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The Interaction of Isocyanides and Fe$_4$S$_4$L$_4$ Clusters

Sir:

Despite the recent, intense interest in the Fe$_4$S$_4$L$_4$ system as a model,[1,2] for biological reducing agents of the ferredoxin type, not a great deal is yet known about the chemical reactivity of this inorganic class.[3-5] As results of a study motivated by an enzyme precedent, videlicet the nitrogenase-mediated conversion of isocyanides to amines,[9] we describe herein the preparation as well as the infrared spectral and electrochemical characterization of Fe$_4$S$_4$L$_4$-isocyanide derived adducts which markedly promote the α,α-addition of mercaptans to isocyanides, the first observed nonenzymic catalytic reaction of this cluster type.

The reaction of p-chlorophenylisocyanide (**1**) with either **2a**$^{2-}$ or **2a**$^{4-}$ [10] in the presence of excess ethanethiol as the proton source exclusively generated N-(p-chlorophenyl) ethylthioformimidate (**5a**),[11] readily hydrolyzable to p-chloroaniline. For reactions run in tetramethylurea (TMU) for 1 h at 22 °C and with 100 molar equiv of isocyanide **1** and 150 molar equiv of ethanethiol, conversions based on isocyanide were 37% from **2a**$^{2-}$ and 73% from **2a**$^{4-}$. A control in which cluster was omitted showed a 1% conversion, while a reaction in which metallic sodium was substituted for **2a** gave a 13% conversion. Solutions of decomposed clusters were not catalytically active. Significantly, replacement of mercaptan by n-C$_4$H$_9$OH, (C$_2$H$_5$)$_3$SiH, CH$_3$(C$_6$H$_5$)PH, or (C$_2$H$_5$)$_2$NH resulted in no consumption of isocyanide under otherwise identical conditions. In light of previously examined metal mediated[12,13] α,α-additions to isocyanide as well as electrochemical and other information presented below, we postulate the reaction sequence outlined in Scheme I.

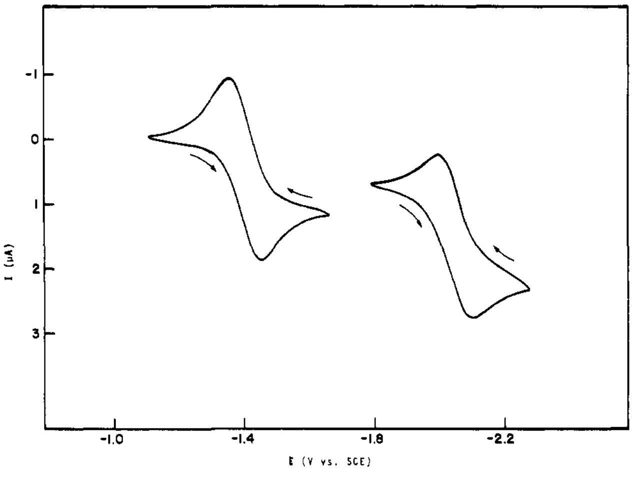
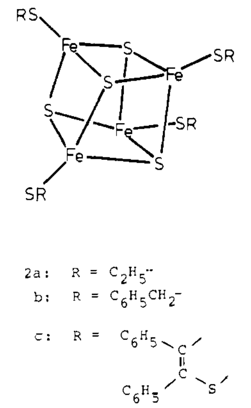


Figure 1. Cyclic voltammograms of 5 mM **2a**$^{2-}$ ⇋ **2a**$^{3-}$ and **2a**$^{3-}$ ⇋ **2a**$^{4-}$.



Cyclic voltammetry[14] of 5 mM (n-Bu$_4$N$^+$)$_2$**2a**$^{2-}$ revealed two chemically reversible one-electron couples (**2a**$^{2-}$/**2a**$^{3-}$ and **2a**$^{3-}$/**2a**$^{4-}$) which could be independently scanned (Figure 1). During cyclic voltammetry monitored titration of the **2a** solution with n-C$_9$H$_{19}$NC, neither the **2a**$^{2-}$/**2a**$^{3-}$ couple nor the **2a**$^{3-}$ to **2a**$^{4-}$ reduction was altered in relative intensity; however, the **2a**$^{4-}$ to **2a**$^{3-}$ oxidation was progressively attenuated while a new couple appeared at −2.26 V vs. SCE (Figure 2a), ascribed to the catalytically active **2a**$^{4-}$-isocyanide adduct.

Confirmation of adduct formation and function was obtained through assay of the catalytic process. TMU solutions of **2a**$^{2-}$ or **2a**$^{4-}$ with varying numbers of molar equivalents of isocyanide **1** were prepared, and after a few minutes, or as many as 96 h, were introduced into TMU solutions of 100- to 1000-fold excess of **1** and ethanethiol. The most active catalyst preparation resulted from equimolar quantities of **2a**$^{4-}$ and isocyanide **1** (98% yield of thioformimidate **5a** after 1 h) and was analyzed by cyclic voltammetry (Figure 2b). The

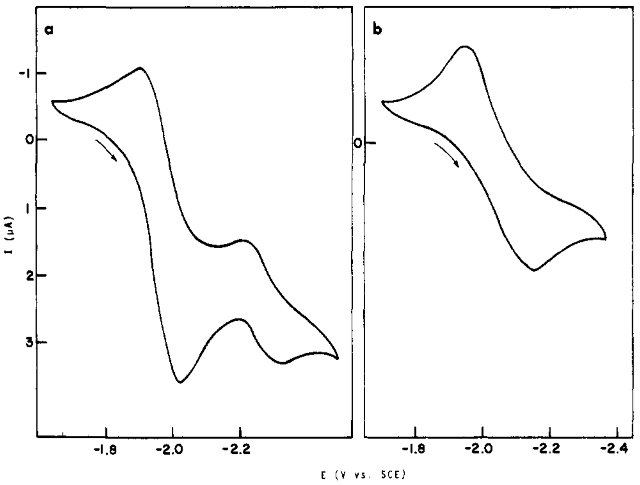
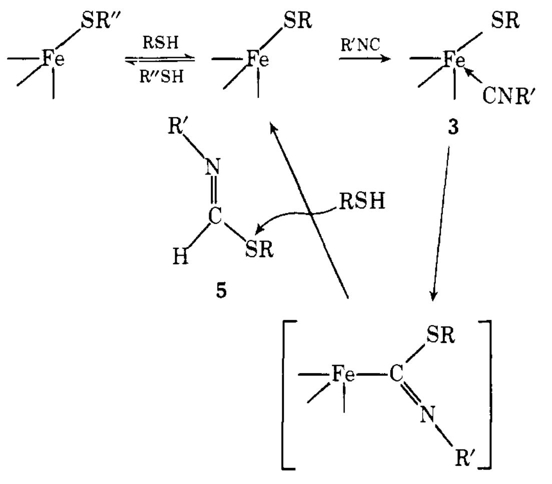


Figure 2. (a) Cyclic voltammogram of 5 mM $\mathbf{2a}^{3-} \rightleftharpoons \mathbf{2a}^{4-}$ with 1.25 mol/mole of n-$C_9H_{19}NC$ added. (b) Cyclic voltammogram of 4 mM $\mathbf{2a}^{4-}/p$-ClC_6H_4NC adduct.

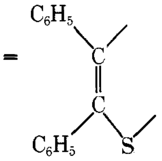
Scheme I



4

a, R″ = R = C_2H_5–; R′ = p-ClC_6H_4–
b, R″ = R = $C_6H_5CH_2$–; R′ = p-ClC_6H_4–
c, R″ = R = C_2H_5–; R′ = $C_{12}H_{25}$–
d, R″ = R = $C_6H_5CH_2$–; R′ = $C_{12}H_{25}$–

e, R″ =



; R = C_2H_5–; R′ = p-ClC_6H_4–

$\mathbf{2a}^{2-}/\mathbf{2a}^{3-}$ couple remained unaltered, but the $\mathbf{2a}^{3-}/\mathbf{2a}^{4-}$ couple was wholly replaced by a new couple at −2.03 V vs. SCE.[15] The greater efficacy of the more reduced cluster adduct contrasts with the activity of other types of transition metal complexes, in which the more oxidized species normally are the more active catalysts.[16]

For infrared spectral studies, a 6 mM solution of $\mathbf{2a}^{2-}$ or $\mathbf{2a}^{4-}$ in TMU was mixed with 0.5-12 molar equiv of t-BuNC, n-BuNC, or p-ClC_6H_4NC (**1**). Variation of isocyanide stretch (2100-2150 cm^{-1})[17] absorbance with concentration of isocyanide in TMU in the absence of **2a** was strictly linear in the concentration range 5 to 100 mM.[18] The t-BuNC absorption was totally unaffected by either $\mathbf{2a}^{2-}$ of $\mathbf{2a}^{4-}$, but the n-BuNC absorption, while linear with concentration beyond 3 mol/mole of $\mathbf{2a}^{2-}$, showed a strong negative deviation from Beer's law at smaller ratios, in keeping with the proposed coordination of isocyanide to cluster followed by attack of mercaptide ligand. The combination $\mathbf{1}/\mathbf{2a}^{2-}$ resulted in the appearance of an additional broadened and red-shifted (35 cm^{-1}) absorbance, attributed to coordinated **1**, as in **3**. Addition of **1** to $\mathbf{2a}^{4-}$ did not result in observable absorption in the isocyanide stretch region, behavior consistent not only with the proposed mechanism but also the observed enhanced activity of the more reduced clusters. The uniqueness of thiol (vide supra) in the operation of the catalytic process supports the postulated **3** ⟶ **4** ⟶ **5** conversion, in that this reagent is necessary, not only to afford product **5**, but also to regenerate the Fe_4S_4 cluster system (**2**) needed for another cycle. The inertness of the starting cluster-isocyanide mixture to other agents lends credence to the belief that the cluster nucleus remains intact during the generation of **5**, and the versatility of simpler transition metal compounds[16] in effecting α,α-addition of various reagents to isocyanides[12,13] implies that in the case at hand no such catalytic species is formed from **2** during thiol addition.

In order to test the generality of the catalysis, cluster **2a**, **2b**,[2] or **2c**[13] was reduced to the 4− state and allowed to react for 24 h with 1 molar equiv of either an aromatic or aliphatic isocyanide in TMU, after which the active catalyst was introduced into the TMU assay solution of mercaptan and more isocyanide, both in great molar excess (Scheme I, b-e). Yields of the various thioformimidates (**5**) were essentially quantitative in all cases, and the products were unambiguously identified by comparison with authentic samples.[11] As in the N_2 fixation studies,[1] success of the reaction is independent of whether the ligand in the starting cluster is mercaptide (**2a**–**b**) or stilbene dimercaptide (**2c**).[19]

Although product at the amine level thus can arise by either enzymatic or nonenzymatic action on isocyanide, the former reaction is reported to yield also methane,[9] whereas the latter path is nonreductive overall. The present finding underlines the behavioral difference between a simple cluster model and the ferredoxin-like holoenzyme, and also raises the question of whether in nature amine might also be generated from isocyanide through a nonreductive cluster-mediated reaction similar to that reported herein.

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(5) Earlier work[1] in this laboratory showed conclusively that $^{15}NH_3$ is generated when $Fe_4S_4(S_2C_2Ph_2)^{4-}$ or $Fe_4S_4(SC_2H_5)^{4-}$ is exposed to the action of an appropriate radical anion reductant in the presence of $^{15}N_2$. However, $^{15}NH_3$ production from $Mo(^{15}N_2)_2(dppe)_2$ under similar conditions is obfuscated by the fact that this coordination compound by itself generates $^{15}NH_3$ merely by treatment with aqueous mineral acid,[6,7] coincidentally one of the operations performed in the analytical method used for $^{15}NH_3$ measurement in this cluster work. These[6,7] latter reports stand in sharp contrast to the earlier indications[8] that through acid treatment or other means NH_3 is not obtainable from $Mo(N_2)_2(dppe)_2$, reports which thus unfortunately had the effect of not only confusing the aforementioned cluster experimentation, but also of temporarily diverting attention from an important but unexpected NH_3-producing reaction exhibited by the $Mo(N_2)_2L_2$ system.

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Trapped Metastable Vibrational Energy Distributions in Laser Pumped Molecules

Sir:

Although certain molecules[1] (e.g., CO_2, N_2O, and SO_2) are known to require many thousands of collisions to transfer energy between vibrational modes, such an occurrence is in fact a rarity. Indeed, for the kinds of molecules and pressure regimes used in many laser decomposition experiments,[2,3] complete intermode energy equilibration involving the *entire* vibrational manifold is expected to occur within a laser pulse-width.[4,5] Thus the achievement of mode specific or bond specific laser driven chemical reactions under such conditions is expected to be difficult. Nevertheless, for at least some laser pumped molecules, intermode relaxation processes can lead *naturally* to localization of energy in a small number of vibrational modes. Such distributions require thousands of collisions to reach equilibrium with the translational and rotational degrees of freedom. Thus the normal energy distribution characterized by a single temperature that is expected for a gas heated by a Bunsen burner does not necessarily apply to a laser pumped gas. Pulsed laser heating leads automatically to a substantial separation of vibrational and translational temperatures which lasts for a time of the order of the overall vibration–translation/rotation (V–T/R) relaxation time. In addition, the intermode energy equilibration processes which occur either during or shortly after the laser pulse almost always require the exchange of a *small* amount of energy with the translational degrees of freedom. Under such conditions the energy distribution in the vibrational modes cannot be described by a single temperature.[6,7] Nevertheless, once the dominant kinetic processes which couple the various vibrational modes are known, the vibrational temperatures of all the modes are well defined in the harmonic oscillator limit.[8] These features can lead to a highly localized metastable vibrational energy distribution as illustrated below for CH_3F, one of the few molecules for which vibrational energy transfer pathways have been reasonably well established.[9–13]

The laser excitation and subsequent dominant vibrational equilibration pathways coupling the fundamental modes of CH_3F are as follows:[9–14]

Characteristic time	Reaction	
τ_{p}	$\mathrm{CH_3F}(0) + h\nu_3 \rightarrow \mathrm{CH_3F}(\nu_3)$	(1)

$$\tau_{\mathrm{VV}} \begin{cases} \mathrm{CH_3F}(\nu_3) + \mathrm{CH_3F} \rightleftarrows \mathrm{CH_3F}(\nu_6) + \mathrm{CH_3F} - 133\ \mathrm{cm^{-1}} & (2) \\ \mathrm{CH_3F}(\nu_6) + \mathrm{CH_3F} \rightleftarrows \mathrm{CH_3F}(\nu_2, \nu_5) + \mathrm{CH_3F} - 284\ \mathrm{cm^{-1}} & (3) \\ 2\mathrm{CH_3F}(\nu_2, \nu_5) \rightleftarrows \mathrm{CH_3F}(2\nu_2, 2\nu_5) + \mathrm{CH_3F}(0) & (4) \\ \mathrm{CH_3F}(2\nu_2, 2\nu_5) + \mathrm{CH_3F} \rightleftarrows \mathrm{CH_3F}(\nu_1, \nu_4) + \mathrm{CH_3F} - 60\ \mathrm{cm^{-1}} & (5) \end{cases}$$

$$\tau_{\mathrm{VT}} \quad \mathrm{CH_3F}(\nu_3) + \mathrm{CH_3F} \rightarrow \mathrm{CH_3F}(0) + \mathrm{CH_3F} + 1049\ \mathrm{cm^{-1}} \qquad (6)$$

The typical laser pulse width τ_{p} is about 10^{-6} s while the four vibration–vibration (V–V) intermode equilibration processes (2–5) can be considered to reach steady state in about 75 gas kinetic collisions (7×10^{-6} s at 1 Torr).[10,14] However, the V–T/R process (eq 6), which restores an energy distribution characteristic of Bunsen burner heating, typically takes 15 000 gas kinetic collisions (1.4×10^{-3} s at 1 Torr) under low level laser excitation conditions.[11] Thus the highly specialized conditions which exist in laser pumped CH_3F at vibrational steady-state after a time τ_{VV} persist for a time τ_{VT} which is at least three orders of magnitude longer than τ_{VV}.

The steady-state equilibrium constant for process 2 in the time domain $\tau_{\mathrm{VV}} < t < \tau_{\mathrm{VT}}$ leads to the following relationship[6,7,12]

$$K_{\mathrm{eq}} = e^{-133/kT'} = \frac{e^{-E_{\nu 6}/kT_{\nu 6}}}{e^{-E_{\nu 3}/kT_{\nu 3}}} \tag{7}$$

with T_{ν_i} defined by

$$N_{\nu_i} = N_0 g_{\nu_i} e^{-E_{\nu_i}/kT_{\nu_i}} \tag{8}$$

E_{ν_i}, T_{ν_i}, g_{ν_i}, N_{ν_i} are the energy, vibrational temperature, degeneracy, and population of level ν_i, respectively; n_0 is the ground state population, and k is Boltzmann's constant ($\mathrm{cm^{-1}/K}$). T' is the steady state translational/rotational temperature which is less than the ambient temperature T since the intermode equilibration pathway for CH_3F requires a loss of translational energy.[15] Equation 7 merely illustrates that the equilibrium constant at steady-state is defined by the bath temperature T' whereas the vibrational state populations are defined by their respective vibrational temperatures or energies. Equation 7 gives immediately the result:

$$\frac{E_{\nu 3}}{T_{\nu 3}} - \frac{E_{\nu 6}}{T_{\nu 6}} = \frac{-133}{T'} \tag{9}$$

This analysis can easily be performed on the remaining V–V processes to yield equations relating the six mode fundamental temperatures with each other and the translational temperature. The remaining vibrational state temperatures are linear combinations of the mode fundamental temperatures in the harmonic oscillator approximation. In addition, the requirement of conservation of particles and total energy at steady state leads to a relation between the fundamental temperatures and the initial experimental conditions. The distribution of fundamental temperatures can thus be obtained in terms of the input laser energy by combining the temperature and conservation equations and solving iteratively on a computer.[16] Since the steady-state vibrational energy expressions are functions of the vibrational temperatures and under most conditions the translational/rotational energy can be expressed by its equipartition limit, $3kT'$, the entire steady-state energy distribution can be calculated for laser pumped CH_3F. These calculations are valid in the time range $\tau_{\mathrm{VV}} < t < \tau_{\mathrm{VT}}$ ignoring