New FeS clusters with NO: associative formation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$, and larger clusters†

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Solutions of $[Fe_2S_2(NO)_4]^{2-}$ or $[Fe_4S_3(NO)_7]^-$ undergo facile aggregation to new clusters $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$, but do not form the known species $[Fe_4S_4(NO)_4]^z$ and $[Fe_6S_6(NO)_6]^{2-}$; reactivities and reactions in solution and gas phases were monitored by electrospray Fourier transform ion cyclotron resonance mass spectrometry, and the probable structures of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ were determined by density functional calculations.

In 1858 Roussin reported salts of $[Fe_2S_2(NO)_4]^{2-}$ **1** and $[Fe_4S_3(NO)_7]^-$ **2**.[1] Since then there have been numerous publications on derivatives of **1** and **2**,[2–6] but $[Fe_4S_4(NO)_4]^z$ (z = 0, −1) **3**[7–9] and $[Fe_6S_6(NO)_6]^{2-}$, **4**[10] are the only other
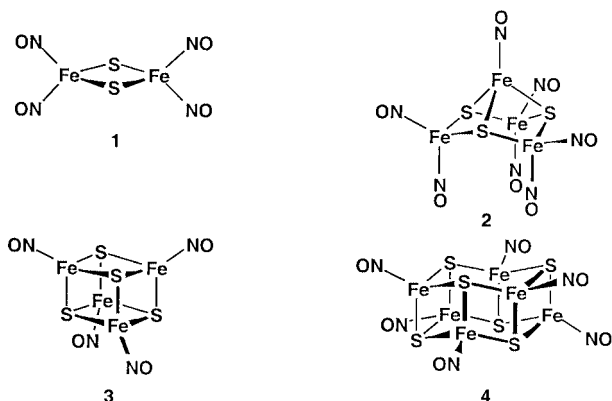
known iron sulfide clusters containing only NO ligands. We report here the formation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ by a facile aggregation process, which also yields other larger clusters.

Negative ion electrospray mass spectrometry (ESMS) of a solution of $Na_2[Fe_2S_2(NO)_4]$ in methanol immediately after preparation shows $[Fe_2S_2(NO)_4H]^-$, which rapidly (*ca.* 15 min at 10^{-4} M concentration, 25 °C) converts to a species of *m/z* 647.† By accurate mass analysis of the isotopomer pattern, and collision induced dissociation of NO, this species was confirmed as $[Fe_5S_4(NO)_8]^-$. Subsequently (40 min), $[Fe_5S_4(NO)_8]^-$ in this methanol solution converts to a mixture of $[Fe_4S_3(NO)_7]^-$ and a new species with *m/z* 883, which is confirmed to be $[Fe_7S_6(NO)_{10}]^-$. A solution of $Na_2[Fe_2S_2(NO)_4]$ in acetonitrile also shows the formation of $[Fe_4S_3(NO)_7]^-$ and $[Fe_5S_4(NO)_8]^-$, and eventually $[Fe_7S_6(NO)_{10}]^-$, together with transitory low intensity species at *m/z* 412, 478, only during the early stages.† Solutions of $Na[Fe_4S_3(NO)_7]$ in methanol also show the formation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$, although generated more slowly (7 to 14 d at 10^{-4} M and 25 °C).

These spectra are significant also for the species that are absent. There is no evidence of $[Fe_4S_4(NO)_4]^{z-}$ or $[Fe_6S_6-$

$(NO)_6]^{z-}$ (z = 1 or 2) in any of the numerous spectra recorded.† Apart from the strong peaks for $[Fe_4S_3(NO)_7]^-$, $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ the spectra are devoid of peaks in the mass range 500–900. Additional high mass peaks above *m/z* 900 have been observed, but not identified unambiguously.

With ESMS there is a fundamental question whether the observed species exist in the electrosprayed solution or are artefacts of the energetic ES desolvation process. The dependence of the spectra on the history of the solutions is strong evidence for the transformations in solution. Further, we have adjusted the ES capillary potential to effect controlled fragmentation, which involves only NO dissociation and occurs well above the threshold capillary voltage for observation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$.† It is significant that induced fragmentation does not disrupt the FeS cores. The stability and coordinative saturation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ are demonstrated by their inertness to reactive $NO_{2\,(g)}$ in the FTICR cell. After controlled partial dissociation of NO from $[Fe_5S_4(NO)_8]^-$ or $[Fe_7S_6(NO)_{10}]^-$ they do react with NO_2, by oxygen addition.

We have not yet been able to crystallise the new species, but have investigated their structures by validated density functional calculations,[11] evaluating the minimised energies of postulated structures. For $[Fe_5S_4(NO)_8]^-$ eight structure types were investigated, and Fig. 1 shows the best structure found, **548A**, which is a flattened FeS_4 tetrahedron with four edge-bridging $Fe(NO)_2$, and a spin doublet ground state (HOMO–LUMO gap of 1.1 eV). This is 22 kcal mol⁻¹ more stable than the next best structure, **548B** (Fig. 1). For $[Fe_7S_6(NO)_{10}]^-$, 29 postulated structures were investigated. The most probable structure, **7610A** (Fig. 2), contains two of the Fe_4S_3 cores fused at one Fe: structures **7610B** and **7610E** are configurational isomers with Fe_4S_3 cores linked by Fe–S bonds; **7610C** also contains the Fe_4S_3 core; while **7610D** is $[Fe_2S_2(NO)_4]$ linked to **548A**. These four isomers are not strongly differentiated in total energy (see Fig. 2). One of the isomers for $[Fe_7S_6(NO)_{10}]^-$ is **5**,
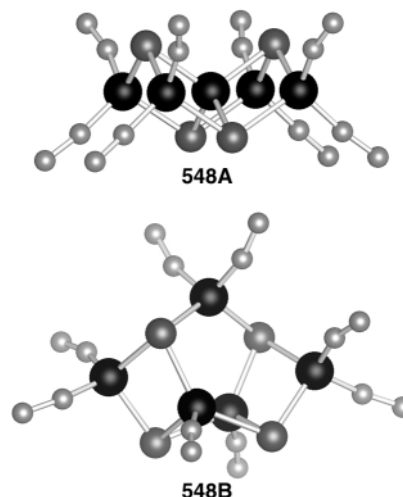

Fig. 1 The optimised structures of isomers **548A** (symmetry D_{2d}) and **548B** (symmetry C_2) of $[Fe_5S_4(NO)_8]^-$: Fe black; S grey, intermediate size; N, O small. The energy of **548B** relative to **548A** is +22 kcal mol⁻¹.
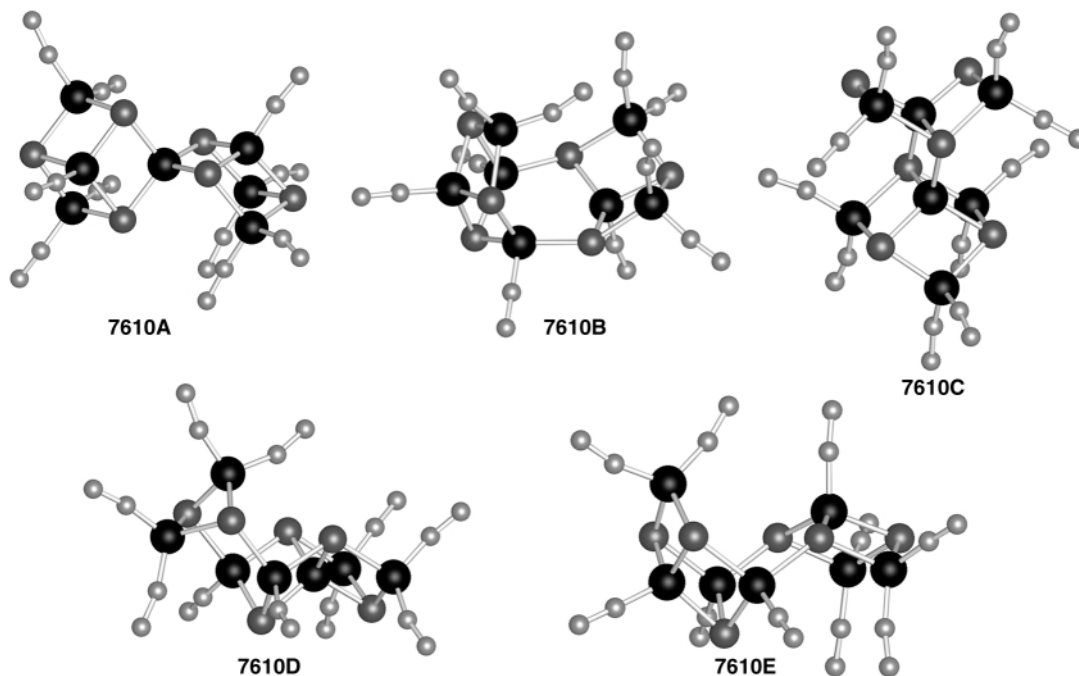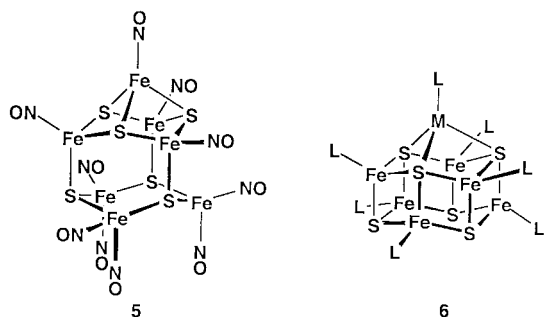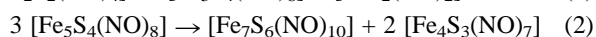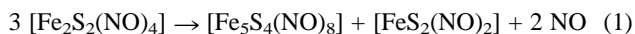
Fig. 2 The optimised structures of the five best isomers of $[Fe_7S_6(NO)_{10}]^-$: Fe black; S grey, intermediate size; N, O small. The symmetries and relative energies (kcal mol^{-1}) are: **7610A**, C_2, 0; **7610B**, C_s, +15; **7610C**, C_s, +18; **7610D**, C_s, +19; **7610E**, C_s, +22.

which is a logical extension of **2**, and is related to the established metal sulfide cluster type **6**,[12] but **5** is 38 kcal mol^{-1} less stable than **7610A**. We believe that our geometry searches have canvassed all reasonable possibilities.

The comparatively fast formation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ suggests facile mechanisms, with uncomplicated connectivity changes between the precursors and the proposed structures. The general absence of observable intermediates during the formation of $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ indicates that the mechanisms are associative. We can propose a facile mechanism for the assembly of **548A** from three $[Fe_2S_2(NO)_4]$, involving the breaking of only three Fe–S bonds and dissociation of two Fe–NO, with reformation of five Fe–S bonds [stoichiometry eqn. (1)]. For the assembly of **7610A** from $[Fe_5S_4(NO)_8]^-$ in solution according to eqn. (2) we can propose a mechanism involving the breaking of a total of only eight Fe–S bonds in concert with transfer of two NO ligands, and reformation of eight Fe–S bonds.

$$3 \ [Fe_2S_2(NO)_4] \rightarrow [Fe_5S_4(NO)_8] + [FeS_2(NO)_2] + 2 \ NO \quad (1)$$

$$3 \ [Fe_5S_4(NO)_8] \rightarrow [Fe_7S_6(NO)_{10}] + 2 \ [Fe_4S_3(NO)_7] \quad (2)$$

An important feature of the reactions observed is that they occur at ambient temperature and low concentration. This is associative cluster formation which is thermodynamically favourable and kinetically facile. In contrast, the formation of **4** (and its precursors) required extended reactions at elevated temperatures.[10] The difference is in the degree of NO

dissociation: the Fe–S–NO clusters easily formed by association in solution retain Fe(NO)$_2$ groups, while other established Fe–S cluster cores have at most one terminal ligand per Fe.

The facility of the associative formation of Fe–S aggregates described here could be relevant to the biosynthesis of Fe–S cofactors.[13–15]

Notes and references

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