$ and d_{z^2} orbitals might lie close to, or even lower than, the $\pi^*(NO)$ orbitals, and significant spin multiplicity could result, the coupling between spins on the metal and NO then being governed by spin-polarization.[14] This could lead to a situation in which the nitric oxide is bound as triplet NO− ($S = 1$) to a high- or intermediate-spin metal ion. This is discussed later in sections 5.1.2 and 5.2.4 in relation to specific examples in iron nitrosyl chemistry.

From the point of view of biologically relevant systems, six-coordinate complexes containing $\{Fe(NO)\}^6$ would normally be expected to have an essentially linear Fe−N−O bond, whereas those containing $\{Fe(NO)\}^7$ would be expected to have a bent arrangement. In cobalt complexes containing $\{Co(NO)\}^8$, the Co−N−O bond should be substantially bent.

Five-coordinate complexes can adopt either tetragonal pyramidal or trigonal-bipyramidal structures. However, five-coordinate macrocyclic complexes of Mn, Fe, and Co nitrosyls almost always have the tetragonal pyramidal arrangement. In this structural arrangement, the simple molecular orbital picture outlined in Figure 5 is still reasonably satisfactory for describing species having linear or bent M−N−O bond angles.

3.1.2. Dinitrosyl Complexes

In dinitrosyl complexes, the NO ligands may be mutually trans or cis, although, given the strong π-acceptor character of nitric oxide, the majority of species adopt a cis geometry. Complexes with an $\{M(NO)_2\}$ configuration could have either linear trans or bent cis structures. While the trans form would clearly minimize the repulsion of the two NO groups, a cis geometry would be favored for species containing $\{M(NO)_2\}^n$, where $n \leq 8$.[15a] To date, only one example of an $\{Fe(NO)_2\}^8$ species, $[Fe(NO)_2(tpp)]$, has been reported,[15b] and although it was suggested that this species contains a trans ON−Fe−NO arrangement, DFT calculations indicate that a cis geometry, with significantly bent Fe−N−O bond angles, is more stable,[15a] a contradiction which remains unresolved.

In species having the configuration $\{M(NO)_2\}^{10}$ containing cis NO groups, the M−N−O bond angles would be essentially linear. In general, the N−M−N bond angle in dinitrosyls lies between 90° and 117°, larger bond angles indicating very substantial population of the N−O π^* orbitals, resulting in ligand−ligand repulsion.

3.2. Bridging Nitrosyl Complexes

Although NO, like CO, can bridge two, three, or even four metal atoms, it is the dinuclear arrangement M−N(O)−M which is most likely to be encountered in systems of relevance to biology, although it is currently rare. The only structurally characterized biomimetic example is the di-copper complex **1** [ligand is 2,6-bis{bis(2-pyridylethyl)aminomethyl}phenolate],[16]
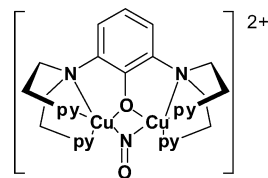
3.3. Isonitrosyl and Other Types of Metal−NO Bonding

In the late 1970s, photolysis of certain transition metal nitrosyls was discovered to cause subtle structural changes in the complexes which did not lead to rapid M−NO bond dissociation. From extremely careful low-temperature X-ray crystallographic studies, these changes were identified as being due to the formation of two metastable states corresponding to

Table 1. NO Stretching Fequencies for Selected Tetragonal Pyramidal Metal Nitrosyl Complexes

complex[a]	coordination core	C.N.[b]	$\{M(NO)\}^n$	S[c]	M−N−O (deg)	ν_{NO} (cm^{-1})[d]
[Fe(NO)(tpp)]	$\{Fe(NO)N_4\}$	5	7	$^1/_2$	149	1670
[Fe(NO)(oep)]	$\{Fe(NO)N_4\}$	5	7	$^1/_2$	144	1666
[Co(NO)(oep)]	$\{Co(NO)N_4\}$	5	8	0	123	1677
[Fe(NO)(TPP)(1-Me-im)]	$\{Fe(NO)N_5\}$	6	7	$^1/_2$	142	1625
[Fe(NO)(oep)]$^+$	$\{Fe(NO)N_4\}$	5	6	0	173	1838
[Fe(NO)(oep)(C$_6$H$_4$F-p)]	$\{Fe(NO)N_4C\}$	6	6	0	157	1839
[Fe(NO(diars)$_2$]$^{2+}$	$\{Fe(NO)As_4\}$	5	7	$^1/_2$	173	1760
[Fe(NO)(diars)$_2$(NCS)]$^+$	$\{Fe(NO)As_4N\}$	6	7	$^1/_2$	159	1620
[Fe(NO)(diars)$_2$(NCS)]$^{2+}$	$\{Fe(NO)As_4N\}$	6	6	0	~180[e]	1885
[Co(NO)(diars)$_2$]$^{2+}$	$\{Co(NO)As_4\}$	5[f]	8	0	179	1852
[Co(NO)(diars)$_2$(NCS)]$^+$	$\{Co(NO)As_4N\}$	6	8	0	132	1587
[Fe(NO)(pyN$_4$]$^{2+}$ (**2^{2+}**)	$\{Fe(NO)N_5\}$	6	7	$^1/_2$	139	1620
[Fe(NO)(pyN$_4$)]$^{3+}$ (**2^{3+}**)	$\{Fe(NO)N_5\}$	6	6	0	~180	1926
[Fe(NO)(salen)] (**6**(CH$_2$CH$_2$))	$\{Fe(NO)N_2O_2\}$	5	7	$^3/_2$	147[g]	1710
				$^1/_2$	127[h]	1630
[Fe(NO)(S$_2$CNMe$_2$)$_2$]	$\{Fe(NO)S_4\}$	5	7	$^1/_2$	170	1690
[Co(NO)(S$_2$CNMe$_2$)$_2$]	$\{Fe(NO)S_4\}$	5	8	0	136	1630

[a] Abbreviations used in this table and throughout this review: tpp, *meso*-tetraphenylporphyrinate(2−); oep, octaethylporphyrinate(2−); ttp, tetra(toluyl)porphyrinate(2−); tpivpp, α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphinato(2−), also known as the dianion of picket-fence porphyrin; porphy, dianion of generalized porphyrin; 1-Me-im, 1-methylimidazole; 2-Me-Him, 2-methylimidazole; iz, indazole; diars, benzene-1,2-bis(dimethylarsine); Me$_3$tacn, *N,N',N'*-trimethyl-1,4,7-triazacyclononane; tmc, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; mnt, maleonitrile-1,2-dithiolate; H$_4$edta, ethylenediaminetetraacetic acid; H$_3$hedta, *N*-(hydroxyethyl)ethylenediaminetriacetic acid. [b] Coordination number. [c] Spin state. [d] Measured in KBr disks or Nujol mulls. [e] Estimated from poor-quality data. [f] Trigonal-bipyramidal structure. [g] 296 K. [h] 98 K.

an isonitrosyl, M−O−N, and a κ^2-M(NO) species, respectively.[17] Among the complexes clearly exhibiting this behavior are [Fe(NO)CN)$_5$]$^{2-}$ and [Ru(NO)-(NH$_3$)$_5$]$^{2+}$, both of which are known to act as "NO donors" under physiological conditions.

The X-ray data obtained from an NO-heme protein found in the saliva of a blood-sucking insect (*Rhodnius prolixus*) were interpreted in terms of both linear and "bent" or side-on ("κ^2") geometries, although the report itself implies that only the bent or loosely bound form is present.[18] Certainly, indications of unconventional nitric oxide bonding in porphyrin complexes have been observed. Thus, for the $\{Fe(NO)\}^7$ complexes [Fe(NO)(ttp)] (for ligand abbreviations, see Table 2), irradiation led to the formation of metastable species whose IR spectroscopic parameters were not inconsistent with isonitrosylmetal binding, Fe−O−N.[19] Similar data were obtained from $\{Ru(NO)\}^6$ complexes [Ru(NO)(oep)X] (X = alkoxide, thiolate, Cl, Py$^+$).[20] DFT calculations of model species [M(NO)(porph)] {porph = porphyrinate(2−)} containing $\{M(NO)\}^n$, $n = 6-8$ and M = Mn, Fe, Co, Ru, Rh, indicated that both isonitrosyl and sideways-bound M(NO) systems could exist, but that the former is likely to be more energetically stable than the latter.[21]

These unusual bonding forms may be of considerable mechanistic importance in terms of the photochemical behavior of complexes of the later first-row transition metal nitrosyls.

4. Spectroscopic Characterization of Nitrosyl Complexes

Infrared and EPR spectroscopy dominate the techniques used to determine the nature of the M−N−O interaction and its implication for molecular structure. The former is convenient to use although sometimes misleading, whereas the latter requires specialist interpretation but is extremely valuable as a probe of electronic configuration at the metal, and

for species at low concentration. EPR data are discussed only in the context of particular complexes in the text. Other spectroscopic techniques include NMR spectroscopy, which is particularly useful for diamagnetic cobalt complexes, and the Mössbauer spectra of iron complexes, which are discussed in connection with individual groups of complexes.

4.1. IR Spectroscopy

The stretching frequency for uncoordinated NO is 1870 cm^{-1}, and on binding to a metal ν_{NO} may increase or decrease, depending on the nature of the co-ligands in the complex, on the electronic configuration of and the charge on the complex, and on the structure of the species.[2] In general, NO stretching frequencies for complexes containing linear M−N−O bonds occur in the range 1950−1450 cm^{-1}, those for complexes containing bent M−N−O bonds in the range 1720−1400 cm^{-1}, and when NO bridges two or more metal atoms, ν_{NO} may occur anywhere between 1650 and 1300 cm^{-1}. These ranges overlap significantly, and there is *no* reliable correlation between the position of ν_{NO} and the M−N−O bond angle. NO stretching frequencies for selected complexes, correlated with coordination number, spin state, and M−N−O bond angle, are listed in Table 1 and underline this point.

4.2. NMR Spectroscopy

This technique largely relies on the use of ^{14}N and ^{15}N NMR studies of diamagnetic complexes, and so is somewhat limited in its use. The ^{14}N nucleus is quadrupolar ($I = 1$) and has a high natural abundance, but possesses small relaxation times. In contrast, ^{15}N ($I = ^1/_2$) has a very low natural abundance but has very long relaxation times. So both nuclei have their uses in NMR, but it is more common to encounter ^{15}N data.[22] In the terms of this review, most N NMR studies have been of metalloporphyrins

Table 2. Spectral Parameters Obtained from Metal Nitrosyl Porphyrinato Complexes

complex[b]	$\{M(NO)\}^n$	CN[c]	M−N−O (deg)	ν_{NO} (cm^{-1})[d]	δ (mm/s)[a]	ΔE_Q (mm/s)[a]	T (K)
[Mn(NO)(tpp)]	6	5	176	1740[e]			
[Fe(NO)(oep)]$^+$ (unsolvated)	6	5	173	1862[e]	0.13	1.55	293
					0.20	1.64	4.2
[Fe(NO)(oep)(1-Me-im)]$^+$	6	6	177	1921	0.02	1.64	4.2
[Fe(NO)(oep)(2-Me-Him)]$^+$	6	6	176	1917	0.05	1.88	4.2
[Fe(NO)(oep)(iz)]$^+$	6	6	178	1914	−0.07	1.99	293
					0.02	1.92	4.2
[Fe(NO)(tpp)(NO$_2$)]	6	6		1877	0.02	1.37	293
					0.13	1.36	4.2
[Fe(NO)(tpivpp)(NO$_2$)]	6	6	169	1893	0.02	1.37	293
					0.13	1.36	4.2
[Fe(NO)(oep)(C$_6$H$_4$F-p)]	6	6	157	1791	0.05	0.56	293
					0.14	0.57	4.2
[Fe(NO)(tpivpp)(NO$_2$)]$^-$ (form 1)	7	6	138[f]	1616	0.22	1.78	200
(form 2)	7	6	137	1668	0.35	1.20	4.2
[Fe(NO)(tpp)]	7	5	149	1670[e]	0.35	1.24	4.2
[Fe(NO)(oep)]	7	5	143	1673	0.35	1.26	100
[Co(NO)(tpp)]	8	5	∼135	1689[e]			
[Co(NO)(oep)]	8	5	123	1675[e]			

^{a} Obtained at zero applied field. ^{b} For abbreviations, see Table 1. ^{c} Coordination number. ^{d} In Nujol mull unless otherwise stated. ^{e} In KBr. ^{f} Average of two molecules in a cell.

(synthetic or natural) and of cobalt and ruthenium complexes. Some ^{59}Co measurements have been also been reported.

The ^{15}N chemical shifts vary over a wide range, and for species containing linear M−N−O, δ_N tends to increase across the transition metal series, and also down a particular group. Generally, ^{15}N chemical shifts in bent nitrosyl species are significantly more deshielded (with respect to MeNO$_2$) than those in linear nitrosyl systems, δ_N for bent M−N−O systems ranging from about 950 to 350 ppm, and for linear M−N−O systems and cis-M(NO)$_2$ from about 200 to −110 ppm.

Significant information can also be obtained from shield tensors, for example in the solid state (by CP-MAS techniques), which gives information on fluxionality between linear and bent M−N−O arrangements and on fluxional behavior in solution.[22] Furthermore, in "bent" nitrosyl complexes such as [Co(NO)(tpp)], shielding tensor analysis yields information on the swinging or spinning of the NO group over the face of the porphyrin ring.

5. Biomimetic Complexes

The role of biomimicry in metal nitrosyl chemistry is to illuminate molecular and/or electronic structural issues, and to facilitate the understanding of the reactivity of the coordinated NO group. It is convenient to develop by categorizing complexes by generic types: heme analogues and related macrocyclic species, non-heme iron complexes, other iron complexes, and complexes of other metals. The reactivity of coordinated NO has been thoroughly reviewed recently, and so it is not discussed here.[23]

5.1. Heme Analogues and Related Macrocyclic Complexes

Because NO synthase, the enzyme which produces NO in the body, and soluble guanylyl cyclase, the enzymatic receptor for NO, both contain heme, iron nitrosyl porphyrinato complexes have received substantial attention. The iron heme nitrosyls containing

$\{Fe(NO)\}^7$ appear, at the time of this writing, to be more prevalent than their oxidized $\{Fe(NO)\}^6$ counterparts. This section also contains brief comments on analogous manganese, ruthenium, and cobalt porphyrins and related complexes.
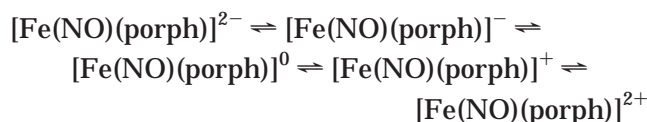
5.1.1. Iron Complexes

Iron nitrosyl porphyrins may be five-coordinate or six-coordinate, the sixth ligand in the well-characterized examples of the latter being either a N-heterocycle, water, alkyl/aryl, or NO$_2^-$. The metal−NO bond angles in the diamagnetic $\{Fe(NO)\}^6$ group of complexes lie between 169° and 180°, i.e. essentially linear, and the Fe−N(O) distances are in the range 1.63−1.67 Å, generally independent of coordination number.[24] Occasionally, a slight off-axis tilt of the Fe−N−O bond system is observed.[25] The nature of the trans axial ligand in the six-coordinate species has relatively little effect on the Fe−N(O) bond length. The NO stretching frequencies of this group, with one significant exception, lie between 1830 and 1937 cm^{-1}, depending on medium, method of preparation, and whether solvent of crystallization is present. The Mössbauer isomer shifts are in the range δ = 0.02−0.24 mm/s (4.2K), reasonable for diamagnetic complexes of this general class (Table 2 and section 5.2).[26,27,28,29] However, this range is wider than that encountered in iron nitrosyl models of non-heme proteins containing the $\{Fe(NO)\}^6$ core.[30,31] It seems that the electronic structure of this group of complexes, be they five- or six-coordinate, can be sensitive to the nature of the ligand trans to NO,[25] although distortions of the porphyrinato ligand do not seem to have a significant effect on the Fe−N−O bond angle.[29]

The major exception to the structural generalities for $\{Fe(NO)\}^6$ porphyrinato complexes referred to above is [Fe(NO)(oep)(C$_6$H$_4$F-p)].[32] This complex has an Fe−N−O bond angle of 157° and the Fe−N(O) distance is 1.73Å, both dimensions more similar to $\{Fe(NO)\}^7$ species, and the Fe−N−O group is tilted significantly off-axis. There is no doubt that this species, and its analogues [Fe(NO)(oep)R] (R = Me, C$_6$H$_5$, etc.), are diamagnetic.[33] The NO stretching

frequency (1791 cm^{-1}) and the Mössbauer isomer shift ($\delta = 0.14$ mm/s) of this complex are significantly different from those of other six-coordinate $\{Fe(NO)\}^6$ species. However, DFT calculations show that the structure of this unusual species represents a minimum energy form. Certainly, the trans axial alkyl or aryl group is likely to exert a significant trans influence, mirrored in ν_{NO}, but so does NO_2^-, and while the Mössbauer isomer shift in [Fe(NO)(tpivpp)-(NO$_2$)] (0.13 mm/s at 4.2K)[27] is close to that of [Fe(NO)(oep)(C$_6$H$_4$F-p)], the NO stretching frequency is more typical of six-coordinate $\{Fe(NO)\}^6$ species. At this point, therefore, [Fe(NO)(oep)(C$_6$H$_4$F-p)] appears to be a rare example of nonconformity with regard to the molecular and electronic generalities for $\{Fe(NO)\}^6$ porphyrinato complexes.

In the Fe(NO)}^{7} group, the Fe$-$N$-$O bond angles are 140$-$150° and the Fe$-$N(O) distances 1.72$-$1.74 Å.[25] The NO stretching frequencies range from 1625 to 1690 cm^{-1}, being dependent on the coordination number and nature of the trans axial ligand in the six-coordinate species. These species are paramagnetic ($S = ^1/_2$), and the Mössbauer spectral isomer shifts vary from 0.22 to 0.35 mm/s.[34]

The five-coordinate iron complexes are electrochemically active, existing within a five-membered electron-transfer chain:[35−38]

$$[Fe(NO)(porph)]^{2-} \rightleftharpoons [Fe(NO)(porph)]^- \rightleftharpoons$$
$$[Fe(NO)(porph)]^0 \rightleftharpoons [Fe(NO)(porph)]^+ \rightleftharpoons$$
$$[Fe(NO)(porph)]^{2+}$$

The anionic species formally contain $\{Fe(NO)\}^8$ and $\{Fe(NO)\}$,[9] although it is possible that the porphyrin ring may be reduced rather than the metal nitrosyl core. Some anionic species are unstable, readily dissociating NO, particularly in the presence of alternative donor ligands.[38,39] However, chemically generated [Fe(NO)(porph)]$^-$ may be reoxidized to its neutral precursor.[36] The monocations presumably contain $\{Fe(NO)\}^6$ and are stable, although the porphyrin rings in these and related dications could be oxidized rather than the metal.[37]

5.1.2. Electronic Structure of Iron Heme Analogues

From detailed IR, Mössbauer, and other spectroscopic studies,[30] it is likely that the $\{Fe(NO)\}^6$ porphyrinato complexes should be regarded as containing Fe^{II} ($S = 0$) bonded by NO$^+$ ($S = 0$), with low-spin Fe^{III} ($S = ^1/_2$) coupled to NO$^•$ ($S = ^1/_2$) as a reasonable alternative.[27] Suggestions have been made that the Mössbauer spectral data obtained from these species are consistent with Fe^{IV} ($S = 1$) coupled antiferromagnetically to NO$^-$ ($S = 1$), but it has been admitted that such a configuration is less satisfactory when all other spectroscopic data are considered.[25]

The spectral data obtained from $\{Fe(NO)\}^7$ complexes may be considered characteristic of complexes containing low-spin Fe^{II} ($S = 0$) coordinated by NO$^•$ ($S = ^1/_2$).[30] However, the assignment of electronic configuration is tentative, and is discussed more fully in section 5.2.4 in connection with non-heme iron model complexes.

5.1.3. Manganese, Cobalt, and Ruthenium Complexes

A comparison of the structures of five-coordinate metal nitrosyl porphyrinato complexes based on the $\{M(NO)\}^6$, $\{M(NO)\}^7$, and $\{M(NO)\}^8$ cores reveals that the M$-$N$-$O bond angle changes from essentially linear in $\{M(NO)\}^6$, as exemplified by [Mn(NO)-(porph)] and [Fe(NO)(porph)]$^+$, through ca. 143° for $\{Fe(NO)\}^7$ (there do not appear to be any other examples of $\{M(NO)\}^7$ except based on Fe), to ca. 122° in $\{M(NO)\}^8$, as in [Co(NO)(porph)].[24] The M$-$N$-$O bond lengths also progressively lengthen, but the displacement of the metal atom out of the N$_4$ porphyrin plane decreases, from ca. 0.31 through 0.28 to 0.16Å.

Cobalt Complexes. A small number of cobalt nitrosyl porphyrinato complexes containing the $\{Co(NO)\}^8$ core have been structurally characterized.[24] All are five-coordinate and essentially square pyramidal, the Co$-$N$-$O bond angle falling close to 120°,[22] although that in [Co(NO)(tpp)] is unexpectedly large (ca. 135°; this may be due to the quality of the X-ray data). This anomaly may be related to the ability of the NO group to swing or rotate about the Co$-$N$-$O bond in the solid state, an effect detected by CPMAS NMR spectral studies (see above).[22] The Co$-$N(O) bond distances average 1.84 Å, and ν_{NO} falls in the range 1675$-$1696 cm^{-1} (KBr or Nujol). Once again, off-axis tilting of the nitrosyl group is detected in [Co(NO)(oep], a phenomenon which appears to be fairly common in other related complexes.

Porphyrinato and related (chlorins, isobateriochlorins) cobalt nitrosyls can be electrochemically oxidized and reduced.[37,40] In general, oxidation is primarily associated with electron loss from the macrocyclic ligands, affording metal(nitrosyl)-stabilized porphyrin π-radical cations. Reduction affords mono- and dianionic species which are unstable and readily lose NO.

Ruthenium Complexes. Porphyrinato ruthenium complexes contain the $\{Ru(NO)\}^6$ group and are six-coordinate.[24] To date, no pure examples of five-coordinate nitrosyls, or of species containing $\{Ru(NO)\}^7$, have been fully characterized. With two exceptions, all six-coordinate ruthenium nitrosyl porphyrinato complexes, [Ru(NO)(porph)L]$^+$ (L = neutral ligand), contain an essentially linear Ru$-$N$-$O bond angle, the Ru$-$N(O) bond distance falling in the range 1.74$-$1.77 Å. The exception to this general rule is [Ru(NO)(porph)(C$_6$H$_4$F-p)] which, like its iron analogue, has a bent Ru$-$N$-$O bond angle, 152$-$155°.[32] The NO stretching frequencies of those species containing linear Ru$-$N$-$O range from 1790 to 1856 cm^{-1} (KBr), whereas those in the alkyl or aryl species are significantly lower (1759$-$1773 cm^{-1}). Once again, the trans σ-bonding alkyl or aryl ligand exerts a powerful influence on the M$-$N$-$O bond angle.
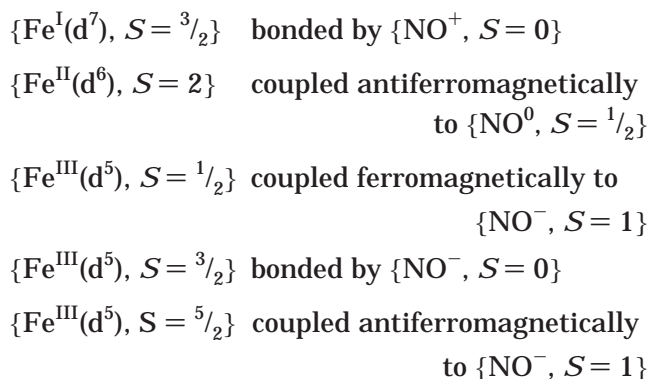
5.2. Non-Heme Model Complexes

The high-spin Fe(II) state of mononuclear non-heme iron proteins is not generally spectroscopically accessible. However, NO can be used most effectively as a probe of such Fe(II) centers, since it can convert the usually EPR-silent $S = 2$ state into an EPR-active $S = ^3/_2$ center. Consequently, enzyme$-$NO adducts

may serve as analogues for possible and/or unstable O_2 intermediates involved in bio-catalysis, thereby facilitating the identification of exogenous ligands such as substrate and solvent molecules in the metal coordination environment.

NO generally prefers to bind to Fe(II), giving $\{Fe(NO)\}^7$ species, so many model complexes containing this core have been investigated in the hope of illuminating the complexities of molecular and electronic structure in the enzyme adducts. Inevitably, species containing this group are paramagnetic, spectroscopic data indicating either an $S = \frac{1}{2}$ or $S = \frac{3}{2}$ ground state. The latter was initially unexpected, but was clearly detected by its characteristic EPR spectral behavior (g at ca. 4 and ca. 2) in a number of enzyme−NO adducts as well as in a number of $\{Fe(NO)\}^7$ complexes.[14]

A range of electronic configurations have been advanced to describe this quartet state and are listed below:[41]

$\{Fe^I(d^7), S = \frac{3}{2}\}$ bonded by $\{NO^+, S = 0\}$

$\{Fe^{II}(d^6), S = 2\}$ coupled antiferromagnetically to $\{NO^0, S = \frac{1}{2}\}$

$\{Fe^{III}(d^5), S = \frac{1}{2}\}$ coupled ferromagnetically to $\{NO^-, S = 1\}$

$\{Fe^{III}(d^5), S = \frac{3}{2}\}$ bonded by $\{NO^-, S = 0\}$

$\{Fe^{III}(d^5), S = \frac{5}{2}\}$ coupled antiferromagnetically to $\{NO^-, S = 1\}$

A variety of physical methods have been used to probe the molecular and electronic complexities of the enzymatic species and appropriate model complexes. These include single-crystal X-ray crystallography, magnetic susceptibility measurements, IR, resonance Raman, EPR, Mössbauer, X-ray absorption spectroscopy, and magnetic circular dichroism, supplemented by DFT and other calculations.

Model complexes containing five- and six-coordinate $\{Fe(NO)\}^7$ cores stabilized by a range of donor atoms incorporated in multidentate or macrocyclic ligands have been described, and many of these are discussed below. While $\{Fe(NO)\}^6$ species are not common among presently characterized enzyme−NO adducts, model complexes have been investigated, occasionally prepared by oxidation of $\{Fe(NO)\}^7$ species. These species are also discussed below.

5.2.1. Six-Coordinate {Fe(NO)}⁶ and {Fe(NO)}⁷ Complexes

Physical data relating to a selection of complexes containing $[N_5]$,[31,42,43] $[N_4X]$ (X = halide[44,45] or O[44,46−48]), $[NS_4]$,[30,49] $[N_3S_2]$,[30,50] and $[N_2S_3]$[51] donor atom sets are shown in Table 3, and representative structures are shown as **2**−**6**. It is possible to discern certain general trends. As expected from studies of heme and related complexes, the few species containing $\{Fe(NO)\}^6$ are diamagnetic, with $\nu_{NO} > 1850$ cm^{-1}. The Mössbauer spectral parameters ($\delta \approx 0.04$ mm/s, $\Delta E_Q = 1.63-1.84$ mm/s) are generally consistent with related

porphyrinato complexes (see Table 2), and the Fe−N−O bond angles in $[Fe(NO)(pyS_4)]^+$ (**3⁺**) and $[Fe(NO)(pyN_4)]^{3+}$ (**2³⁺**) are essentially linear.[30,31]

2 [Fe(NO)(pyN₄)]ᶻ, z = +2, +3

3 [Fe(NO)(pyS₄)]ᶻ, z = 0, +1

4 [Fe(NO)(tdcn)]
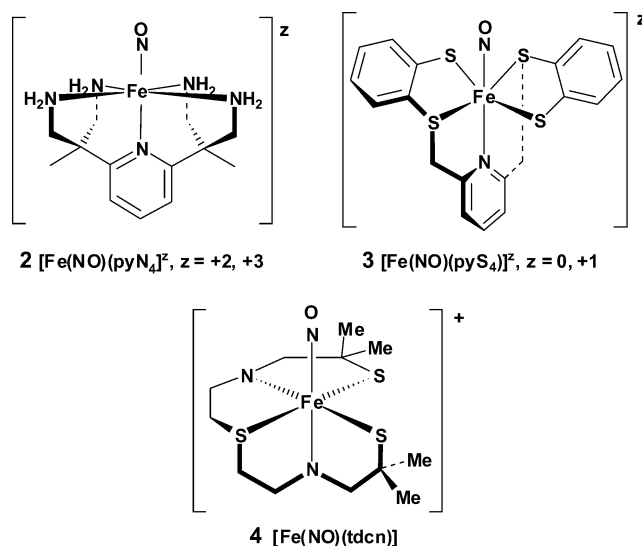
The NO stretching frequencies in the $\{Fe(NO)\}^7$ species are partly a function of donor atom set and also of charge, falling in the range 1620−1810 cm^{-1}. The differences between ν_{NO} for **2²⁺** and **2³⁺** (300 cm^{-1}) and **3** and **3⁺** (245 cm^{-1}) are very substantial, suggesting that oxidation of $\{Fe(NO)\}^7$ to $\{Fe(NO)\}^6$, in these species at least, results in a major reduction in population of the NO π^* orbitals. The electronic consequences of this are discussed further later.

The Fe−N(O) bond distance in most $\{Fe(NO)\}^7$ complexes in this group are in the range 1.68−1.76 Å, averaging 1.73 Å. The Fe−N−O bond angles in the $\{Fe(NO)\}^7$ species listed in Table 3 deviate to varying degrees from linearity, from 24° in $[Fe(NO)(Me_3tacn)(N_3)_2]$ ($\angle$(Fe−N−O) = 156°, established crystallographically and by EXAFS)[41,42] to 41° in $[Fe(NO)(pyN_4)]^{2+}$ (**2²⁺**) ($\angle$(Fe−N−O) = 139°).[31] No simple rationale has yet been advanced to account for these bond angle data.
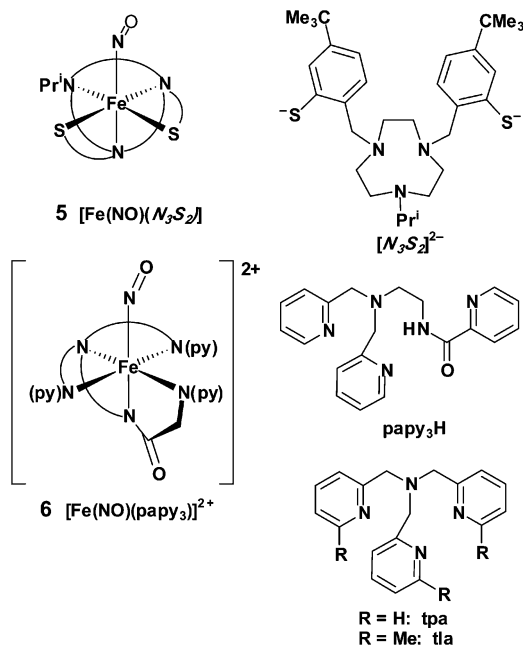

5 [Fe(NO)(N₃S₂)]

[N₃S₂]²⁻

6 [Fe(NO)(papy₃)]²⁺

papy₃H

R = H: tpa
R = Me: tla

Table 3. Physical Properties of Some Non-Heme Iron Nitrosyl Model Complexes

complex	ref	config	ν_{NO} (cm^{-1})	Fe−N−O (deg)	EPR^a	δ (mm/s)	ΔE_Q (mm/s)	redox^b	S^c	proposed electronic configuration^d
Coordination Core: [Fe(NO)N₅]										
[Fe(NO)(pyN₄)]²⁺ (**2²⁺**)	29	{Fe(NO)}⁷	1620	139	¹⁴N	0.31	0.84	1e ox 1e red	¹/₂	Fe^{II}(0)/NO⁰(¹/₂)
[Fe(NO)(PyN₄)]³⁺ (**2³⁺**)	29	{Fe(NO)}⁶	1926	~180		0.04	1.84		0	Fe^{II}(0)/NO⁺(0)
Fe(NO){Me₃tacn}(N₃)₂]	39	{Fe(NO)}⁷	1712	173	g = 4	0.62	−1.28		³/₂	
Fe(NO)(papy₃)]²⁺ (**6**)	40	{Fe(NO)}⁶	1919						0	Fe^{II}(0)/NO⁺(0)?
Coordination Core: [Fe(NO)N₄X]										
trans-[Fe(NO)(cyclam)Cl]⁺ (**12⁺**)	41	{Fe(NO)}⁷	1611	144	¹⁴N	0.27	1.26	1e ox 1e red	¹/₂	Fe^{II}(0)/NO⁰(¹/₂)
trans-[Fe(NO)(cyclam)Cl]²⁺ (**12²⁺**)	41	{Fe(NO)}⁶	1902			0.04	2.05		0	Fe^{II}(0)/NO⁺(0)
trans-[Fe(NO)(cyclam)Cl]⁰ (**12⁰**)	41	{Fe(NO)}⁸	>1500			0.27	0.77			
cis-[Fe(NO)(cyclam)Cl]⁺	41	{Fe(NO)}⁷	1802						³/₂	
cis-[Fe(NO)(cyclam)I]⁺	41		1726		g = 4	0.64	−1.78		³/₂	
[Fe(NO)(tmc)(OH)]²⁺	43	{Fe(NO)}⁶	1890	178						Fe^{II}(0)/NO⁺(0)?
[Fe(NO)(tacn)(NO₂)(ONO)]⁺	41	{Fe(NO)}⁶	1907, 1885	171		0.03	1.37		0	Fe^{II}(0)/NO⁺(0)
[Fe(NO)(tacn)(NO₂)₂]⁺	41		1890							
[Fe(NO)(tla)(O₂CCOPh)]⁺	44	{Fe(NO)}⁷	1802						³/₂	
[Fe(NO)(tpa)(O₂CCOPh)]⁺	44		1794 1716	162 155					³/₂	
[Fe(NO){L¹:OEt/CO₂Et} (MeOH)]	45		1744	150					³/₂ ↔ ¹/₂	
[Fe(NO){L¹:OEt/CN}(MeOH)] (**10a** (form 1))	45			150					³/₂	Fe^{II}(*2*)/NO⁰(¹/₂)?
Coordination Core: [Fe(NO)NS₄]										
[Fe(NO)(pyS₄)] (**3⁰**)	28, 46	{Fe(NO)}⁷	1648	150	¹⁴N	0.33	−0.40		¹/₂	Fe^{II}(0)/NO⁰(¹/₂)
[Fe(NO)(pyS₄)]⁺ (**3⁺**)	28, 46	{Fe(NO)}⁶	1893	180		0.04	−1.63		0	Fe^{II}(0)/NO⁺(0)
Coordination Core: [Fe(NO)N₃S₂]										
[Fe(NO)(*N₃S₂*)] (**5**)	28	{Fe(NO)}⁷	1682	147	¹⁴N	0.38 0.55	0.56 1.42		¹/₂ (58%) ³/₂ (42%)	Fe^{II}(0)/NO⁰(¹/₂) Fe^{III}(⁵/₂)/NO⁻(1)
[Fe(NO)(*Me₆N₃S₂*)]⁺ (**14**)	47	{Fe(NO)}⁶	1822	172					0	Fe^{III}(¹/₂)/NO⁰(¹/₂)
Coordination Core: [Fe(NO)N₂S₃]										
[Fe(NO)(tdcn)]⁺ (**4**)	48	{Fe(NO)}⁶	1856	177		0.06	1.75		0	Fe^{II}(0)/NO⁺(0)
Coordination Core: [Fe(NO)N₂O₄]										
[Fe(NO)(H₂EDTA]	13, 49	{Fe(NO)}⁷	1776	~156	g = 4				³/₂	Fe^{III}(⁵/₂)/NO⁻(1)
Coordination Core: [Fe(NO)N₄]										
[Fe(NO)(tmc)]²⁺	43	{Fe(NO)}⁷	1840	178	g = 4	0.46 0.59	0.53 0.65		³/₂ ¹/₂	Fe^{III}(⁵/₂)/NO⁻(1)? Fe^{II}(0)/NO⁰(¹/₂)?
[Fe(NO)(tact)] (**9a**)	45		1629	140				2 × 1e ox 1e red	¹/₂	Fe^{II}(0)/NO⁰(¹/₂)
[Fe((NO)(btact)] (**9b**)	45		1637	145				1e ox 1e red		Fe^{II}(0)/NO⁰(¹/₂)
[Fe(NO)(dbtact)] (**9c**)	45		1675	152				1e ox 1e red		Fe^{II}(0)/NO⁰(¹/₂)
[Fe(NO)(ᶦPr₃-tcbma)]⁻ (**13**)	50		1729	178	g = 4	0.43	1.29	1e ox 1e red	³/₂	Fe^{III}(⁵/₂)/NO⁻(1)
[Fe(NO){(cyp)₃-tcbma}]⁻ (**13**)	50		1739	173	g = 4	0.41	1.34	1e ox 1e red	³/₂	Fe^{III}(⁵/₂)/NO⁻(1)
[Fe(NO){(dmp)₃-tcbma}]⁻ (**13**)	50		1750	160	g = 4	0.43	1.33	1e ox	³/₂	Fe^{III}(⁵/₂)/NO⁻(1)
[Fe(NO)(tc-5,5)] (**15**)	68		1692	174	E	0.06	1.39	2 × 1e red	¹/₂	Fe^{III}(³/₂)/NO⁻(1)?; [Fe^{III}(¹/₂)/NO−(1)?
Coordination Core: [Fe(NO)N₂O₂]										
[Fe(NO){L¹:OEt/CN}] (**10a**)	45	{Fe(NO)}⁷	1812					1e red	³/₂	Fe^{III}(⁵/₂)/NO⁻(1)? or Fe^{II}(*2*)/NO(¹/₂)?
[Fe(NO){L¹:Me/COMe}] (**10a**)	45		1790					1e red	³/₂ ↔ ¹/₂	
[Fe(NO){L¹:Me/CO₂Et} (**10a**)	45		1776					1e red		
[Fe(NO){L¹:Ph/CO₂Et}] (**10a**)	45		1778							
[Fe(NO){L²:Ph/CO₂Et}] (**10b**)	45		1700					1e red	³/₂ ↔ ¹/₂	
[Fe(NO)(salen)] (**7**)	51		1710 1630	144, 150 122, 132		0.44 0.28	0.35 1.95		³/₂ ¹/₂	Fe^{III}(⁵/₂)/NO⁻(1)? Fe^{II}(0)/NO⁰(¹/₂)?
[Fe(NO)(5-Cl-sal)] (**7**)	52					0.65	0.58		³/₂	Fe^{III}(⁵/₂)/NO−(1)
[Fe(NO)(salphen)] (**7**)	53		1724 1643			0.42 0.27	0.18 1.76		³/₂ ¹/₂	Fe^{II}(0)/NO⁰(¹/₂)
[Fe(NO)(naphthen)] (**8**)	58		1710						³/₂	Fe^{III}(⁵/₂)/NO⁻(1)?
[Fe(NO)(naphthph)] (**8**)	58		1770						³/₂	Fe^{III}(⁵/₂)/NO⁻(1)?
[Fe(NO)(naphthmph)] (**8**)	58		1755						³/₂	Fe^{III}(⁵/₂)/NO⁻(1)?

Table 3 (Continued)

complex	ref	config	ν_{NO} (cm^{-1})	Fe–N–O (deg)	EPR[a]	δ (mm/s)	ΔE_Q (mm/s)	redox[b]	S^c	proposed electronic configuration[d]
Coordination Core: [Fe(NO)N₂S₂]										
[Fe(NO){$Me_2N_2S_2$(H)}]⁺ (**11**(H))	54	{Fe(NO)}⁶	1800	173		0.02	0.92		0?	Fe^{III}(1/2)/NO⁰(1/2)
						0.04	0.92			or Fe^{II}(0)/NO⁺(0)?
[Fe(NO){$Me_2N_2S_2$(NO₂)}]⁺ (**11**(Me))	54		1802			0.10	1.38		0	Fe^{III}(1/2)/NO⁰(1/2)
						0.03	1.41			or Fe^{II}(0)/NO⁺(0)?
[Fe(NO){$Et_2N_2S_2$(NO₂)}]⁺ (**11**(Et))	54		1804			0.09	1.54		0	Fe^{III}(1/2)/NO⁰(1/2)
						0.03	1.50			or Fe^{II}(0)/NO⁺(0)?
Coordination Core: [Fe(NO)N₂S₂]										
[Fe(NO){$Pr_2N_2S_2$(NO₂)}]⁺ (**11**(ⁿPr))	54		1808	176		0.08	1.35		0	Fe^{III}(1/2)/NO⁰(1/2)
						0.03	1.37			or Fe^{II}(0)/NO⁺(0)?
[Fe(NO){$Bu_2N_2S_2$(NO₂)}]⁺ (**11**(ⁿBu))	54		1796			0.11	1.40		0	Fe^{III}(1/2)/NO⁰(1/2)
						0.05	1.46			or Fe^{II}(0)/NO⁺(0)?
Coordination Core: [Fe(NO)S₄]										
[Fe(NO)(mnt)₂]²⁻	50, 51	{Fe(NO)}⁷	1641	160	¹⁴N	0.33	0.78	1e ox 1e red	1/2	Fe^{II}(0)/NO⁰(1/2)
[Fe(NO)(mnt)₂]⁻	50, 51	{Fe(NO)}⁶	1806			0.03	1.70		0	Fe^{II}(0)/NO⁺(0)
[Fe(NO)(S₂C₂Ph₂)₂]	50, 51	{Fe(NO)}⁵	1760			0.06	1.60	1e ox 2 × 1e red	1/2	
[Fe(NO)(S₂C₂Ph₂)₂]⁻	50	{Fe(NO)}⁶	1777						0	Fe^{II}(0)/NO⁺(0)?
[Fe(NO)(S₂C₂Ph₂)₂]²⁻	50	{Fe(NO)}⁷	1620		¹⁴N				1/2	Fe^{II}(0)/NO⁰(1/2)?
[Fe(NO){S₂C₂(tol)₂}₂]	50, 51	{Fe(NO)}⁵	1798			0.06	1.71	1e ox 2 × 1e red	1/2	
[Fe(NO){S₂C₂(an)₂}₂]	50, 51	{Fe(NO)}⁵	1764			0.08	1.59	2 × 1e red	1/2	
[Fe(NO)(S₂CNEt₂)₂]	57	{Fe(NO)}⁷		160 (rt) 170 (lt)	?	0.28 0.34	0.89 0.87		1/2	Fe^{II}(0)/NO⁰(1/2)?

[a] ¹⁴N denotes a rhombic signal pattern with ¹⁴N hyperfine coupling. [b] Electrochemical oxidation (ox) and/or reduction (red). [c] Spin ground state. [d] Fe^{ox}(spin state)/NO^z(spin state), ? implies suggestion. [e] Exhibits EPR spectrum with rhombic symmetry, but ¹⁴N hyperfine coupling not observed.
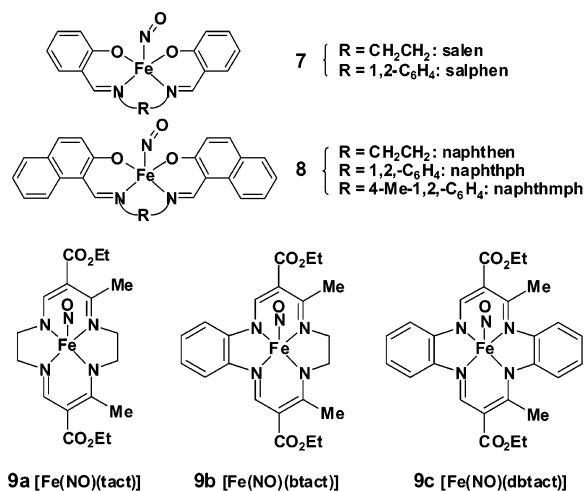
Magnetic susceptibility studies show that, while many complexes have either a doublet or quartet ground state, there is obviously a temperature-dependent equilibrium between these states in many, if not all, complexes. While both [Fe(NO)(pyN₄)]²⁺ and [Fe(NO)(pyS₄)] have $S = {}^1/_2$ configurations, [Fe(NO)L³] (**4**) clearly displays spin equilibrium behavior, $S = {}^1/_2 \rightleftharpoons S = {}^3/_2$,[30] and it was suggested that this last behavior was due to valence tautomers rather than to a simple high-spin/low-spin crossover.

From an EXAFS examination of what is probably [Fe(NO)(H₂edta)], obtained by addition of NO to [Fe^{II}(edta)(H₂O)]²⁻, the Fe–N–O bond angle and the Fe–N(O) bond length were estimated to be 156° and 1.78 Å, respectively.[14,41] The precise coordination number of the species was not established, but the dimensions are consistent with a {Fe(NO)}⁷ configuration, the EPR spectrum indicating an $S = {}^3/_2$ ground state.

### 5.2.2. Tetragonal Pyramidal Five-Coordinate {Fe(NO)}⁷ Complexes

These complexes contain [N₄],[41,48,52] [N₂O₂],[48,53–55] [N₂S₂],[56] and [S₄][57–59] donor atom sets, and their physical data are summarized in Table 3. Almost all complexes have essentially square-pyramidal structures with only some slight distortion toward trigonal-bipyramidal forms. The iron atoms are displaced from the basal donor atom planes toward the NO group. The Fe–N(O) bond lengths are similar to those of their six-coordinate analogues, averaging 1.72 Å in species containing the [N₄] donor atom set, and slightly larger (1.78 Å) in [Fe(NO)(salen)] (**7**, R = CH₂CH₂; [N₂O₂] donor atom set, RT). The Fe–N–O bond angle is always significantly bent (122–150°),

with one exception, [Fe(NO)(tmc)]²⁺ (**178°**), which has a distorted geometry midway between tetragonal pyramidal and trigonal bipyramidal.[41,46] The structure of [Fe(NO)(salen)] (**7**, R = CH₂CH₂) was determined at two temperatures, 98 and 296 K.[54] The room temperature form, which has an $S = {}^3/_2$ ground state, has a slightly shorter Fe–N(O) bond length and a less bent Fe–N–O bond angle than the low-temperature form ($S = {}^1/_2$).


7 { R = CH₂CH₂: salen
R = 1,2-C₆H₄: salphen

8 { R = CH₂CH₂: naphthen
R = 1,2-C₆H₄: naphtph
R = 4-Me-1,2,-C₆H₄: naphthmph

9a [Fe(NO)(tact)]　　**9b** [Fe(NO)(btact)]　　**9c** [Fe(NO)(dbtact)]

A number of other five-coordinate complexes have $S = {}^3/_2$ ground states, for example [Fe(NO)(naphthen)][60] (**9a**) and its analogues **9b** and **9c**,[48] and several complexes in the series [Fe(NO){L¹:R¹/R²}] (**10a**).[48] A few species exhibit spin-state equilibria, $S = {}^3/_2 \rightleftharpoons S = {}^1/_2$, e.g., [Fe(NO)(tmc)]²⁺,[41,46] [Fe(NO){L¹:Me/CO₂Et}] (**10a**), and [Fe(NO){L²:Ph/CO₂Et}] (**10b**).[48] The rest have doublet ground states, in-

cluding [Fe(NO)(tact)] (**9a**)[48] and its analogues, and all the complexes containing the [S$_4$] donor atom set.[57-59]
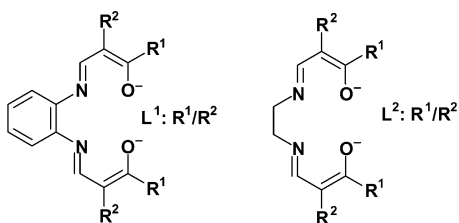
10a [Fe(NO)(L^1:R^1/R^2)]   **10b** [Fe(NO)(L^2:R^1/R^2)]

The NO stretching frequencies of this group of complexes fall in the range 1629–1812 cm^{-1}, being a function of substituents on the ligands. The one exception to this is [Fe(NO)(tmc)]$^{2+}$, $\nu_{NO} = 1840$ cm^{-1}, whose anomalous behavior in this regard, and with respect to the Fe–N–O bond angle, may be due to its distorted geometry, as mentioned earlier.
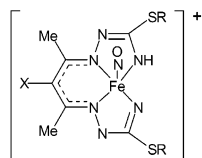
11 (H) [Fe(NO){N_2S_2(H)}] (X = H, R = Me))

11 (R) [Fe(NO){N_2S_2(NO$_2$)}] (X =NO$_2$, R = alkyl))

Several of these five-coordinate species, particularly [Fe(NO)(tact)] (**9a**) and its analogues[48] and *trans*-[Fe(NO)(cyclam)Cl]$^+$ (**12**)$^+$,[44] undergo one-electron oxidation and reduction processes, corresponding to the formation, formally, of {Fe(NO)}^{6} and {Fe(NO)}^{8} species, as shown:

$$[\{Fe(NO)\}^8]^- \rightleftharpoons [\{Fe(NO)\}^7]^0 \rightleftharpoons$$
$$[\{Fe(NO)\}^6]^+ \{\rightleftharpoons [\{Fe(NO)\}^5\}]^{2+}\}$$
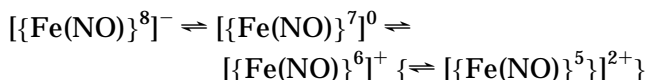
While the former have some stability in solution, they were not characterized, and the reduced species were unstable, losing NO readily. [Fe(NO)(tact)] (**9a**) exhibited a second oxidation process which seemed to be NO-ligand based. No Mössbauer spectral data have been reported for this group of complexes. None of these species were sufficiently stable to be isolated, and there are no IR or Mössbauer spectral data available.
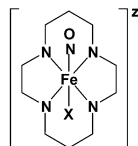
12 *trans*-[Fe(NO)(cyclam)X]^z, z = 0, +1, +2

5.2.3. Trigonal Bipyramidal Iron Non-Heme Protein Models

There are very few examples of {Fe(NO)}^{7} complexes which have trigonal-bipyramidal coordination and an $S = 3/2$ ground state, and this geometry has not yet been identified in non-heme iron proteins. The anionic species [Fe(NO)(R$_3$-tcbma)]$^-$ [**13**, R = ^{i}Pr,

cyclopentyl (cyp), or 3,5-dimethylphenyl (dmp)] were designed to have this structure and a quartet ground state, but the Fe–N–O bond angles vary according to the substituent, R, viz., 178° (R = ^{i}Pr), 173° (R = cyp), and 160° (R = dmp), respectively.[52] This bond angle variation is caused by restrictions in the cavity size defined by the R groups, being most confined when R = ^{i}Pr and least so when R = dmp. These complexes undergo a reversible one-electron oxidation and a quasi-reversible one-electron reduction, but neither the oxidized nor reduced species were sufficiently stable for characterization.
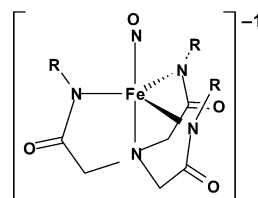

13 [Fe(NO)(R$_3$-tcbma)]$^-$

5.2.4. Electronic Description of Iron Non-Heme Protein Models

As can be inferred from the data provided in Table 3, there are four potential configurations for five- and six-coordinated iron nitrosyls: {Fe(NO)}^{5}, {Fe(NO)}^{6}, {Fe(NO)}^{7}, and {Fe(NO)}^{8}. There are many examples of biological species adopting the {Fe(NO)}^{7} configurations, fewer which are described as {Fe(NO)}^{6}, and none yet which appear to contain {Fe(NO)}^{5} or {Fe(NO)}^{8}. However, there are several examples of the last group found in coordination compounds.

The electronic descriptions of these complexes rely substantially on zero-field, applied-field, and variable-temperature Mössbauer spectral studies, complemented by DFT calculations which are supported, when possible, by crystallographic data, sometimes at two different temperatures, and by EPR spectral measurements.

The Mössbauer isomer shifts of the complexes reported in Table 3 fall into three broad groups: (a) $\delta = 0.03-0.06$ mm/s, (b) $\delta = 0.25-0.38$ mm/s, and (c) $\delta = 0.55-0.67$ mm/s. Complexes containing {Fe(NO)}^{6}, $S = 0$, are in group (a), and it has been proposed that the electronic structure of the iron–nitrosyl core can be described as low-spin Fe^{II} ($S = 0$) coordinated formally by NO$^+$ ($S = 0$).[30] This is consistent with the relatively high NO stretching frequencies in this group of complexes ($\nu_{NO} = 1893-1926$ cm^{-1}). Variations within this range are likely to be due to the charge on the complex and the effect of varying donor atom sets. The electronic description is less certain for that group of complexes where ν_{NO} falls below 1850 but above 1770 cm^{-1}, although δ (low temperature) falls between 0.03 and 0.06 mm/s. It seems reasonable to regard these species also as Fe^{II} ($S = 0$) coupled to NO$^+$ ($S = 0$), since earlier proposals that some of the complexes might contain high- or intermediate-spin Fe^{III} ($S = 5/2$ or $3/2$) or Fe^{IV} ($S = 1$) antiferromagnetically coupled to NO$^-$ ($S = 1$)[44] appear to have been re-evaluated.[30] However, although there are no supporting Mössbauer data, the {Fe-(NO)}^{6} complex [Fe(NO)($Me_6N_3S_2$)]$^+$ (**14**), which has

an Fe−N−O bond angle of 172° and $\nu_{NO} = 1822$ cm^{-1}, is described as containing Fe^{III} coordinated by NO$^\bullet$.[50]
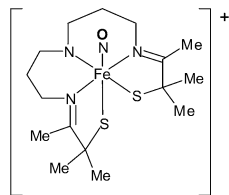
14 [Fe(NO)(*Me$_6$N$_3$S$_2$*)]$^+$

Group (b) contains complexes having the configuration {Fe(NO)}^{7} with an $S = {}^1/_2$ ground state. The electronic structure of these complexes may be represented as low-spin Fe^{II} ($S = 0$) coordinated by NO$^\bullet$ ($S = {}^1/_2$).[30] The NO stretching frequencies of this group are certainly significantly lower than those of group (a), in the range 1611−1682 cm^{-1}, as shown by *trans*-[Fe(NO)(cyclam)Cl]$^+$ (**12$^+$**), [Fe(NO)(pyN$_4$)]$^{2+}$ (**2^{2+}**), the low-temperature form of [Fe(NO)(salen)] (**7**), [Fe(NO)(mnt)$_2$]$^{2-}$, the low-temperature form of [Fe(NO)(salphen)] (**7**, R = 1,2,C$_6$H$_4$), [Fe(NO)(pyS$_4$)]$^+$ (**3$^+$**), and the low-spin form of [Fe(NO)(N_3S_2)] (**5**). Furthermore, the EPR spectra of these complexes, where reported, exhibit rhombic site symmetry at low temperature and ^{14}N hyperfine coupling, which is consistent with the coordination of NO$^\bullet$ and a bent Fe−N−O bond. The five-coordinate species [Fe(NO)-(tact)] (**9a**), [Fe(NO)(btact)] (**9b**), and [Fe(NO)(dbtact)] (**9c**) have $S = {}^1/_2$ ground states and ν_{NO} between 1629 and 1675 cm^{-1}, but there are no Mössbauer spectral data. It is tempting to describe them as Fe^{II} ($S = 0$) coupled to NO$^\bullet$ ($S = {}^1/_2$), although intermediate-spin Fe^{III} ($S = {}^3/_2$) coupled antiferromagnetically to NO$^-$ ($S = 1$) has been suggested as an alternative on the basis of comparability with analogues not containing NO.[48]

Group (c) also contains {Fe(NO)}^{7} complexes but having $S = {}^3/_2$. It has been suggested that these be regarded as containing high-spin Fe^{III} ($S = {}^5/_2$) antiferromagnetically coupled to NO$^-$ ($S = 1$).[14,30] The NO stretching frequencies of this group of complexes range from 1682 to 1802 cm^{-1}, and several of these complexes exhibit $g = 4$ as well as $g = 2$ signals in their EPR spectra. Complexes with these properties include one form of [Fe(NO)(N_3S_2)] (**5**), [Fe(NO)(Me$_3$tacn)N$_3$)$_2$], and *cis*-[Fe(NO)(cyclam)I]$^+$ (**12$^+$**, X = I). It has also been suggested that [Fe(NO)-(H$_2$edta)] ($S = {}^3/_2$) contains Fe^{III} ($S = {}^5/_2$) antiferromagnetically coupled to NO$^-$ ($S = 1$).[14] A number of other complexes have spin states at room temperature and NO stretching frequencies which fall within the ranges described above, but have δ values less than 0.55 mm/s. This group includes the high-spin, high-temperature (220 K) forms of [Fe(NO)(salen)] ($\delta = 0.44$ mm/s) and [Fe(NO)(salphen)] (**7**, R = 1,2-C$_6$H$_4$, $\delta = 0.42$ mm/s), [Fe(NO)(tmc)]$^{2+}$ ($\delta = 0.46$ mm/s), and [Fe(NO)(R$_3$-tcmba)] (**13**, $\delta = 0.41-0.43$ mm/s).

A number of five- and six-coordinate species [Fe-(NO){L^n:R^1/R^2}] (n = 1 or 2) and [Fe(NO){L^1:R^1/R^2}-(MeOH)] (**10a** and **10b**) exhibit spin-crossover behavior, $S = {}^3/_2 \rightleftharpoons S = {}^1/_2$, but no Mössbauer spectral or EPR spectral data are available to assist in

determining the electronic configurations of these species.[48] These complexes have NO stretching frequencies in the range 1700−1812 cm^{-1}. At low temperature, magnetic and crystallographic data seem to be consistent with a description as Fe^{III} ($S = {}^5/_2$) coupled to NO$^-$ ($S = 1$) for [Fe(NO){L^1:OEt/CN}] (**10a**), whose $S = {}^3/_2$ state is stable down to 30 K, although Fe^{II} ($S = 2$) coupled to NO$^\bullet$ ($S = {}^1/_2$) has been suggested as an alternative.[48] In the absence of detailed Mössbauer spectral analyses, no clear conclusions can be drawn.

A few species containing {Fe(NO)}^{8} have been identified electrochemically, but only one has been isolated, [Fe(NO)(cyclam)Cl]^0 (**12^0**).[44,45] It was originally but very tentatively proposed that this complex ($\nu_{NO} < 1500$ cm^{-1}; $\delta = 0.27$ mm/s) be described as low-spin Fe^{III} ($S = {}^1/_2$) coupled antiferromagnetically to the dianionic radical NO^{2-} ($S = {}^1/_2$), leading to a significantly bent Fe−N−O bond angle.[44] However, in view of the later assignment of [Fe(NO)(cyclam)-Cl]$^+$ (**12$^+$**) as low-spin Fe^{II} ($S = 0$) coupled to NO$^\bullet$ ($S = {}^1/_2$),[30] it seems more reasonable to view the neutral species as also containing low-spin Fe^{II} ($S = 0$) but coupled to singlet NO$^-$ ($S = 0$). This description has been proposed for related ruthenium complexes.[61] The trigonal-bipyramidal complexes [Fe(NO)L$_4$]$^+$, in which L is a π-acceptor ligand, have ν_{NO} at 1730 $\pm$ 20 cm^{-1} and linear Fe−N−O bond angles, and have been regarded as containing low-spin Fe^{II} ($S = 0$) coordinated by singlet NO$^-$ ($S = 0$). However, an alternative description as Fe^0 ($S = 0$) bound by NO$^+$ has been proposed as being more consistent with Mössbauer spectral data, particularly those obtained from [Fe(NO){P(OEt)$_3$}$_4$]$^+$ ($\delta = -0.02$ mm/s).[44]

Several five-coordinate {Fe(NO)}^{7} complexes have no Mössbauer spectral data but exhibit ν_{NO} below 1700 cm^{-1} and have $S = {}^1/_2$, e.g. [Fe(NO)(tact)] (**9a**) and its analogues **9b** and **9c**. It has been suggested that these species could be described as intermediate-spin Fe^{III} ($S = {}^3/_2$) antiferromagnetically coupled to coordinated triplet NO$^-$ ($S = 1$),[48] but in view of more recent data obtained from other {Fe(NO)}^{7} species,[30] it seems more likely that they should be regarded as containing Fe^{II} ($S = 0$) coordinated by NO$^\bullet$ ($S = {}^1/_2$). Oxidation and reduction of these complexes, giving {Fe(NO)}^{6} and {Fe(NO)}^{8}, would then be regarded as generating species with Fe^{II}(NO$^+$) and [Fe^{II}(NO$^-$) configurations, respectively. It has been remarked, however, that oxidation of [Fe(NO)(btact)] (**9b**) and [Fe(NO)(dbtact)] (**9c**) appeared to be a macrocyclic ligand-based process, reminiscent of the behavior of porphyrinato complexes.[48]

The highly oxidized species [Fe(NO)(tact)]$^{2+}$ (**9a^{2+}**) and [Fe(NO)(S$_2$C$_2$Ph$_2$)$_2$]^0 present an interesting challenge. It has been suggested that the former be formulated as Fe^{IV}(NO$^\bullet$), but this seems implausible.[48] Assuming that the species does not contain an oxidized macrocyclic ligand, an alternative description, based on the earlier suggestion for [Fe(NO)-(tact)]$^+$ (**9a$^+$**), might involve Fe^{III} (S unknown) bound to NO$^+$. In the absence of IR, magnetic susceptibility measurements, and Mössbauer spectral data, this proposal must remain speculative. The dithiolene

$[Fe(NO)(S_2C_2Ph_2)_2]^0$ and its analogues have Mössbauer isomer shifts close to those of $\{Fe(NO)\}^6$, although the complexes are paramagnetic ($g = 2.003$, no ^{14}N hyperfine couplings) and the NO stretching frequencies are less than 1800 cm^{-1}.[57,58] No clear assignment has yet been suggested, but dithiolene complexes are well-known to exhibit "non-innocent" behavior,[62] so the sulfur ligands may be coordinated as radical anions. A possible formulation might be $[Fe^{II}(NO^{\bullet})\{(S_2C_2Ph_2)^{\bullet-}\}_2]$, in which the NO$^{\bullet}$ ($S = 1/2$) is antiferromagnetically coupled to one of the unpaired spins on a sulfur ligand.[58]

However one may view these electronic descriptions and the prediction of specific electronic arrangements, two things are clear. The first is that particular descriptions must rely strongly on the nature of the ligand field provided by the ligands surrounding the $\{Fe(NO)\}^n$ core: examples in Tables 2 and 3 bear this out. The second is that there remains a considerable degree of conjecture in the extrapolation of Mössbauer spectral information to actual charge and electron distribution in the highly covalent systems.

5.3. Other Iron Complexes

Reaction of aquated Fe^{2+} salts with NO affords what may be regarded as the archetypal iron nitrosyl, $[Fe(NO)(H_2O)_5]^{2+}$, an $\{Fe(NO)\}^7$ species. This complex is also formed in the so-called "brown ring" test for NO$_2^-$ used in simple qualitative analysis. The previous description of the cation as Fe^I ($S = 1/2$) bonded by NO$^+$ has recently been re-examined.[63] The IR spectrum ($\nu_{NO} = 1810$ cm^{-1}), EPR spectrum ($g \approx 4$ and 2), and Mössbauer spectral parameters ($\delta = 0.76$ mm/s; $\Delta E_Q = 2/1$ mm/s) are typical of an $S = 3/2$ ground state for this species, which is appropriately described as high-spin Fe^{III} ($S = 5/2$) antiferromagnetically coupled to NO$^-$ ($S = 1$).

A group of iron dinitrosyl complexes of the type $[Fe(NO)_2(SR)_2]^-$ can be formed in vivo and in vitro.[64] These $\{Fe(NO)_2\}^9$ species are, of course, paramagnetic (in "organometallic" terminology they have 17 valence electrons) and exhibit characteristic EPR signals at $g \approx 2.03$. These species are related to the so-called Roussin red esters, $[Fe_2(NO)_4(\mu\text{-}SR)_2]$, which may apparently be reduced in two steps, affording $[Fe_2(NO)_4(\mu\text{-}SR)_2]^-$ and $[Fe_2(NO)_4(\mu\text{-}SR)_2]^{2-}$.[65] There is some controversy surrounding the existence of the monoanion.[66] There is little structural information about the mononuclear species, although the EPR spectrum of the isolated 1-aminobenzenethiolato complex $[Fe(NO)_2\{S(NH_2)C_6H_4\}]$ ($\nu_{NO} = 1800, 1740$ cm^{-1}), which is likely to be tetrahedral, has $g = 2.03$.[67] In the preparation of tetrahedral $[Fe(NO)_2(1\text{-}Me\text{-}im)_2]$ (1-Me-im = 1-methylimidazole), EPR signals with $g \approx 2.03$ were identified as arising from the paramagnetic intermediate $[Fe(NO)_2(1\text{-}Me\text{-}im)_2]^+$.[68] These observations may have implications for biological species containing $\{Fe(NO)_2\}$ groups.

The trigonal-bipyramidal tropocoronand complex $[Fe(NO)(tc\text{-}5,5)]$ (**15**), which can disproportionate NO into N$_2$O and NO$_2$, has IR ($\nu_{NO} = 1692$ cm^{-1}) and Mössbauer spectral parameters ($\delta = 0.06$ mm/s, ΔE_Q

$= 1.39$ mm/s) consistent with an $\{Fe(NO)\}^7$ configuration, although the Fe$-$N$-$O bond angle was 174°.[69] The low-temperature EPR spectrum exhibited a rhombic pattern, the spin ground state $S = 1/2$, and there was no evidence for spin-crossover behavior. The unusual Mössbauer isomer shift, more commonly found in $\{Fe(NO)\}^6$ species, coupled with the NO stretching frequency, was interpreted as indicating a low-spin $[Fe^{III}(NO^-)]^{2+}$ center, which was consistent with the relatively short Fe$-$N(macrocycle) bond lengths when compared with regular Fe^{II} analogues.
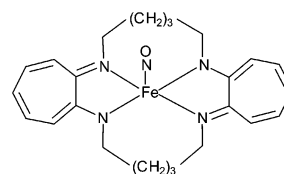
15 [Fe(NO)(tc-5,5)]

The dinuclear carboxylato-bridged dinitrosyl species $[Fe_2(NO)_2(Et\text{-}htpb)(O_2CPh)][BF_4]_2$ (**16**) was prepared as a potential mimic of the nitrosylated diiron sites in hemerythrin and ribonucleotide reductase (R2).[70] This species had ν_{NO} at 1785 cm^{-1} and Mössbauer parameters ($\delta = 0.67$ mm/s and $\Delta E_Q = 1.44$ mm/s) consistent with $\{Fe(NO)\}^7$ centers, each iron having an $S = 3/2$ spin state. The two iron centers were antiferromagnetically coupled, $J = -23$ cm^{-1}. It would appear that the electronic configuration of the individual iron centers fall into group (c) described above, viz, high-spin Fe^{III} ($S = 5/2$) coupled antiferromagnetically to NO$^-$ ($S = 1$). The average Fe$-$N$-$O bond angle was 167°, and theoretical calculations indicated that this angle was determined by Fe$-$N π-bonding interactions, and not by the HOMO, which was largely Fe$-$N π-antibonding.
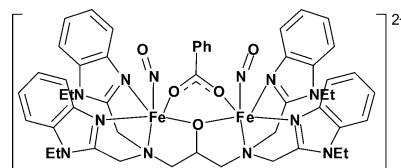
16 [Fe$_2$(NO)$_2$(Et-htpb)(O$_2$CPh)]$^{2+}$

In the search for nickel/iron heterobimetallic species related to the proposed active site in [NiFe] hydrogenase, a number of dinitrosyl iron complexes have been characterized. These involve nickel complexes containing di- or tricyclic sulfur ligands which function as donors to either $\{Fe(NO)_2\}^9$ or $\{Fe(NO)_2\}^{10}$ groups. The structure of complex **17** ($\nu_{NO} = 1767, 1725$ cm^{-1}) reveals that the Ni$-$N$-$O bond angle is nearly linear (175°) and the Fe$-$N$-$O bond angles are slightly distorted from linearity, the NO groups tilting toward each other.[71] The molecule is paramagnetic, with an EPR spectrum ($g = 2.03$, no ^{14}N hyperfine splitting) similar to those of other tetrahedral species $[Fe(NO)_2X_2]^-$ (X = halide, SR), the iron center being described as $\{Fe(NO)_2\}^9$ and the nickel group as $\{Ni(NO)\}$.[10] Complex **17** (M = H$^+$; ν_{NO}

= 1740, 1695 cm^{-1}) also contains {Fe(NO)$_2$},[9] but when M = Ni^{II} (ν_{NO} = 1675, 1630 cm^{-1}), the iron core becomes {Fe(NO)$_2$},[10] reflecting the change in oxidation state of the nickel center ({Ni^0(NO)$^+$ to Ni^{2+}).[72] The Ni···Fe distances in **17** and **18** (M = Ni^{II}) are the same, 2.8 Å, close to that in [NiFe] hydrogenase (2.9 Å). Species **17** is oxidized and reduced in quasi-reversible one-electron steps, and chemical oxidation causes loss of the EPR signal, while reduction caused the generation of a new but unidentified paramagnetic species.

17   **18**

19 [{Fe(NO)(*NS₃*)}NiCl(dppe)]
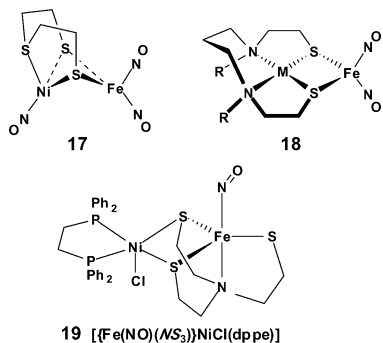
Complex **19** ([{Fe(NO)(*NS₃*)}NiCl(dppe)] (ν_{NO} = 1667 cm^{-1}) was also designed to model aspects of [NiFe] hydrogenase.[73] The Fe−N−O bond angle, somewhat disordered, is significantly bent, averaging 141°, and the Ni···Fe distance is 3.02 Å. The Mössbauer spectral parameters (δ = 0.40 mm/s, ΔE_Q = 1.26 mm/s) are consistent with a {Fe(NO)}^{7} configuration and an electronic description as Fe^{III}(S = $^5/_2$) coupled antiferromagnetically to NO$^-$ (S = 1). Similar trinuclear species [M{Fe(NO)(*NS₃*)}$_2$] (M = Fe, Co, Ni, and Cu) have also been described.

5.4. Other Metal Complexes

5.4.1. Ruthenium Nitrosyls

A number of ruthenium complexes, like their iron analogues, have the ability to scavenge and to release NO, being therefore of considerable interest in environmental remediation and in biomedical applications. Generally, ruthenium complexes are more kinetically stable than their iron analogues, and the relevant oxidation states, Ru^{II} and Ru^{III}, are low spin, in contrast to the variable spin behavior of Fe^{II} and Fe^{III}.

Reduction of [Ru(NO)(hedta)] (ν_{NO} = 1846 cm^{-1}), which is described as {Ru(NO)}^{6} containing Ru^{II} (S = 0) bonded by NO$^+$ (S = 0), affords [Ru(NO)(hedta)]$^-$ (ν_{NO} = 1858 cm^{-1}), formally containing {Ru(NO)}^{7}, and [Ru(NO)(hedta)]$^{2-}$ (ν_{NO} = 1383 cm^{-1}), formally described as {Ru(NO)}^{8}.[74] From extensive electrochemical and ^{15}N NMR spectral examination, it has been concluded that the monoanion is best described as Ru^{II} (S = 0) coupled to NO$^•$ (S = $^1/_2$) and the dianion also as Ru^{II} (S = 0) but coupled to singlet NO$^-$ (S = 0). The ^{15}N NMR spectra data obtained from [Ru(NO)(hedta)]$^{2-}$ are consistent with a bent Ru−N−O bond, which is rare in coordination complexes of σ-bonding ligands but has been identified in complexes containing π-acceptor ligands, such as [Ru(NO)$_2$(PPh$_3$)$_2$Cl]$^+$ (one linear, one bent Ru−N−O

bond). The neutral species [Ru(NO)(hedta)] exists as a single cis equatorial isomer **20a**, whereas [Ru(NO)(hedta)]$^{2-}$ exists as both a cis and trans equatorial form, **20b**. That the NO stretching frequency of [Ru(NO)(hedta)] is lower than that of [Ru(NO)(hedta)]$^-$ appears counter-intuitive. However, Ru^{II} is a strong π donor, and $d_\pi - \pi^*$(NO) back-donation will be more efficient in the neutral species than in the monoanion, which contains an unpaired electron in the π^*(NO) orbital. A similar argument can explain why the NO stretching frequency in the structurally similar [Ru(NO)(edta)] (pendant carboxylate in place of hydroxyethyl) occurs at 1880 cm^{-1}, only 30 cm^{-1} higher than the hedta analogue. The edta species contains Ru^{III} coordinated by NO$^+$, but Ru^{III} (low-spin d^5) is not as effective a π-donor as Ru^{II} (low-spin d^6).

20a *cis*-equatorial   **20b** *trans*-equatorial
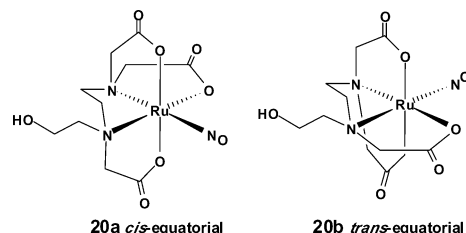
The {Ru(NO)}^{6} complex *trans*-[Ru(NO)(cyclam)-Cl]$^{2+}$ has ν_{NO} in the range 1852−1869 cm^{-1}, depending on counterion, and an essentially linear Ru−N−O bond, as expected.[75] This species undergoes two irreversible one-electron reductions in aqueous media. The first process appears to lead to [Ru(NO)-(cyclam)Cl]$^+$, since ν_{NO} is reduced by 22−30 cm^{-1}, but this species decomposes with loss of Cl$^-$, affording [Ru(NO)(cyclam)(H$_2$O)]$^{2+}$, which then slowly releases NO to give *trans*-[Ru(cyclam)(H$_2$O)$_2$]$^{2+}$. EPR spectral examination of [Ru(NO)(cyclam)(H$_2$O)]$^{2+}$ revealed signals with rhombic symmetry and ^{14}N hyperfine splittings, similar to the EPR spectrum of [Ru(NO)-(NH$_3$)$_4$(H$_2$O)]$^+$. Reduction of [Ru(NO)(cyclam)(H$_2$O)]$^{2+}$ afforded unstable [Ru(NO)(cyclam)(H$_2$O)]$^+$, which also decomposed to *trans*-[Ru(cyclam)(H$_2$O)$_2$]$^{2+}$. The dication is therefore described as Ru^{II} coordinated by NO$^+$, the one-electron reduction product as Ru^{II} coordinated by NO$^•$ (S = $^1/_2$) with a bent Ru−N−O bond, and [Ru(NO)(cyclam)(H$_2$O)]$^+$ as Ru^{II} coordinated by singlet NO$^-$ (S = 0).

5.4.2. Cobalt Nitrosyls

Neutral cobalt nitrosyl Schiff base complexes **21** have the configuration {Co(NO)}^{8}, and so would be expected to contain bent Co−N−O bonds (ca. 125°). This has been confirmed by several crystallographic

21
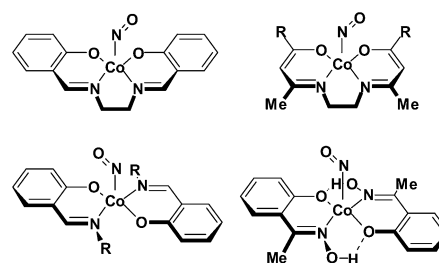
studies, and by judicious use of $^{14/15}$N NMR spectroscopy in solution and in the solid state.[60,76] These diamagnetic complexes, like their porphyrinato analogues, are of interest because of the relative ease with which the Co−NO bond may be photolyzed. Also, NO reacts with reduced vitamin B$_{12}$, affording nitrosyl species.

The electronic description of these complexes cannot be probed as effectively as those of their iron analogues discussed above, but the alternatives are Co^{III} ($S = 0$) bonded to NO$^-$ ($S = 0$) or Co^{II} ($S = \frac{1}{2}$) antiferromagnetically coupled to NO$^\bullet$ ($S = \frac{1}{2}$). The former is preferred since ^{59}Co NMR chemical shifts of the nitrosyls are similar to those of Co^{III} complexed by "innocent" σ-bonding ligands.

5.4.3. Copper Complexes

Copper-containing enzymes play a central role in denitrification, whereby bacteria use NO$_3^-$ and NO$_2^-$ as terminal electron acceptors, ultimately producing NO, N$_2$O, and/or N$_2$. A copper−NO species has been proposed as a key intermediate in biological nitrogen oxide reduction, and NO adducts of other copper proteins have been proposed. A single copper nitrosyl species in nitrite reductase obtained from *Achromobacter cycloclastes* has been proposed as an intermediate involved in conversion of NO$_2^-$ to NO or, in some instances, to N$_2$O. The site binding NO$_2^-$ or NO is believed to be pseudo-tetrahedral, and the nitrosyl adduct, which has the configuration {Cu(NO)}^{10}, is described as Cu^I bound by NO$^+$.[77]

There are remarkably few copper nitrosyl coordination compounds, the first well-characterized species being derived from a dinucleating ligand and containing a bridging NO group, viz., **1**.[16] The Cu−N−O bond angles are 130°, the N−O bond distance is 1.18 Å, typical of N=O, and ν_{NO} = 1536 cm^{-1}. The coordination around each copper atom is distorted square pyramidal, and the Cu···Cu distance is 3.14 Å, i.e. nonbonding. The complex is regarded as containing Cu^{II} and the nitrosyl group as μ-NO$^-$.

However, complexes perhaps more attractive as models for the active site of nitrite reductases have been obtained using sterically hindered tris(pyrazolyl)borato ligands, [Tp$^{R',R''}$]$^-$, where R$'$ = 3-^{t}Bu, Ph, CF$_3$, or mesityl (Mes) and R$''$ = 5-H, Ph, or Me.[77,78] Nitric oxide addition to [Cu$^I_2$(Tp$^{R',R''}$)$_2$] afforded [Cu-(NO)Tp$^{R',R''}$], the structure of the complex with R$'$ = ^{t}Bu, R$''$ = H confirming the expected tetrahedral (idealized C_{3v} symmetry) geometry with a short Cu−N(O) bond (1.76 Å) and Cu−N−O = 163°. NO addition was reversible, and the complexes reacted with oxygen to form [Cu^{II}(O$_2$NO)Tp$^{R',R''}$]. The EPR spectra of the species where R$'$ = ^{t}Bu, R$''$ = H and R$'$,R$''$ = Ph had g < 2.00 and relatively large ^{14}N and ^{63,65}Cu hyperfine splittings. In contrast, those species where R$'$ = CF$_3$, R$''$ = Me and R$'$ = mes, R$''$ = H were "EPR-silent", but the latter exhibited sharp ^{1}H NMR signals, albeit isotropically shifted by contact and/or dipolar interactions. The NO stretching frequencies of these species occurred between 1712 and 1753 cm^{-1}, the actual position being a function of the R$'$ group. It was suggested that these {Cu(NO)}^{11} species should be described as Cu^I coupled to NO$^\bullet$ ($S =$

$\frac{1}{2}$), and so they have one more electron than the proposed active site in nitrite reductase. However, the fact that two of these species, whose structures appear to be very similar, do not exhibit EPR signals indicates that the formulation of the active site in the enzyme as Cu^I bound by NO$^+$ should be treated with caution.

6. Conclusions

This review has described the structural and electronic issues surrounding the coordination of NO to Fe, Ru, Co, and Cu complexes. As explained in the Introduction, because enzymes and other proteins containing these metals (Ru excepted) have dominated the research into the physiological generation and behavior of NO and the use of iron nitrosyls as analogues for unstable iron-based oxygenases, etc., the discussion of metal nitrosyl chemistry has been limited. This does not mean that other transition metal nitrosyls, such as those containing V, Mo, or W, are not important in biology and medicine—just that they have yet to be identified in such milieu. It is probably only a matter of time before they are detected.

7. References

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