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The Interconversion of Heptanitrosyltri-μ_3-thioxotetraferrate(1–) and Pentacyanonitrosylferrate(2–)

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Recent interest [1, 2] in the chemistry of Roussin's red salts which contain the anion $[Fe_2S_2(NO)_4]^{2-}$, tetranitrosylbis-μ_2-thioxodiferrate(2–) has prompted us to report some of our work on Roussin's black salts, which contain the anion $[Fe_4S_3(NO)_7]^-$ heptanitrosyltri-μ_3-thioxotetraferrate(1–): this anion was first prepared by Roussin in 1858, although its composition and constitution were not properly established at that time [3, 4], and it has been characterised by X-ray analyses of its caesium [5] and tetraphenylarsonium salts [6]. In his original paper Roussin [3] was concerned to establish a relationship between the anion $[Fe_4S_3(NO)_7]^-$ and the nitroprusside ion $[Fe(CN)_5NO]^{2-}$ which itself had only recently been described for the first time [7]: he showed that the solution resulting from the prolonged action of nitric oxide on aqueous iron(II) sulphate reacted with sulphide ion to yield $[Fe_4S_3(NO)_7]^-$ or with cyanide ions to yield $[Fe(CN)_5NO]^{2-}$. He also claimed to have achieved the direct interconversion of these two anions by simple means. In view of the completely different structures of these ions [5, 6, 8], the very high formation constant of the nitroprusside ion, and the known reaction of nitroprusside with sulphide ions to form first $[Fe(CN)_5NOSH]^{3-}$ then $[Fe(CN)_5NOS]^{4-}$ and finally $[Fe(CN)_5H_2O]^{3-}$, such interconversions seemed scarcely credible. However we have now repeated Roussin's original work and can confirm it in every detail.

Treatment of aqueous sodium nitroprusside with hydrogen sulphide gas, followed by boiling, gave a green solution which after filtration and evaporation to dryness yielded a blue-green mass: extraction with ether gave the sodium salt $Na[Fe_4S_3(NO)_7]$ in 78% isolated yield. The ether-insoluble residue contained sulphur, together with a blue material: this was not investigated, but may well have contained Prussian blue or similar solids. Conversely, treatment of aqueous $NH_4[Fe_4S_3(NO)_7]$ with a large excess of potassium cyanide gave over a period of *ca.* 1 hour an essentially quantitative conversion to nitroprusside, determined spectrophotometrically. Over longer periods of time the reaction proceeds further to give $Fe(CN)_6{}^{4-}$: this arises not from direct reaction of cyanide ion with $[Fe(CN)_5NO]^{2-}$ but *via* the nitrito species $[Fe(CN)_5NO_2]^{4-}$, formed from nitroprusside at the high pH prevailing in this reaction mixture:

$$[Fe(CN)_5NO]^{2-} + 2OH^- \rightarrow H_2O + [Fe(CN)_5NO_2]^{4-}$$

$$[Fe(CN)_5NO_2]^{4-} \xrightarrow{\text{slow}} NO_2{}^- + [Fe(CN)_5]^{3-}$$

$$[Fe(CN)_5]^{3-} + CN^- \xrightarrow{\text{fast}} [Fe(CN)_6]^{4-}$$

At $pH < 10$, cyanide ions show no reaction with $[Fe(CN)_5NO]^{2-}$.

Closely related to the anion $[Fe_4S_3(NO)_7]^-$ is the cubane-like neutral molecule $Fe_4S_4(NO)_4$, tetranitrosyltetra-μ_3-thioxo-*tetrahedro*-tetrairon, originally prepared [9] by reaction of $Hg[Fe(CO)_3NO]_2$ with elemental sulphur, which has been shown [6] to yield the ion $[Fe_4S_3(NO)_7]^-$ upon reduction with sodium amalgam. We have demonstrated that prolonged reflux of salts of $[Fe_4S_3(NO)_7]^-$ with elemental sulphur yields this cubane derivative in 72% yield, thus completing a second reversible transformation:

$$[Fe_4S_3(NO)_7]^- \xrightleftharpoons[\text{Na/Hg}]{S_8} Fe_4S_4(NO)_4$$

in addition to that involving the nitroprusside ion:

$$[Fe_4S_3(NO)_7]^- \xrightleftharpoons[H_2S]{CN^-} [Fe(CN)_5NO]^{2-}$$

Furthermore, Roussin's black and red salts are themselves interconvertible [1, 10]:

$$[Fe_4S_3(NO)_7]^- \xrightleftharpoons[\text{Acid}]{\text{Base}} [Fe_2S_2(NO)_4]^{2-}$$

When the mercurial $Hg[Fe(CO)_3NO]_2$ is treated with sodium polysulphide instead of elemental sulphur, the product is $Na[Fe_4S_3(NO)_7]$ (obtained in 68% yield) rather than $Fe_4S_4(NO)_4$.

These transformations, enabling the synthesis of both $[Fe_4S_3(NO)_7]^-$ and $Fe_4S_4(NO)_4$ to be achieved by several different routes, naturally open up the possibility of preparing selenium analogues, and we shall report upon these in a future communication.

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