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Mononitrosyl Iron Complexes Supported by Sterically Hindered Carboxylate Ligands

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Complexes that feature a single NO bound to Fe, as postulated in various carboxylate-rich metalloproteins, were prepared by mixing Fe^{II} salts, NO, and the sterically encumbered 2,6-dimesitylbenzoate ($Mes_2ArCO_2^-$). Among the compounds isolated are the potentially useful heterobimetallic synthon $Tl(\mu\text{-}Mes_2ArCO_2)_3Fe(NO)$ and a novel cubane $Fe_4(Mes_2ArCO_2)_4(NO)_4(\mu_3\text{-}OH)_4$ that forms in the presence of added H_2O and features *syn*-$[FeNO]_2$ units.

Carboxylate-rich non-heme diiron protein active sites, exemplified by those in the R2 subunit of ribonucleotide reductase (RNR) and the hydroxylase component of soluble methane monooxygenase (MMOH), bind and activate O_2 in order to oxidize substrate(s).[1] In studies aimed at probing the initial O_2 binding events during catalysis, reactions of the surrogate nitric oxide[2,3] with the reduced Fe^{II}_2 forms of RNR[4a,b] and MMOH[4b] revealed coordination of a single NO molecule to each Fe center. These $[Fe(NO)]_2$ assemblies undergo slow reduction of the coordinated NO to give N_2O and a (μ-oxo)diiron(III) unit.[4] A similar reduction of NO to N_2O comprises the natural function of other Fe_2 enzymes, such as the bacterial nitric oxide reductases (NOR) isolated from *P. denitrificans*[5] and *P. Aeruginosa*[6] and the flavodiiron protein (FprA) isolated from *M. thermoacetica*.[7] Bacterial NOR contains both heme and non-heme Fe centers, while FprA features a non-heme Fe_2 center with three histidines, three carboxylate-containing residues, and two H_2O/hydroxo ligands. Coordination of a single NO to each Fe and N_2O evolution via a pathway(s) involving two such [FeNO] units are postulated to be common to all of the non-heme Fe systems.[2,4,7a] In view of these hypotheses and the more general significance of iron nitrosyls in biology, understanding the properties of carboxylate-rich non-heme iron nitrosyls and elucidating their reactivity are important research goals.

The combination of sterically demanding terphenylcarboxylate ligands and Fe salts has been demonstrated to be a useful strategy for the synthesis of viable synthetic models of non-heme Fe active sites comprising multiple carboxylates.[8−12] This approach has been used to study the reaction of NO with Fe and Co complexes supported by 2,6-di-*p*-tolylbenzoate, but only complexes with $M(NO)_2$ units were observed.[13] We envisioned that alternate metal nitrosyl species might result from studies of Fe complexes of 2,6-dimesitylbenzoate ($Mes_2ArCO_2^-$) because variation of terphenylcarboxylate substituents is known to result in differences in metal complex chemistry.[12] Herein, we report preliminary results from explorations of the reactions of NO, Fe salts, and Mes_2ArCO_2M (M = Li, Tl). Novel carboxylate-rich complexes comprising [FeNO] units have been isolated, and their nature has been found to be dependent on the counterions, the solvent, and the presence of adventitious H_2O in the reaction mixture.

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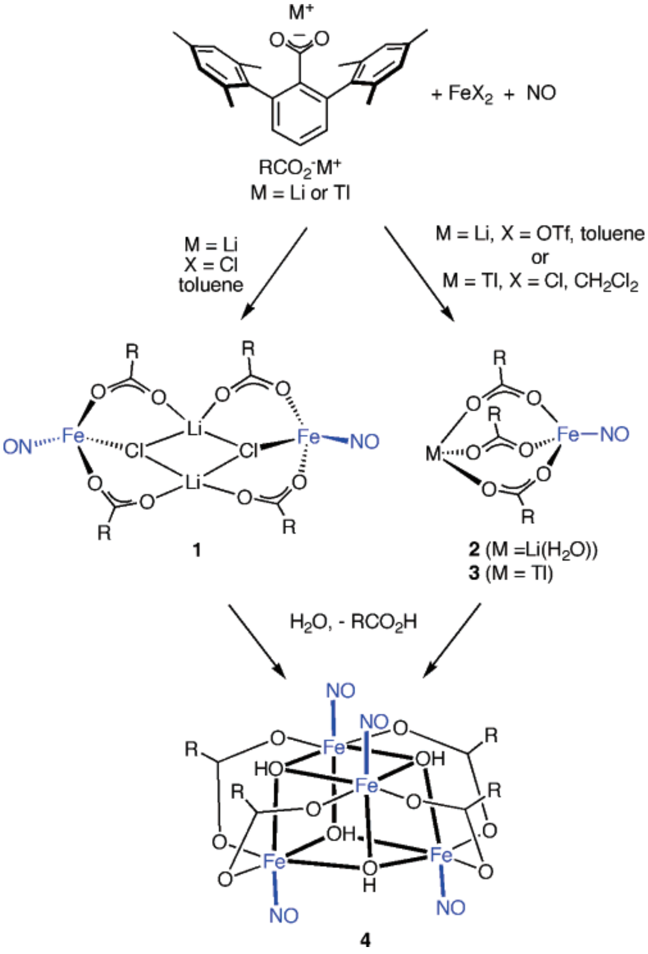
Scheme 1



The reaction of gaseous NO with mixtures of FeX$_2$·nCH$_3$CN (X = Cl, n = 0; X = OTf, n = 2) salts and Mes$_2$ArCO$_2$M (M = Li, Tl) in CH$_2$Cl$_2$ or toluene leads to colored solutions, from which {[Fe(Mes$_2$ArCO$_2$)$_2$(NO)Cl]Li}$_2$ (**1**), (H$_2$O)Li(μ-Mes$_2$ArCO$_2$)$_3$Fe(NO) (**2**), Tl(μ-Mes$_2$ArCO$_2$)$_3$Fe(NO) (**3**), and Fe$_4$(Mes$_2$ArCO$_2$)$_4$(NO)$_4$(μ_3-OH)$_4$ (**4**) could be isolated (Scheme 1). Cluster **4** is thermodynamically favored and is the primary product crystallized in all cases unless meticulous care is taken to exclude H$_2$O from the glassware (silylation), solvents, and atmosphere. When such care is exercised, **1**−**3** may be isolated, although the extreme moisture and temperature sensitivity of **2** has inhibited its characterization by methods other than an X-ray crystal structure. X-ray structures of **1**−**4** were determined, but only those of **3** and **4** are of sufficient quality to assess bond distances; the data sets for **1** and **2** only enable atom connectivity to be established.

Complex **1** is a dimer with four-coordinate Fe centers bridged by Li$^+$ ions through chloride and carboxylate ligands (Figure S1 in the Supporting Information). The remaining Fe coordination site is occupied by a NO unit. UV−vis and IR spectra of solutions of **1** corroborate the presence of the [FeNO] moiety: λ_{max} (ϵ, M^{-1} cm^{-1}; toluene) = 354 (1400), 463 (440), and 634 (200) nm and ν(NO) = 1821 cm^{-1} (CH$_2$Cl$_2$). Complexes **2** (Figure S2 in the Supporting Information) and **3** (Figure 1) also feature four-coordinate iron nitrosyl centers, but with each Fe atom bound to three carboxylates that bridge to either a Li$^+$ (**2**) or Tl$^+$ (**3**) ion. The [FeNO] unit is essentially linear (Fe−N−O angle = 178° for **3**). Examples of tetrahedral binding in iron nitrosyls are rare, with only a few reported examples from organometallic chemistry[14] and a recent report of an iron thiolate complex [Fe(SBu^t)$_3$NO]$^-$.[15] Complex **3** is an unusual bimetallic complex containing both Fe and Tl and, to the best of our knowledge, is one of only a few examples of carboxylate complexes containing both of these ions.[16] The electron paramagnetic resonance (EPR) spectrum of a frozen toluene solution of **3** at 20 K exhibits signals at g = 4.03, 3.99, and 2.01 that are typical for an $S = {}^3/_2$ {FeNO}^{7} system.[17] The UV−vis and IR data for **3** in solution are also diagnostic: λ_{max} (ϵ, M^{-1} cm^{-1}; toluene) = 344 (3800), 442 (920), and 648 (450) nm and ν(NO) = 1815 cm^{-1} (CH$_2$Cl$_2$).[18]

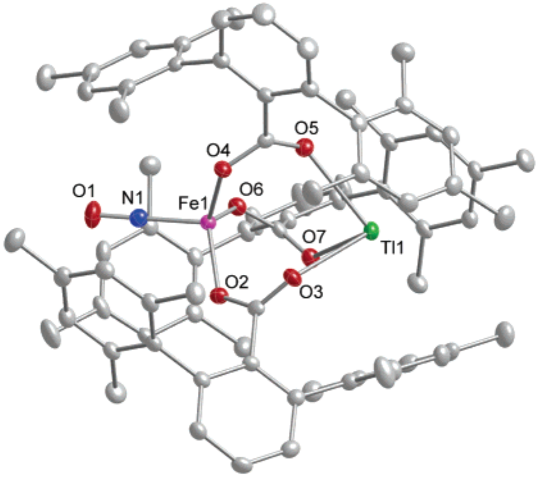


Figure 1. Molecular structure of **3** showing all non-H atoms as 50% ellipsoids. Selected bond distances (Å) and angles (deg): Fe1−O2, 1.928(2); Fe1−O4, 1.931(2); Fe1−O6, 1.932(2); Fe1−N1, 1.740(3); N1−O1, 1.151(4); Fe1−N1−O1, 177.8(3).

In preparations of **1**−**3** performed without rigorous effort to exclude moisture or upon the addition of degassed H$_2$O (10 equiv) to CH$_2$Cl$_2$ solutions of **1**−**3**, IR bands appear at 1772 and 1741 cm^{-1} due to the formation of **4** [ν(NO)] and Mes$_2$ArCO$_2$H [ν(C=O)], respectively. Complex **4** may also be synthesized independently by the reaction of NO-saturated CH$_2$Cl$_2$ suspensions containing Fe(OTf)$_2$·2CH$_3$CN and 2 equiv of Mes$_2$ArCO$_2$Li with a 2-fold excess of H$_2$O. An X-ray structural determination of **4** (Figure 2) revealed an Fe$_4$(μ_3-OH)$_4$ cubane, with terminal coordination of one NO to each Fe site and four face-capping carboxylate ligands. The core of **4** (sans NO ligands) resembles Fe$_4$(ArCO$_2$)$_4$(μ_3-OR′)$_4$ (Ar = benzoate or hindered benzoate; R′ = Me or

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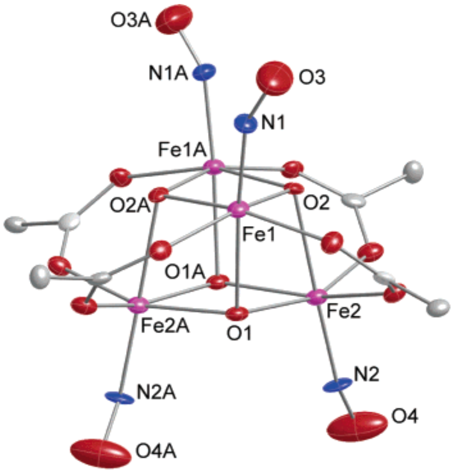

Figure 2. Molecular structure of **4**, shown for clarity without the terphenyl portion of the carboxylates nor the carboxylate atom labels. Ellipsoids are shown at 50% probability, and H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe−Fe, 3.333 (average); Fe1−O1, 2.145(7); Fe1−O2, 2.090(6); Fe1−N1, 1.771(5); N1−O3, 1.131(7); Fe1−N1−O3, 155.3(5).

H),[19] and the overall structure of **4** bears some similarity to the nitrosylated Fe−S cluster $Fe_4S_4(NO)_4$.[20] Notwithstanding some disorder evidenced by the distorted thermal ellipsoids for the nitrosyl O atoms, the NO ligands in **4** are bound in nearly linear fashion, with an average Fe−N−O angle of 155° and an average N−O distance of 1.137 Å, typical for NO in an $\{FeNO\}^7$ system.[21] Also typical is the UV−vis spectrum: λ_{max} (approximate ϵ at 0.6 mM, M^{-1} cm^{-1}, toluene) = 344 (830), 445 (500), and 586 (140) nm.

Of particular significance is the Fe−Fe distance in **4** of 3.333 Å, which is similar to that observed in the nitric oxide reducing enzyme FprA (3.4 Å).[7a] The NO-reducing ability of FprA, RNR, and MMOH is thought to be the result of such a short Fe−Fe distance and the syn bonding of the NO ligands;[3,4,7] these aspects are replicated in **4**, although N_2O was not observed upon decomposition of the compound when allowed to stand in solution. The syn orientation of the nitrosyl ligands has been seen previously in a dinuclear model complex of a N-rich heptadentate ligand, which also did not produce N_2O.[8]

In summary, the reaction of gaseous NO with mixtures of Fe^{II} salts and the bulky carboxylate $Mes_2ArCO_2^-$ resulted in the formation of novel nitrosyl iron complexes **1**−**4**, which feature coordination of a single nitric oxide to each Fe center. The mononuclear Fe complexes **1**−**3** are highly sensitive to the presence of adventitious H_2O, and when exposed to H_2O, convert to **4**. Complex **4** is the first example of a tetranuclear cluster containing NO ligands without the presence of sulfide. Attempts to further exploit the chemistry of **1**−**4** are underway.

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Supporting Information Available: Synthesis, crystallographic data, and spectroscopic characterization for **1**−**4** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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