Reactions of Nucleophiles with Bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)(2−), $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$, and of Electrophiles with Heptanitrosyltri-μ$_3$-thio-tetraferrate(1−), $[Fe_4S_3(NO)_7]^-$: New Routes to Bis(μ-organothiolato)-bis(dinitrosyliron) Complexes $[Fe_2(SR)_2(NO)_4]$ and the Crystal and Molecular Structure of Trimethylsulphonium Heptanitrosyltri-μ$_3$-thio-tetraferrate(1−), $SMe_3[Fe_4S_3(NO)_7]$†

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Sodium bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)(2−), $Na_2[Fe_2(S_2O_3)_2(NO)_4]$, reacts rapidly in aqueous solution with a range of thiols RSH [R = alkyl (C_1—C_5), CH_2CO_2Me, CH_2CH_2OH, or 2-pyrimidinyl] in the presence of sodium thiosulphate to give the neutral complexes $[Fe_2(SR)_2(NO)_4]$ generally in yields of 50—65%. With sodium sulphide a mixture of the Roussin red and black salts, $Na_2[Fe_2S_2(NO)_4]$ and $Na[Fe_4S_3(NO)_7]$ respectively, is formed, readily separable by solvent extraction with diethyl ether. The latter salt reacts with arenediazonium tetrafluoroborates $RN_2^+BF_4^-$ to yield the corresponding bis(μ-arenethiolato)-bis(dinitrosyliron) complexes $[Fe_2(SR)_2(NO)_4]$. Alkylation of $Na[Fe_4S_3(NO)_7]$ with $R_3O^+BF_4^-$ (R = Me or Et) yields $[Fe_2(SR)_2(NO)_4]$ but with $Me_3S^+BF_4^-$ or $Me_3SO^+BF_4^-$ metathesis, rather than alkylation, occurs to provide Me_3S^+ (or Me_3SO^+)$[Fe_4S_3(NO)_7]^-$. Crystals of $[SMe_3][Fe_4S_3(NO)_7]$ are triclinic, with space group $P\bar{1}$, $a = 9.655(2)$, $b = 11.707(3)$, $c = 8.968(1)$ Å, $\alpha = 106.11(2)$, $\beta = 91.78(3)$, $\gamma = 84.92(2)°$, and $Z = 2$: The compound is a salt with no close contacts between cation and anion. Reduction of the anion in $[SMe_3][Fe_4S_3(NO)_7]$ to the more nucleophilic dianion causes alkylation and formation of $[Fe_2(SMe)_2(NO)_4]$.

We recently reported[1] the synthesis and characterisation of some salts containing the bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)(2−) anion, $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$. Here we report some reactions of this anion which lead to a convenient synthesis of neutral Roussin esters $[Fe_2(SR)_2(NO)_4]$: we also report some new routes to the neutral Roussin esters based upon reactions of the readily accessible tetranuclear anion $[Fe_4S_3(NO)_7]^-$ with strongly electrophilic reagents, along with the crystal and molecular structure of the salt $[SMe_3][Fe_4S_3(NO)_7]$, which results from the reaction of the salt $Na[Fe_4S_3(NO)_7]$ with the electrophilic $Me_3S^+I^-$.

Experimental

Light petroleum had b.p. 40—60 °C, and was dried by reflux over sodium diphenylketyl; dichloromethane was dried by reflux over calcium hydride. The salts $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ and $Na[Fe_4S_3(NO)_7]$ were prepared as previously described.[1,2] Arenediazonium tetrafluoroborates $RN_2^+BF_4^-$ were prepared by reaction of the amines RNH_2 with sodium nitrite and aqueous fluoroboric acid: they were purified using repeated reprecipitation by diethyl ether from solution in acetonitrile. All amines were purified by distillation, or by reprecipitation from aqueous acidic solution, before use. Other reagents were the best commercially available grade, and were used as received.

Elemental analyses were by the Microanalytical Laboratory of this Department. Infra-red spectra were measured using Perkin-Elmer model 1710 (FTIR) or 1330 spectrophotometers. N.m.r. spectra were recorded in CD_2Cl_2 or tetrahydrofuran (thf) solutions using Bruker AM-300 (for ^1H, ^{13}C, and ^{15}N) or WP-80 (for ^{19}F) spectrometers: ^{19}F spectra were recorded at 75.3 MHz, relative to internal CCl_3F. E.s.r. spectra were measured in 1-mm quartz capillaries using a Bruker ER200 D spectrometer: di-t-butylaminyl oxide was used as the standard for the measurement of line positions. Mass spectra were measured using an INCOS-50 GC/MS system. All operations were carried out in dinitrogen atmospheres, using Schlenk techniques or a glove-box as appropriate.

Conversion of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *in* $[Fe_2(SR)_2(NO)_4]$ *using Thiolates.*—(*a*) *Preparation of* $[Fe_2(SCH_2CO_2Me)_2(NO)_4]$. To a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (2.0 g, 4.0 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (2.0 g, 8.0 mmol) in water (50 cm^3) was added a solution of methyl thioglycolate (6.0 g, 56 mmol) and NaOH (2.5 g) in water (100 cm^3). After brief stirring, the mixture was extracted with CH_2Cl_2 (3 × 50 cm^3), and the organic fraction was dried. The solvent was removed, and the residual black solid was recrystallised from warm CH_2Cl_2 to give $[Fe_2(SCH_2CO_2Me)_2(NO)_4]$ as shiny black rectangular plates, m.p. 120—122 °C, yield 1.04 g, 2.3 mmol (58%) (Found: C, 16.4; H, 2.1; N, 12.6. $C_6H_{10}Fe_2N_4O_8S_2$ requires C, 16.3; H, 2.3; N, 12.6%). N.m.r. (CD_2Cl_2): δ_H 3.66, 3.72 (2 × s, 3 H, 2 × CH_3) and 3.70, 3.74 (2 × s, 2 H, s × CH_2); δ_C 42.6(q) and 44.8(q) (2 × CH_3), 53.1(t) and 53.2(t) (2 × CH_2), and 169.3(s) CO. Mass spectrum: *m*/*z* 412, $[M - NO]^+$; 382, $[M - 2NO]^+$; 352, $[M - 3NO]^+$. Infra-red (CH_2Cl_2): ν(NO) 1 788 and 1 760; ν(CO) 1 745 cm^{-1}.

(*b*) *Preparation of* $[Fe_2(SCH_2CH_2OH)_2(NO)_4]$. To a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2.0 mmol) and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: G = 10^{-4} T.

$Na_2S_2O_3{\cdot}5H_2O$ (1.0 g, 4.0 mmol) in water (30 cm^3) was added a solution of $HSCH_2CH_2OH$ (1.5 g, 20 mmol) and NaOH (1.0 g) in water (30 cm^3). Dichloromethane (75 cm^3) was then added, and the mixture was stirred for 10 min. The organic layer was removed, and to the aqueous fraction was added glacial acetic acid–water (1:1 v/v; 100 cm^3) and CH_2Cl_2 (100 cm^3). After extraction, the organic layer was separated. The combined organic fractions were washed with water (3 × 100 cm^3) and then dried. The solvent was removed to yield 0.3 g of a dark brown solid. Recrystallisation from CH_2Cl_2 gave black crystals of $[Fe_2(SCH_2CH_2OH)_2(NO)_4]$, m.p. 108—110 °C, yield 0.20 g, 0.50 mmol (26%) (Found: C, 12.6; H, 2.3; N, 14.3. $C_4H_{10}Fe_2N_4O_6S_2$ requires C, 12.5; H, 2.6; N, 14.5%). Infra-red (CH_2Cl_2 solution): ν(NO) 1 780 and 1 753 cm^{-1}. N.m.r. (thf): δ_H 3.16 and 3.20 (2 × t, 4 H, 2 × CH_2S), 3.84 (m, 5 H, 2 × CH_2O), and 4.42 (m, 2 H, 2 × OH); δ_C 48.1 and 49.1 (2 × t, 2 × CH_2S), and 64.1 (t, 2 × CH_2O).

(*c*) *Preparation of* $[Fe_2(SC_4H_3N_2)_2(NO)_4]$. To a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2.0 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (1.0 g, 4.0 mmol) in water (30 cm^3) was added a solution of 2-pyrimidinethiol ($C_4H_3N_2SH$) (2.24 g, 20 mmol) and NaOH (2 g), in water (30 cm^3). After brief stirring, the mixture was extracted with CH_2Cl_2 (2 × 200 cm^3). The organic fraction was dried, and the solvent was removed. Recrystallisation of the resulting solid from warm CH_2Cl_2 gave black crystals of $[Fe_2(SC_4H_3N_2)_2(NO)_4]$, yield 0.48 g, 1.04 mmol (52%) (Found: C, 21.6; H, 1.2; N, 25.9. $C_8H_6Fe_2N_8O_4S_2$ requires C, 21.2; H, 1.3; N, 24.7%). Infra-red ν(NO) (CH_2Cl_2 solution) 1 798 and 1 765; (Nujol) 1 794 and 1 741 cm^{-1}. N.m.r. (CD_2Cl_2): δ_H 7.1 (m, 2 H) and 8.6 (m, 4 H).

(*d*) *Preparation of* $[Fe_2(SR)_2(NO)_4]$ (*R* = *alkyl.*) In like manner to the foregoing were prepared $[Fe_2(SR)_2(NO)_4]$ for R = Me, Et, Pr^i, Bu^t, Bu^i, Bu^s, Pr^n, Bu^n, or $(CH_2)_4Me$: yields were in the range 55—65%. These known products were identified by their i.r. and ^1H and ^{13}C n.m.r. spectra.[2–6]

Reaction of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *with* Na_2S.—To a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2.0 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (1.0 g, 4.0 mmol) in water (30 cm^3) was added a solution of $Na_2S{\cdot}9H_2O$ (7.2 g, 30 mmol) in water (30 cm^3). The mixture was stirred during 30 min, during which time the colour changed from green-black to dark red. The solvent was removed, and the resulting solid was extracted with thf (4 × 50 cm^3): the extracts were then evaporated to dryness. The i.r. spectrum of the resulting solid, in thf solution, showed the presence of both $[Fe_4S_3(NO)_7]^-$ and $[Fe_2S_2(NO)_4]^{2-}$. Extraction of the solid with diethyl ether gave $Na[Fe_4S_3(NO)_7]$ (26%): the residual solid was found by i.r. spectroscopy[7] to contain $[Fe_2S_2(NO)_4]^{2-}$ as the sole iron nitrosyl complex present.

Conversion of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *into* $[Fe_2(SR)_2(NO)_4]$ *using Halides.*—To a mixture of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2.0 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (1.0 g, 4.0 mmol) in water (30 cm^3) was added a solution of $Na_2S{\cdot}9H_2O$ (5.8 g, 24 mmol) and NaOH (1g) in water (30 cm^3). After brief stirring, thf (60 cm^3) was added and the mixture was filtered. To the filtrate was added methyl iodide (3.0 g, 21 mmol) and the solution was stirred for 30 min. The mixture turned green and a strong smell of methanethiol was detected. The solution was extracted with CH_2Cl_2 (3 × 50 cm^3): the extract was reduced to small volume, and chromatographed on silica. Elution with CH_2Cl_2 gave $[Fe_2(SMe)_2(NO)_4]$, yield 0.13 g, 0.4 mmol (20%). A similar reaction using Ph_2CHCl instead of MeI gave a 7% yield of a poorly stable product, i.r. ν(NO) 1 793 and 1 761 cm^{-1}, tentatively identified as $[Fe_2(SCHPh_2)_2(NO)_4]$.

Conversion of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *into* $[Fe(NO)(S_2CNR_2)_2]$ (*R* = Me, Et, *or* Pr^n).—In a typical reaction, a mixture of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2.0 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (1.0 g, 4.0 mmol) in water (30 cm^3) was added to a solution of sodium diethyldithiocarbamate trihydrate (2.0 g, 8.9 mmol) in dilute aqueous sodium hydroxide (30 cm^3). After brief stirring, the solution was extracted with CH_2Cl_2 (3 × 50 cm^3): the extract was washed with water (2 × 100 cm^3) and dried. The solvent was removed, and the residue crystallised from boiling ether to provide $[Fe(NO)(S_2CNEt_2)_2]$[8] in 72% yield. In a similar manner were prepared $[Fe(NO)(S_2CNMe_2)_2]$[8] (64%) and $[Fe(NO)(S_2CNPr_2)_2]$[8] (68%).

Reactions of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *with Arenediazonium Tetrafluoroborates.*—(*a*) *p*-$FC_6H_4N_2{}^+BF_4{}^-$. A solution of $Na[Fe_4S_3(NO)_7]$ (1.18 g, 2.1 mmol) in MeCN (20 cm^3) was cooled to 0 °C. Freshly recrystallised *p*-$FC_6H_4N_2{}^+BF_4{}^-$ (3.0 g, 14.3 mmol) was added in one portion, and the solution was then stirred for 20 min. Water (200 cm^3) was added, and the mixture filtered. The solid product was washed with water (2 × 50 cm^3), then dissolved in CH_2Cl_2 (200 cm^3): this solution was dried and reduced to small volume. Chromatography on silica (CH_2Cl_2 eluant) gave the product $[Fe_2(SC_6H_4F\text{-}p)_2(NO)_4]$, m.p. 150 °C (decomp.) which was recrystallised from CH_2Cl_2–MeOH in overall yield of 97% (Found: C, 29.6; H, 1.6; N, 11.2. $C_{12}H_8F_2Fe_2N_4O_4S_2$ requires C, 29.7; H, 1.7; N, 11.5%). N.m.r. (CD_2Cl_2): δ_H 6.85 (d × d, $^3J_{HH}$ 7.0, $^4J_{HF}$ 5.2, H^2), and 7.05 (d × d, $^3J_{HH}$ 7.0, $^3J_{HF}$ 8.1, H^3); δ_C 115.6 ($^2J_{CF}$ 22.3, C^3) 131.3 ($^3J_{CF}$ 8.5) and 131.3 ($^3J_{CF}$ 8.3), (C^2), 133.5 ($^4J_{CF}$ 2.9) and 133.7 ($^4J_{CF}$ 3.2), (C^1), 161.4 ($^1J_{CF}$ 250.3) and 161.7 ($^1J_{CF}$ 250.3), (C^4); δ_F 112.8 (t × t, $^3J_{FH}$ 8.1, $^4J_{FH}$ 5.2) and 113.4 (t × t, $^3J_{FH}$ 8.1, $^4J_{FH}$ 5.2 Hz). Mass spectrum: *m/z* 486, M^+; 456, $[M - NO]^+$; 426, $[M - 2NO]^+$; 396, $[M - 3NO]^+$, and 366, $[M - 4NO]^+$, $[Fe_2(SC_6H_4F)_2]^+$. Infra-red (CCl_4 solution): ν(NO) 1 789 and 1 763 cm^{-1}.

(*b*) $PhN_2{}^+BF_4{}^-$, *p*-$MeC_6H_4N_2{}^+BF_4{}^-$, *p*-$MeOC_6H_4N_2{}^+BF_4{}^-$, *and p*-$MeCOC_6H_4N_2{}^+BF_4{}^-$. From reactions similar to the foregoing were obtained respectively the known[9] $[Fe_2(SPh)_2(NO)_4]$ and $[Fe_2(SC_6H_4Me\text{-}p)_2(NO)_4]$, and labile $[Fe_2(SC_6H_4OMe\text{-}p)_2(NO)_4]$ [n.m.r. (CD_2Cl_2 solution), δ_H 3.60 (s, 3 H, CH_3) and 6.9—7.1 (m, 4 H, C_6H_4); mass spectrum, *m/z* 510 M^+, 480 $[M - NO]^+$, 450 $[M - 2NO]^+$, 420 $[M - 3NO]^+$, and 390 $[M - 4NO]^+$; i.r. (CH_2Cl_2 solution) ν(NO) 1 784 and 1 756 cm^{-1}] and $[Fe_2(SC_6H_4COMe\text{-}p)_2(NO)_4]$ [n.m.r. (CD_2Cl_2 solution) δ_H 2.59 (s, 6 H, CH_3) and 7.2—7.9 (m, 8 H, aromatic), δ_C 26.6 (q, 2 × CH_3), 128.7 (d, aromatic C^2 or C^3), 130.6(d) and 130.8(d) (aromatic C^3 or C^2), 135.6(d) and 136.7(d) (aromatic CS), 145.1(d) and 145.3(d) (aromatic *C*–$COCH_3$), and 196.8 (s, CO); mass spectrum, *m/z* 534 M^+, 504 $[M - NO]^+$, 474 $[M - 2NO]^+$, 444 $[M - 3NO]^+$, and 414 $[M - 4NO]^+$; i.r. (CH_2Cl_2 solution) ν(NO) 1 792 and 1 765, ν(CO) 1 688 cm^{-1}.

(*c*) *p*-$ClC_6H_4N_2{}^+BF_4{}^-$, *p*-$NCC_6H_4N_2{}^+BF_4{}^-$, *and p*-$O_2NC_6H_4N_2{}^+BF_4{}^-$. From reactions similar to the foregoing were obtained extremely air-sensitive and labile products tentatively identified respectively as $[Fe_2(SC_6H_4Cl\text{-}p)_2(NO)_4]$, [i.r. ($CH_2Cl_2$ solution) ν(NO) 1 787 and 1 759 cm^{-1}], $[Fe_2(SC_6H_4CN\text{-}p)_2(NO)_4]$ [i.r. (thf solution) ν(NO) 1 791 and 1 763, ν(CN) 2 229 cm^{-1}], and $[Fe_2(SC_6H_4NO_2\text{-}p)_2(NO)_4]$ (Found: C, 26.5; H, 1.4; N, 15.4. $C_{12}H_8Fe_2N_6O_8S_2$ requires C, 26.7; H, 1.5; N, 15.6%); i.r. (CH_2Cl_2 solution) ν(NO) 1 790 and 1 760 cm^{-1}; n.m.r. δ_C 125.3(d), 131.6(d), 143.1(s), and 147.9(s).

Reactions of $Na[Fe_4S_3(NO)_7]$ *with Onium salts.*—(*a*) $Et_3O^+BF_4{}^-$. A single portion of $Na[Fe_4S_3(NO)_7]$ (0.5 g, 0.9 mmol) was added to a solution of $Et_3O^+BF_4{}^-$ (20 cm^3, 1 mol dm^{-3} in CH_2Cl_2, 20 mmol). The mixture was stirred overnight and water (100 cm^3) was then added and the whole shaken. The organic layer was separated, dried, and reduced to small volume. Chromatography on silica (CH_2Cl_2 eluant) gave $[Fe_2(SEt)_2(NO)_4]$ (0.12 g, 0.34 mmol, 21%).

(*b*) $Me_3O^+BF_4^-$. A similar reaction using $Me_3O^+BF_4^-$ gave $[Fe_2(SMe)_2(NO)_4]$ (22%).

(*c*) $Me_3S^+I^+$. To a solution of $Na[Fe_4S_3(NO)_7]$ (0.5 g, 0.9 mmol) in water (50 cm^3) was added a solution of $Me_3S^+I^-$ (1.0 g, 4.9 mmol) in water (50 cm^3). The resulting precipitate was filtered off, washed with water (2 × 100 cm^3), and dissolved in acetone (100 cm^3). Light petroleum (b.p. 60—80 °C) was added and the volume of the solution was then reduced to afford lustrous black crystals of $[SMe_3][Fe_4S_3(NO)_7]$, yield 0.35 g, 0.57 mmol (64%) (Found: C, 6.0; H, 1.3; N, 16.1. $C_3H_9Fe_4N_7O_7S_4$ requires C, 5.9; H, 1.5; N, 16.1%). Infra-red: $\nu(NO)$ (MeCN solution) 1 800w, 1 747vs, and 1 711m; (Nujol mull) 1 797w, 1 735vs, 1 716s, and 1 701m cm^{-1}. When a portion of $[SMe_3][Fe_4S_3(NO)_7]$ was refluxed in MeCN solution, with or without added base, no change was detected either by i.r. spectroscopy or by t.l.c.; the solid was recovered unchanged in 98% yield.

(*d*) $Me_3SO^+I^-$. To a solution of $Na[Fe_4S_3(NO)_7]$ (1.0 g, 1.8 mmol) in methanol (2.0 cm^3) was added a solution of $Me_3SO^+I^-$ (0.40 g, 1.8 mmol) in methanol–water (1:1 v/v, 20 cm^3). The resulting precipitate was filtered off, washed with water (4 × 50 cm^3), and dried over phosphoric oxide: the yield of $[SMe_3O][Fe_4S_3(NO)_7]$ was 0.79 g, 1.27 mmol (70%) (Found: C, 6.2; H, 1.3; N, 15.4. $C_3H_9Fe_4N_7O_8S_4$ requires C, 5.8; H, 1.5; N, 15.7%). Infra-red: $\nu(NO)$ (CH_3CN solution) $\nu(NO)$ 1 800w, 1 747vs, and 1 711m cm^{-1}; (Nujol mull) 1 798w, 1 765s, 1 740vs, 1 713s, and 1 691m cm^{-1}. After reflux of a portion of $[SMe_3O][Fe_4S_3(NO)_7]$ in methanol (1:1 v/v) during 6 h, the salt was recovered unchanged.

Reduction of $[SMe_3][Fe_4S_3(NO)_7]$.—An ether solution of sodium diphenylketyl (1.6 mmol) was filtered into a solution of $[SMe_3][Fe_4S_3(NO)_7]$ (1.0 g, 1.65 mmol) in ether (20 cm^3), and the mixture stirred during 8 h. The solvent was removed; the resulting solid was dissolved in the minimum volume of CH_2Cl_2 and chromatographed on silica (CH_2Cl_2 eluant) to afford $[Fe_2(SMe)_2(NO)_4]$ in 23% yield.

Crystal Structure Determination.—Crystals of $[SMe_3][Fe_4S_3(NO)_7]$ suitable for *X*-ray examination were grown from acetone.

Crystal data. $C_3H_9Fe_4N_7O_7S_4$, $M = 606.81$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.655(2)$, $b = 11.707(3)$, $c = 8.968(1)$ Å, $\alpha = 106.11(2)$, $\beta = 91.78(3)$, $\gamma = 84.92(2)°$, $U = 970.04$ Å^3, $Z = 2$, $D_c = 2.08$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 33.86$ cm^{-1}, $\lambda = 0.710\ 69$ Å, $F(000) = 516$.

Data collection.[10] CAD4 diffractometer using graphite-monochromated Mo-K_α radiation; ω—2θ scan mode, $1.5 \leqslant \theta \leqslant 25°$. 3 666 Reflections measured, of which 3 406 unique and 2 553 with $F_o \geqslant 3\sigma(F_o)$ used for the analysis and refinement.

Structure solution and refinement. Patterson method, followed by SFLS and Fourier-difference cycles. The asymmetric unit comprises one cation and one anion. The orientation of the cation was disordered, and three partial sulphur atoms were included in the refinement with site occupation factors (s.o.f.s) 0.7 [S(4)], 0.2 [S(4a)], and 0.1 [S(4b)]. In addition, further partially occupied methyl carbon sites were included, although most density was localised at the major sites C(1)–C(3). All non-hydrogen atoms were refined anisotropically. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\ 02F_o^2]$ gave final R and R' values of 0.039 and 0.042 for 257 refined parameters. Programs and computers used, and sources of scattering factor data, were as given in ref. 11.

Final refined co-ordinates are given in Table 1, selected geometric parameters in Table 2, and a perspective view of the ion pair, showing the atom numbering scheme, is given in the Figure.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Conversion of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *into* $[Fe_2(SR)_2(NO)_4]$.—We observed[1] previously that tetrahydrofuran (thf) solutions of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ react with thiols RSH in the presence of NEt_3 as proton acceptor to provide useful yields of the neutral Roussin esters $[Fe_2(SR)_2(NO)_4]$. However these conversions, which involve ligand-substitution reactions at iron, were found to be slow, which we attribute to the fact that $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ remains largely in dinuclear form in solvents such as thf. Since we have found[2] that mononuclear intermediates of type $[Fe(SR)_2(NO)_2]^-$ are very labile to ligand-substitution reactions, we reasoned that prior conversion of the dinuclear anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ into the known[1] intermediate $[Fe(NO)_2(S_2O_3)_2]^{3-}$ by reaction with thiosulphate could lead to very much faster reaction with thiols: for this purpose we chose to use water as the solvent rather than thf, as being most amenable to the formation of $[Fe(NO)_2(S_2O_3)_2]^{3-}$.

Consistent with this, we have found that addition of the thiols RSH [R = Me, Et, Pr^i, Bu^t, Bu^i, Bu^s, Pr^n, Bu^n, or $(CH_2)_4Me$] in aqueous alkaline solution to a 1:2 molar mixture of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ and $Na_2S_2O_3$ {a mixture which is effectively equivalent to $Na_3[Fe(S_2O_3)_2(NO)_2]$ as shown[1] by e.s.r. spectroscopy} rapidly gave good yields (55—65%) of the known[2–6] Roussin esters $[Fe_2(SR)_2(NO)_4]$, according to equation (1).

$$[Fe_2(S_2O_3)_2(NO)_4]^{2-} + 2S_2O_3^{\,2-} \longrightarrow 2[Fe(S_2O_3)_2(NO)_2]^{3-} \xrightarrow{2RS^-} 4S_2O_3^{\,2-} + [Fe_2(SR)_2(NO)_4] \quad (1)$$

The same method was used to produce two neutral esters containing functionalised substituents: $[Fe_2(SCH_2CO_2Me)_2(NO)_4]$ and $[Fe_2(SCH_2CH_2OH)_2(NO)_4]$. The ^1H and ^{13}C n.m.r. spectra show that as usual[2–6] two isomers of each complex of C_{2v} and C_{2h} symmetry respectively are present in solution in equal abundance. In the same type of reaction, 2-pyrimidinethiol reacted to form $[Fe_2(SC_4H_3N_2)_2(NO)_4]$.

The simplest possible thiolate anion is SH^-, and reaction of a $Na_2[Fe_2(S_2O_3)_2(NO)_4]$–$Na_2S_2O_3$ mixture with aqueous sodium sulphide gave a mixture of Roussin's Red Salt, $Na_2[Fe_2S_2(NO)_4]$, and Roussin's Black Salt, $Na[Fe_4S_3(NO)_7]$. Since $Na[Fe_4S_3(NO)_7]$, but not $Na_2[Fe_2S_2(NO)_4]$, is freely soluble in diethyl ether, extraction of the mixed salt with ether removes the tetranuclear anion to leave only $Na_2[Fe_2S_2(NO)_4]$. This procedure probably represents the most convenient preparation available for $Na_2[Fe_2S_2(NO)_4]$. The usual preparation of $Na_2[Fe_2S_2(NO)_4]$ by the reaction of $[NH_4][Fe_4S_3(NO)_7]$ with concentrated aqueous sodium hydroxide[11,12] is invariably accompanied by the production of hydrated iron(III) oxides: the preparation of $Na_2[Fe_2S_2(NO)_4]$ from $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ and sodium sulphide is free from such contamination.

The anion $[Fe_2S_2(NO)_4]^{2-}$ has long been known to react readily with halogenoalkanes,[12] and this reaction has been extensively exploited[6,7,14] for the synthesis of neutral Roussin esters $[Fe_2(SR)_2(NO)_4]$: the tetranuclear anion $[Fe_4S_3(NO)_7]^-$ by contrast does not react with simple halogenoalkanes. Consequently it is possible to use without separation the crude mixture of $[Fe_2S_2(NO)_4]^{2-}$ and $[Fe_4S_3(NO)_7]^-$ formed in the reaction between $Na_2[Fe_2(S_2O_3)_2(NO)_4]$–$Na_2S_2O_3$ and sodium sulphide in reactions with halogenoalkanes to form $[Fe_2(SR)_2(NO_4)]$. By use of methyl iodide, a 20% yield of $[Fe_2(SMe)_2(NO_4)]$ was obtained: use of chlorodiphenylmethane gave a low yield of a poorly stable product, which could not be obtained in analytically pure form but which exhibited the characteristic pattern[2,4] of nitrosyl stretches in the i.r. spectrum indicative of a neutral Roussin ester; hence we tentatively identify this material as $[Fe_2(SCHPh_2)_2(NO)_4]$.

Intermediates in the Reactions of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *with Thiols*.—In these reactions the principal effect of change of solvent from thf[1] to water is to increase the rate: the products are identical and the overall yields are similar. We have investigated briefly the formation of paramagnetic mononuclear intermediates using thf as solvent: the slower reactions in thf render more convenient the observation of such intermediates by e.s.r. spectroscopy, and the use of the thf permits the reaction solutions to be cooled to 240—260 K which we have found[3,9] to give enhanced resolution of the e.s.r. spectra.

Solutions of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ in thf give extremely weak e.s.r. spectra, in which no fine structure can be resolved: the spectra are probably best assigned to solvo complexes similar to those found[1] for neutral $[Fe_2(SR)_2(NO)_4]$. Addition of triethylamine caused no change. Addition of a small quantity of Pr^iSH to the mixed thf–NEt_3 solution caused the rapid development of an intense e.s.r. spectrum arising from two distinct complexes. One was a dinitrosyl complex, characterised by $g = 2.027$, $A(^{14}N) = 2.5$ G(2N), $A(^1H) = 1.3$ G(2H), and identified[2] as $[Fe(SPr^i)_2(NO)_2]^-$, a well established[2] precursor of $[Fe_2(SPr^i)_2(NO)_4]$: the other was a mononitrosyl complex, characterised by $g = 2.021$, $A(^{14}N) = 4.0$ G(1N) with no hyperfine coupling to hydrogen atoms, and identified[3,9,11] as $[Fe(SPr^i)_3(NO)]^-$. Increase in the quantity of Pr^iSH added caused a decrease in the intensity of the $[Fe(SPr^i)_3(NO)]^-$ signal, and its replacement by that of a second mononitrosyl complex, having $g = 2.040$, $A(^{14}N) = 13.2$ G, identified[3,9] as $[Fe(SPr^i)_3(NO)]^{3-}$.

Very similar results were obtained using Bu^tSH instead of Pr^iSH: initially the complexes[3,9,11] $[Fe(SBu^t)_2(NO)_2]^-$ and $[Fe(SBu^t)_3(NO)]^-$ were formed, while further addition of Bu^tSH caused replacement of $[Fe(SBu^t)_3(NO)]^-$ by $[Fe(SBu^t)_3(NO)]^{3-}$. The reduction of complexes $[Fe(SR)_3(NO)]^-$ to $[Fe(SR)_3(NO)]^{3-}$ by excess of thiolate RS^- has been established in previous work,[3,9] as has the slow conversion of both $[Fe(SR)_3(NO)]^-$ and $[Fe(SR)_3(NO)]^{3-}$, by routes and mechanisms unknown, to give $[Fe(SR)_2(NO)_2]^-$ as the sole paramagnetic iron nitrosyl complex left in the system: this latter dinitrosyl complex, as noted above, is readily converted[2] into $[Fe_2(SR)_2(NO)_4]$, for a wide range of organic substituents R. The essential independence of these processes from the choice of solvent was demonstrated by repetition of the e.s.r. experiments using Pr^iSH in dimethylformamide (dmf) as solvent: the results were unchanged.

We have observed in previous work[2] that the rate of thiolate exchange in $[Fe_2(SR)_2(NO)_4]$ is strongly correlated with the donor capacity of the solvent and with the ease with which mononuclear intermediates of types $[Fe(NO)_2L_2]^+$ and $[Fe(SR)(NO)_2L]$ (L = solvent) are formed. The e.s.r. results reported here indicate that the part of the reaction between RS^- and $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ which proceeds *via* mononuclear intermediates is in fact far more complex than a simple exchange of sulphur ligands: both nitrosyl transfer and redox reactions also occur.

Conversion of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *into* $[Fe(NO)(S_2CNR_2)_2]$.—The reactions of a 1:2 mixture of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ and $Na_2S_2O_3$ with dialkyldithiocarbamate salts $Na^+S_2CNR_2^-$ (for R = Me, Et, or Pr^n) provided good yields (65—70%) of the mononitrosyl complexes $[Fe(NO)(S_2CNR_2)_2]$. This reaction thus provides a further example in which a precursor complex containing the dinitrosyliron fragment $\{Fe(NO)_2\}^9$ is converted in good yield into a product containing the mononitrosyliron fragment $\{Fe(NO)\}^7$: previously recorded examples include the reactions of $[Fe_2(SR)_2(NO)_4]$ (R = alkyl) with $Me_2NCS_2^-$ to give $[Fe(NO)(S_2CNMe_2)_2]$,[3] and with $[MoS_4]^{2-}$ to give $[Fe(NO)(S_2MoS_2)_2]^{2-}$.[9] This behaviour appears to be characteristic of chelating anionic ligands of restricted bite, although no tractable product could be obtained from the reactions of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ with ammonium tetrathiomolybdate.

Conversion of $Na[Fe_4S_3(NO)_7]$ *into* $[Fe_2(SR)_2(NO)_4]$.—There are conflicting reports in the literature concerning the reactions of the black Roussin salt, $Na[Fe_4S_3(NO)_7]$ with arenediazonium salts. The *p*-nitro derivative, p-$O_2NC_6H_4N_2^+BF_4^-$, was reported[15] to yield a paramagnetic product, described on the basis of partial evidence as the tetranuclear complex $[p$-$O_2NC_6H_4N_2Fe_4S_3(NO)_4]$, in which the dinitrogen group of the diazonium cation is retained, whereas the *p*-fluoro salt p-$FC_6H_4N_2^+BF_4^-$ was reported[16] to give a diamagnetic dinuclear complex $[Fe_2(SC_6H_4F$-$p)_2(NO)_4]$, which does not retain the dinitrogen group of the diazonium cation, and which was identified unambiguously by *X*-ray analysis. Because of this reported difference, and in the hope of characterising further the paramagnetic tetranuclear product, we have studied the reactions of $Na[Fe_4S_3(NO)_7]$ with a range of arenediazonium tetrafluoroborates, p-$XC_6H_4N_2^+BF_4^-$, for X = H, Me, F, Cl, MeO, MeCO, CN, or NO_2.

When X = H, Me, or F the reactions between $Na[Fe_4S_3(NO)_7]$ and p-$XC_6H_4N_2^+BF_4^-$ in acetonitrile solution yielded the known[9,16] dinuclear products $[Fe_2(SC_6H_4X$-$p)_2(NO)_4]$. The product having X = F was not characterised in solution in the earlier work,[16] but the ^{13}C and ^{19}F n.m.r. spectra (see Experimental section) both consist of the superimposition of two equivalent spectra, of equal intensity, each straightforwardly analysed as arising from a 1,4-FC_6H_4Y fragment. From this we deduce that, like complexes $[Fe_2(SR)_2(NO)_4]$ having R = alkyl[2–6] and like $[Fe_2(SPh)_2(NO)_4]$,[9,14] the *p*-fluoro complex $[Fe_2(SC_6H_4F$-$p)_2(NO)_4]$ exists in solution as a mixture of two geometric isomers, in equal abundance. In contrast to the solution behaviour, $[Fe_2(SC_6H_4F$-$p)_2(NO)_4]$ exists in the solid state only as the centrosymmetric *trans* isomer,[16] as also do the alkyl analogues $[Fe_2(SR)_2(NO)_4]$ when R = Me,[17] Et,[18], n-C_5H_{11},[17] or Bu^t.[17]

When X = MeO or MeCO the products were too labile to be characterised by microanalysis, but each exhibited in the i.r. spectrum a nitrosyl stretching pattern characteristic[2,4] of $[Fe_2(SR)_2(NO)_4]$ complexes and each showed in the mass spectrum not only a molecular ion, but four further ions at intervals of 30 mass units corresponding to successive loss of four nitrosyl ligands: this is typical of $[Fe_2(SR)_2(NO)_4]$. For X = MeO the ^{13}C n.m.r. spectrum showed clearly the presence of two isomeric forms, present in roughly equal abundance. When X = Cl, CN, or NO_2 the products were extremely labile and air sensitive: for X = Cl and CN, only the i.r. spectra gave an indication of the formation of dinuclear $[Fe_2(SC_6H_4X$-$p)_2(NO)_4]$ accompanied by complete loss of $Na[Fe_4S_3(NO)_7]$. However no evidence whatever was found to support a formulation, in the case of X = NO_2, of any product as $[p$-$O_2NC_6H_4N_2Fe_4S_3(NO)_4]$ as previously reported.[15]

The above results show that, although there is no reaction between the anion $[Fe_4S_3(NO)_7]^-$ and weakly electrophilic reagents such as halogenoalkanes, reaction does occur with most powerful electrophiles such as RN_2^+. The course of this reaction is presumably initiated by attack of sulphur, as

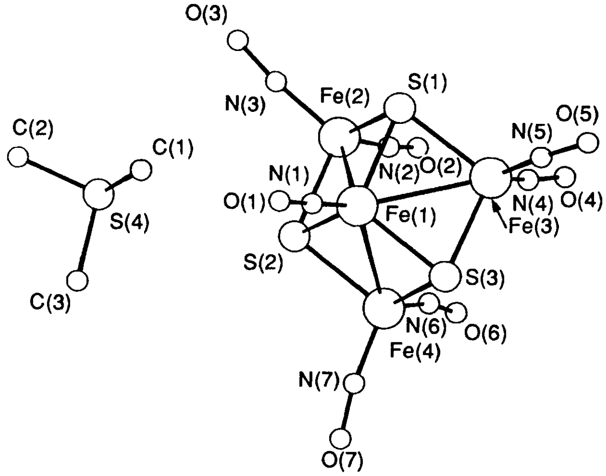

Figure. Perspective view of the ion pair showing the atom-numbering scheme: the principal orientation of the cation is shown. For details of the disorder see Table 1 and the text

Table 1. Fractional atomic co-ordinates (× 10^4) for $[SMe_3][Fe_4S_3(NO)_7]$

Atom	*x*	*y*	*z*
Fe(1)	253(1)	1 509(1)	2 979(1)
Fe(2)	2 479(1)	1 317(1)	1 160(1)
Fe(3)	−461(1)	3 468(1)	2 000(1)
Fe(4)	1 777(1)	3 019(1)	5 092(1)
S(1)	213(2)	1 607(1)	560(2)
S(2)	2 452(2)	1 163(1)	3 612(2)
S(3)	−469(2)	3 306(1)	4 442(2)
S(4)	3 952(6)	−2 165(5)	3 127(7)
S(4a)	3 387(13)	−2 901(11)	3 375(13)
S(4b)	3 686(31)	−1 603(27)	4 055(57)
N(1)	−700(5)	455(4)	3 192(5)
N(2)	3 331(6)	2 468(5)	1 118(6)
N(3)	3 041(6)	−8(6)	−19(6)
N(4)	647(6)	4 411(4)	1 787(5)
N(5)	−2 093(6)	3 804(5)	1 565(6)
N(6)	2 739(5)	4 011(5)	4 715(6)
N(7)	1 765(6)	2 990(5)	6 941(6)
O(1)	−1 358(6)	−300(5)	3 326(6)
O(2)	4 071(6)	3 162(6)	952(7)
O(3)	3 614(6)	−796(6)	−940(7)
O(4)	1 216(6)	5 172(4)	1 537(6)
O(5)	−3 143(6)	4 251(5)	1 211(7)
O(6)	3 486(6)	4 741(5)	4 749(7)
O(7)	1 899(7)	3 147(5)	8 269(5)
C(1)	2 090(8)	−2 042(7)	2 639(10)
C(2)	4 466(11)	−3 669(10)	2 403(13)
C(3)	3 863(11)	−2 049(13)	5 193(12)
C(a)	5 008(36)	−1 348(32)	2 922(40)
C(b)	3 750(55)	−2 344(46)	1 936(62)
C(c)	4 855(64)	−1 742(55)	2 341(68)

Occupancies of methyl carbon atoms are: C(1) 1.0, C(2) 0.75, C(3) 0.80, C(a) 0.25, C(b) 0.10, and C(c) 0.10. Occupancies of sulphonium sulphur atoms are: S(4) 0.7, S(4a) 0.2, and S(4b) 0.1.

nucleophile, on the terminal nitrogen atom of the diazo group as occurs with, for example, arenethiolates $R'S^-$ to yield sulphides RSR';[19] arenesulphinates $R'SO_2^-$ to yield diazosulphones $RN{=}N{-}SO_2R'$,[20] and sulphite to yield diazosulphonates $[RN{=}N{-}SO_3]^-$.[21] The subsequent course of the reaction, involving at least two major stages in the loss of dinitrogen, and the change of nuclearity from four to two, remains obscure: it may, as appears[14] to be common in reactions of $[Fe_4S_3(NO)_7]^-$, involve fragmentation of the tetrairon core to mononuclear fragments, followed by reassembly to give dinuclear products.

Reactions of $Na[Fe_4S_3(NO)_7]$ *with Onium Salts.*—Alkanediazonium salts are generally very hazardous, so that for direct alkylation of $Na[Fe_4S_3(NO)_7]$ we turned to trialkyloxonium and trialkylsulphonium cations as electrophiles. Each of $Me_3O^+BF_4^-$ and $Et_3O^+BF_4^-$ reacted with a suspension of $Na[Fe_4S_3(NO)_7]$ in CH_2Cl_2 to provide $[Fe_2(SR)_2(NO)_4]$ for R = Me or Et respectively. Hence the sulphur of the $[Fe_4S_3(NO)_7]^-$ is again presumably acting as the nucleophilic centre towards R_3O^+, with further steps to change the nuclearity.

With the less potent electrophile, $Me_3S^+I^-$, a simple salt $Me_3S^+[Fe_4S_3(NO)_7]^-$ was obtained, with no evidence at all for methyl transfer to cluster sulphur. Likewise $Me_3SO^+I^-$ gave the salt $Me_3SO^+[Fe_4S_3(NO)_7]^-$. No methyl transfer was induced for either of the salts upon prolonged reflux.

The i.r. spectra, measured in acetonitrile solutions, of $[SMe_3][Fe_4S_3(NO)_7]$, $[SMe_3O][Fe_4S_3(NO)_7]$, and $[AsPh_4][Fe_4S_3(NO)_7]$ are all identical in the ν(NO) region: exactly the same ν(NO) pattern was found for $[AsPh_4][Fe_4S_3(NO)_7]$ in the solid state.[22] However, the solid-state spectrum of $[SMe_3][Fe_4S_3(NO)_7]$ is quite different from that in solution, suggesting that there may exist some association between the ions in the solid state sufficient to perturb the i.r. spectrum. This point was further investigated by a determination of the crystal and molecular structure of $[SMe_3][Fe_4S_3(NO)_7]$.

Reduction of the anion $[Fe_4S_3(NO)_7]^-$ can be achieved[23] in a series of reversible one-electron steps to produce in turn $[Fe_4S_3(NO)_7]^{2-}$, $[Fe_4S_3(NO)_7]^{3-}$, and $[Fe_4S_3(NO)_7]^{4-}$. Since such reduced anions are more electron-rich than $[Fe_4S_3(NO)_7]^-$, they may be expected to be also more strongly nucleophilic. Accordingly, *in situ* reduction of $Me_3S^+[Fe_4S_3(NO)_7]^-$ using sodium diphenylketyl, which causes[23] reduction of $[Fe_4S_3(NO)_7]^-$ to $[Fe_4S_3(NO)_7]^{2-}$, does indeed provide evidence of methyl transfer, with an isolated yield of $[Fe_2(SMe)_2(NO)_4]$ of 23%.

These observations may be relevant to the biosynthetic pathway to the naturally occurring tumour promoter $[Fe_2(SMe)_2(NO)_4]$, readily obtained from plant material incubated with dilute aqueous sodium nitrite solutions:[24–26] since the anion $[Fe_4S_3(NO)_7]^-$ can be easily produced,[27] in good yield, from the reaction of nitrite with pre-formed {2Fe-2S} and {4Fe-4S} clusters of redox protein type, biochemical reduction followed by methylation, *e.g.* by *S*-adenosylmethionine, provides a plausible route to $[Fe_2(SMe)_2(NO)_4]$.

Crystal Structure of $[SMe_3][Fe_4S_3(NO)_7]$.—The structure consists of isolated ions with no contacts between ions within the sums of the van der Waals radii. The structure of the anion is very similar to that found[22] in the Ph_4As^+ salt. Although the mean values for given geometric parameters are almost the same in the two determinations, the anion in $[SMe_3][Fe_4S_3(NO)_7]$ approximates much more closely to C_{3v} symmetry than the anion in $[AsPh_4][Fe_4S_3(NO)_7]$: thus the three independent iron-iron distances around the base of the tetrahedron involving Fe(2), Fe(3), and Fe(4) are 3.575(5), 3.588(5), and 3.589(5) Å (range 0.014, mean 3.584 Å) in the Me_3S^+ salt, but 3.519(2), 3.564(2), and 3.628(2) Å (range 0.109, mean 3.570 Å) in the Ph_4As^+ salt. The apical iron, Fe(1), carries a single nitrosyl ligand for which the Fe–N–O angle 179.0(5)° is close to 180°. The basal iron atoms each form $Fe(NO)_2$ fragments in which the Fe–N–O groups are bent towards one another, with mean Fe–N–O angle 167.4°: the structure of $M(NO)_2$ has been discussed by Summerville and Hoffmann.[28] Within each basal $Fe(NO)_2$ the mean equatorial Fe–N distance is not significantly different from the mean axial Fe–N distance: this contrasts with

Table 2. Selected bond lengths (Å) for $[SMe_3][Fe_4S_3(NO)_7]$

Fe(2)–Fe(1)	2.695(4)	Fe(3)–Fe(1)	2.703(4)
Fe(4)–Fe(1)	2.704(4)	S(1)–Fe(1)	2.203(4)
S(2)–Fe(1)	2.212(4)	S(3)–Fe(1)	2.213(4)
N(1)–Fe(1)	1.657(7)	Fe(3)–Fe(2)	3.575(5)
Fe(4)–Fe(2)	3.589(5)	S(1)–Fe(2)	2.256(4)
S(2)–Fe(2)	2.257(4)	N(2)–Fe(2)	1.649(8)
N(3)–Fe(2)	1.671(8)	Fe(4)–Fe(3)	3.588(5)
S(1)–Fe(3)	2.253(4)	S(3)–Fe(3)	2.251(4)
N(4)–Fe(3)	1.654(7)	N(5)–Fe(3)	1.652(8)
S(2)–Fe(4)	2.261(4)	S(3)–Fe(4)	2.249(4)
N(6)–Fe(4)	1.660(7)	N(7)–Fe(4)	1.668(7)
C(1)–S(4)	1.840(11)	C(2)–S(4)	1.733(14)
C(3)–S(4)	1.824(14)	O(1)–N(1)	1.167(7)
O(2)–N(2)	1.170(8)	O(3)–N(3)	1.164(8)
O(4)–N(4)	1.163(7)	O(5)–N(5)	1.175(8)
O(6)–N(6)	1.159(7)	O(7)–N(7)	1.159(7)

a recent study[29] of $[AsPh_4][Fe_4Se_3(NO)_7]$ where the mean equatorial Fe–N distance was found to be longer than the mean axial distance. The cation is heavily disordered, and three partial sulphur sites and six carbon sites were necessary to fit the data: the site occupation factors are in Table 1. There is no indication from the structure either of a close approach between one of the sulphur atoms in the anion and one of the methyl carbons of the cation, or of a close approach of the sulphur of the cation to the basal triangle of the anion with incipient closure of an Fe_4S_4 cuboid framework.

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