Synthesis and Properties of the Bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)(2−) Anion. Crystal and Molecular Structure of Bis[bis(triphenylphosphoranylidene)-ammonium] Bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)†

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Salts of the bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)(2−) anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ can be prepared by reaction of iron(II)/thiosulphate mixtures either with nitric oxide or with sodium nitrite: the preparation using nitrite provides a convenient route to the ^{15}N labelled anion $[Fe_2(S_2O_3)_2(^{15}NO)_4]^{2-}$. The anion reacts readily with thiols RSH to provide good yields of $[Fe_2(SR)_2(NO)_4]$. Crystals of $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$ are triclinic, $a = 10.999(5)$, $b = 12.748(4)$, $c = 14.020(7)$ Å, $\alpha = 67.13(4)$, $\beta = 83.31(4)$, $\gamma = 93.87(3)°$, space group $P\bar{1}$ with $Z = 1$: the structure was solved using diffractometer data and refined to an R value of 0.034. The anion lies across a centre of inversion, and hence adopts the *trans* conformation. The ^{15}N n.m.r. spectrum of $[Fe_2(S_2O_3)_2(^{15}NO)_4]^{2-}$ shows the presence of only the *trans* conformer in solution, and that upon exposure to air $[Fe_2(S_2O_3)_2(^{15}NO)_4]^{2-}$ is readily converted into $[Fe_4S_3(^{15}NO)_7]^-$.

The Roussin esters, readily prepared by reaction of nitric oxide with mixtures of thiols RSH and iron(II) salts, have long been known to exist as dimers $[Fe_2(SR)_2(NO)_4]$, and in recent years their chemical[1–4] and structural[5–10] properties have been intensively studied. The stoicheiometrically related thiosulphato complex $[\{Fe(S_2O_3)(NO)_2\}_n]^{m-}$, although it was first reported[11] in 1895, has been much less well studied. Apart from its diamagnetism[11] and its i.r. spectrum,[12] no properties have been described: even the ratio m/n appears uncertain, with values of 3[12] and 1[13] recorded; in either case the observed diamagnetism requires n to be even.

The early preparative methods for this thiosulphato complex were based upon $[Fe_2I_2(NO)_4]$: we have now developed convenient methods based upon the reactions of iron(II) salts and thiosulphate with either nitric oxide gas or sodium nitrite. In this paper, we report these synthetic methods and some reactions, the crystal and molecular structure of the $[N(PPh_3)_2]^+$ salt, which shows the anion to be dimeric ($n = 2$, $m = 2$), and a ^{15}N n.m.r. study of both the anion and its decomposition products in solution.

Experimental

The salt $Na[^{15}NO_2]$ (99% enriched) was purchased from MSD isotopes, and was used as received. Elemental analyses were by the Microanalytical Laboratory of this Department. Nitrogen-15 n.m.r. spectra were recorded on 2% (w/v) solutions in CD_2Cl_2 or $CDCl_3$, using a Bruker AM-300 spectrometer, at 30.42 MHz relative to external $CH_3{}^{15}NO_2$. E.s.r. spectra were recorded using a Bruker ER200D spectrometer. All operations were carried out in dinitrogen atmospheres, using Schlenk techniques or a glove-box as appropriate.

Preparation of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *using* NO *gas*.—A solution of $FeSO_4{\cdot}7H_2O$ (10.8 g, 39 mmol) in water (20 cm^3) was added, under N_2, to a stirred solution of $Na_2S_2O_3{\cdot}5H_2O$ (20 g, 80 mmol) in water (80 cm^3). Nitric oxide was bubbled through the solution for 2 h. The mixture was filtered, and the filtrate evaporated to dryness: the solid residue was extracted with dry acetone (4 × 200 cm^3). The combined extracts were reduced to small volume and cooled in an ice-bath. Slow addition of CH_2Cl_2 caused the precipitation of the brown crystalline product. Yield of crude $Na_2[Fe_2(S_2O_3)_2(NO)_4]$: 9.0 g, 17.9 mmol, 90%.

Conversion to $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$. To a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2 mmol) in water (40 cm^3) at 60 °C was added, under N_2, $[N(PPh_3)_2]Cl$ (2.3 g, 4 mmol). The mixture was stirred for 20 min, filtered, and the solid product was washed with a little warm water. The solid was dissolved in CH_2Cl_2 (150 cm^3) and the solution was dried over $MgSO_4$. The solution was reduced to small volume and cooled in an ice-bath to give the product as brown needles, in almost quantitative yield (Found: C, 56.3; H, 3.9; N, 5.4. $C_{72}H_{60}Fe_2N_6O_{10}P_4S_4$ requires C, 56.4; H, 3.9; N, 5.5%). Infra-red (CH_2Cl_2 solution): ν(NO) 1 787 and 1 757 cm^{-1}.

Preparation of $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ *Salts using* $NaNO_2$.—To a well stirred solution of $NaNO_2$ (2.84 g, 41 mmol) and $Na_2S_2O_3{\cdot}5H_2O$ (9.9 g, 40 mmol) in water (40 cm^3) was added, under N_2, a solution of $FeSO_4{\cdot}7H_2O$ (5.52 g, 19.8 mmol) in water (30 cm^3). After stirring for 2 h, the mixture was filtered, and the filtrate evaporated to dryness. The solid residue was extracted with dry acetone (4 × 200 cm^3) to leave a green residue. The combined extracts were reduced to small volume: addition of CH_2Cl_2–light petroleum (b.p. 40—60 °C) (1 : 5 v/v) caused precipitation of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.5 g, 3 mmol, 30%). Conversion into the $[N(PPh_3)_2]$ salt gave a product identical to that described above.

The green residue was dissolved in the minimum volume of water, and $NBu^n{}_4Br$ (8 g, 25 mmol) was added. The green solution was extracted with CH_2Cl_2 until the aqueous layer was colourless. The combined CH_2Cl_2 extracts were evaporated to dryness and the residual solid was washed with warm water (4 × 250 cm^3). The solid was dried under vacuum, and recrystallised from ethanol to give $[NBu^n{}_4]_2[Fe_2(S_2O_3)_2$-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. units employed: G = 10^{-4} T, 1 eV ≈ 1.60×10^{-19} J.

Table 1. Fractional atomic co-ordinates (× 10^4) for $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	4 469.7(3)	4 128.6(2)	4 802.3(2)	C(13)	690(2)	2 995(2)	9 041(2)
S(1)	4 391.8(5)	4 246.9(4)	6 363.1(4)	C(14)	1 219(3)	2 719(2)	8 229(2)
S(2)	4 347.8(6)	6 846.9(5)	2 756.4(4)	C(15)	648(3)	2 939(3)	7 360(2)
N(1)	3 045(2)	4 156(2)	4 509(2)	C(16)	−455(3)	3 417(3)	7 295(2)
N(2)	5 219(2)	3 028(2)	4 816(2)	C(17)	−974(3)	3 683(2)	8 092(2)
O(1)	2 087(2)	4 051(2)	4 272(3)	C(18)	−411(2)	3 475(2)	8 972(2)
O(2)	5 576(2)	2 198(2)	4 800(2)	C(19)	1 532(2)	1 332(2)	12 857(2)
O(3)	6 054(2)	3 756(2)	7 842(2)	C(20)	1 683(3)	177(2)	13 132(2)
O(4)	6 608(2)	3 065(2)	6 517(2)	C(21)	2 779(3)	−201(3)	13 447(3)
O(5)	4 820(2)	2 136(2)	7 850(2)	C(22)	3 711(3)	541(3)	13 481(3)
P(1)	1 438.8(5)	2 786.7(4)	10 163.1(4)	C(23)	3 570(3)	1 688(3)	13 218(2)
P(2)	188.4(5)	1 917.4(4)	12 330.7(4)	C(24)	2 480(3)	2 082(3)	12 900(2)
N(3)	444(2)	2 701(2)	11 112(1)	C(25)	−1 027(2)	763(2)	12 634(2)
C(1)	2 565(2)	4 026(2)	9 792(2)	C(26)	−1 619(2)	663(2)	11 857(2)
C(2)	2 470(2)	4 739(2)	10 333(2)	C(27)	−2 600(3)	−192(3)	12 099(3)
C(3)	3 281(3)	5 740(2)	9 986(2)	C(28)	−2 990(3)	−927(3)	13 128(3)
C(4)	4 165(3)	6 028(2)	9 127(2)	C(29)	−2 403(3)	−839(3)	13 895(3)
C(5)	4 278(3)	5 313(2)	8 600(2)	C(30)	−1 428(3)	−1(2)	13 668(2)
C(6)	3 487(2)	4 311(2)	8 940(2)	C(31)	−397(2)	2 730(2)	13 037(2)
C(7)	2 187(2)	1 519(2)	10 397(2)	C(32)	−1 145(3)	3 568(2)	12 578(2)
C(8)	3 405(3)	1 467(3)	10 525(2)	C(33)	−1 728(3)	4 101(3)	13 167(3)
C(9)	3 867(4)	403(4)	10 785(3)	C(34)	−1 575(3)	3 809(3)	14 185(2)
C(10)	3 129(4)	−553(3)	10 896(3)	C(35)	−841(3)	2 985(3)	14 637(2)
C(11)	1 923(4)	−504(2)	10 771(2)	C(36)	−246(3)	2 448(3)	14 068(2)
C(12)	1 449(3)	534(2)	10 517(2)				

Table 2. Bond distances (Å) and angles (°) for the anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$

Fe(1)–Fe(1′)	2.713(4)	N(1)–O(1)	1.156(5)
Fe(1)–S(1)	2.244(3)	N(2)–O(2)	1.161(4)
Fe(1)–S(1′)	2.252(3)	S(1)–S(2)	2.171(3)
Fe(1)–N(1)	1.665(4)	S(2)–O(3)	1.425(4)
Fe(1)–N(2)	1.669(4)	S(2)–O(4)	1.418(4)
		S(2)–O(5)	1.430(4)
S(1)–Fe(1)–S(1′)	105.7(2)	Fe(1)–S(1)–Fe(1′)	74.3(2)
S(1)–Fe(1)–N(1)	107.6(2)	Fe(1)–S(1)–S(2)	107.5(2)
S(1)–Fe(1)–N(2)	109.3(2)	Fe(1′)–S(1)–S(2)	108.6(2)
S(1′)–Fe(1)–N(1)	107.3(2)	S(1)–S(2)–O(3)	102.3(2)
S(1′)–Fe(1)–N(2)	107.8(2)	S(1)–S(2)–O(4)	108.0(2)
N(1)–Fe(1)–N(2)	118.3(2)	S(1)–S(2)–O(5)	100.1(2)
Fe(1)–N(1)–O(1)	170.7(3)	O(3)–S(2)–O(4)	113.8(2)
Fe(1)–N(2)–O(2)	169.9(2)	O(4)–S(2)–O(5)	116.6(2)
		O(5)–S(2)–O(3)	113.6(2)

Primed atoms related to unprimed atoms by symmetry operation $1 - x, 1 - y, 1 - z$.

$(NO)_4]$ (2.0 g, 2 mmol, 20%). Infra-red (CH_2Cl_2 solution): ν(NO) 1 787 and 1 758 cm^{-1}.

Preparation of $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(^{15}NO)_4]$.—As described above, but using $Na[^{15}NO_2]$ (99% isotopic enrichment). Infra-red (CH_2Cl_2 solution): ν(NO) 1 748 and 1 718 cm^{-1}. ^{15}N N.m.r.: ($CDCl_3$ solution) +30 °C, δ +36.0 (s), $\nu_{\frac{1}{2}}$ 3.9; −60 °C, +35.9 (s), $\nu_{\frac{1}{2}}$ 3.0; (CD_2Cl_2 solution) +30 °C, δ + 35.8 (s) p.p.m., $\nu_{\frac{1}{2}}$ 4.3 Hz. The spectrum of a sample sealed under N_2 was unchanged after 10 d at ambient temperature: upon exposure to air, a solution in CD_2Cl_2 rapidly developed further resonances: δ +16.0 (s), +41.5 (d, *J* = 4.2), +81.1 (d, *J* = 4.2 Hz), assigned[7] to $[Fe_4S_3(^{15}NO)_7]^-$; +0.8 ($^{15}NO_3^-$); and +191.7 p.p.m. ($^{15}NO_2^-$).

Conversion of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ *to* $[Fe_2(SR)_2(NO)_4]$ (R = Me_2CH, Me_2CHCH_2, *or* n-C_5H_{11}).—Typically, to a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ (1.0 g, 2 mmol) in dry tetrahydrofuran (thf) (30 cm^3), was added under N_2, RSH (5 mmol) (R = Me_2CH, Me_2CHCH_2, or n-C_5H_{11}) and triethylamine (1.0 g, 10 mmol). The mixture was stirred for 4 h, and then toluene (500 cm^3) was added. The solution was then evaporated to dryness and the residue extracted with light petroleum (b.p. 40—60 °C) (4 × 50 cm^3). The resulting red solution was filtered, reduced to small volume, and chromatographed on silica (15 × 5 cm, eluted with light petroleum). The eluate was reduced to small volume, and cooled in an ice-bath, when crystals of $[Fe_2(SR)_2(NO)_4]$ were deposited: typical yields were 40—70%.

Crystal Structure Determination.—Crystals of $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$ suitable for *X*-ray examination were grown from 1,2-dichloroethane.

Crystal data. $C_{72}H_{60}Fe_2N_6O_{10}P_4S_4$, $M = 1\,533.13$, triclinic, $a = 10.999(5)$, $b = 12.748(4)$, $c = 14.020(7)$ Å, $\alpha = 67.13(4)$, $\beta = 83.31(4)$, $\gamma = 93.87(3)°$, $U = 1\,785.2$ Å^3, space group $P\bar{1}$ (no. 2), $Z = 1$, $D_c = 1.43$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 6.17$ cm^{-1}, $\lambda = 0.710\,69$ Å, $F(000) = 790$.

Data collection.[14] CAD4 diffractometer using graphite-monochromated Mo-K_α radiation ω—2θ scan mode, $1.5 \leqslant \theta \leqslant 25°$. 6 152 Reflections measured, of which 5 954 unique and 5 183 with $F_o \geqslant 4\sigma(F_o)$.

Structure solution and refinement. Patterson method, followed by SFLS and Fourier-difference cycles. The asymmetric unit comprises one $[N(PPh_3)_2]^+$ cation and half of an anion. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined with individual isotopic thermal parameters. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.000\,54F_o^2]$ gave final *R* and *R′* values of 0.034 and 0.056, with 563 refined parameters. Programs and computers used, and sources of scattering factor data, were as given in ref. 14.

Final refined co-ordinates for the non-hydrogen atoms are given in Table 1. Bond lengths and angles for the anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ are in Table 2. A perspective view of the anion, showing the atom-numbering scheme, is given in Figure 1, a view of the unit cell contents, showing the *trans* conformation of the anion, is given in Figure 2.

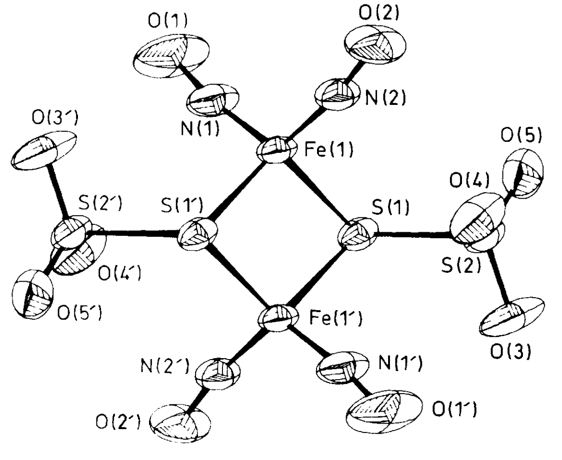

Figure 1. Perspective view of the anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ showing the atom-numbering scheme

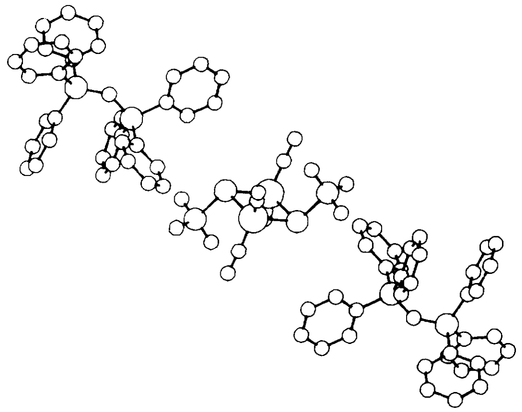

Figure 2. Perspective view of the unit cell contents showing the *trans* conformation of the anion

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

EHMO Calculations.—Extended Hückel molecular orbital calculations[15,16] were based on experimental geometries, and employed atomic parameters from the literature:[17–20] the calculations were performed using a VAX 11/785 computer.

Results and Discussion

Synthesis and Reactions.—Iron(II) sulphate reacts readily in aqueous solution with sodium thiosulphate and nitric oxide to give high (*ca.* 90%) yields of the sodium salt of the bis(μ-thiosulphato-*S*)-bis(dinitrosylferrate)(2−) anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ (see below for a description of the structure of the anion). The sodium salt is easily converted into the $[N(PPh_3)_2]^+$ salt by metathesis to provide a product amenable to combustion analysis and readily soluble in common organic solvents.

In a similar manner, the same product can be obtained, but in lower yield, by the use of sodium nitrite instead of nitric oxide. Despite the more modest yield (*ca.* 50%) of this route, the use of sodium nitrite makes this a convenient route to the ^{15}N-labelled product $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(^{15}NO)_4]$, useful for ^{15}N n.m.r. studies in organic solvents.

Salts of the $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ anion are dark brown in colour, and are stable for long periods, even in solution, in the absence of oxygen.

The preparation of the sodium salt by the sodium nitrite method produces, as well as brown $Na_2[Fe_2(S_2O_3)_2(NO)_4]$, a very air-sensitive green, water-soluble solid from which $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ can be extracted into CH_2Cl_2 in the presence of large organic cations. The colour of this material and its chemical behaviour are both reminiscent of the green mononuclear thiolato-complexes $[Fe(NO)_2(SR)_2]^-$, which are easily formed from,[1] and converted into,[1] the red-brown Roussin esters $[Fe_2(SR)_2(NO)_4]$. When the green solid was dissolved in methanol, the solution exhibited at 260 K an e.s.r. spectrum characterised by $g = 2.029$, $A(^{14}N) = 2.6$ G (2 N), typical[1–4] of a mononuclear dinitrosyl complex of type $[Fe(NO)_2X_2]^{n\pm}$. The identical spectrum was obtained by addition of excess of a saturated solution of sodium thiosulphate in methanol to a solution of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$, also in methanol, and hence we assign this spectrum to the mononuclear anion $[Fe(NO)_2(S_2O_3)_2]^{3-}$, formed as in equation (1). Similarly we tentatively identify the green solid, above, as $Na_3[Fe(NO)_2(S_2O_3)_2]$, although an analytically pure sample has not been obtained, because of its extreme air-sensitivity.

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

The reactions of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ with thiols RSH in the presence of NEt_3 as proton acceptor in thf solutions provide good yields of the Roussin esters $[Fe_2(SR)_2(NO)_4]$ for a range of R groups. E.s.r. examination of such a reaction mixture when R = Me_2CH revealed the presence of a single paramagnetic intermediate, a mononitrosyl characterized by $g = 2.040$ and $A(^{14}N) = 13.5$ G. Intermediates of this type have been observed[1,2] also in the reactions of $[Fe_4S_4(NO)_4]$ with Me_3CS^- or HS^- in dimethylformamide (dmf), and of $[Fe_2I_2(NO)_4]$ with Me_2CHSH in NEt_3–thf solutions, and have been assigned[2] constitutions of type $[Fe(NO)(SR)_3]^{3-}$. When the identical reaction of $Na_2[Fe_2(S_2O_3)_2(NO)_4]$ and Me_2CHSH was carried out in dmf rather than in thf, the same $g = 2.040$ species was observed, along with the well characterized[1] $[Fe(NO)_2(SCHMe_2)_2]^-$.

Crystal Structure of $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(NO)_4]$.—The structure consists of isolated ions, as expected. The anion is found to be dinuclear, and to lie across a centre of inversion: the central Fe_2S_2 ring is therefore strictly planar, and the pendant SO_3 groups are on opposite sides of the Fe_2S_2 ring, giving a *trans* conformation (Figure 2), precisely as observed for the neutral Roussin esters $[Fe_2(SR)_2(NO)_4]$ [R = Me,[10] Et,[5] n-C_5H_{11},[10] and Me_3C[10]]. The molecular dimensions (Table 2) are very similar to those found[5,10] in the neutral species: in particular the Fe–N–O angles are always found to be *ca.* 170°, and the Fe–Fe distances within the narrow range 2.686—2.713 Å. The two Fe–N–O fragments in each $Fe(NO)_2$ group are bent towards each other: the relationship between M–N–O bending and the N–M–N angles in $M(NO)_2$ groups has been discussed by Summerville and Hoffman,[21] and the $[Fe_2(SR)_2(NO)_4]$ and $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ structures are all consistent with their description. The dimensions of the S–SO_3 fragment are unexceptional and are very similar to those found, for example, in the $[S(S_2O_3)_2]^{2-}$ and $[S_2(S_2O_3)_2]^{2-}$ anions.[22,23] As in these two anions, the S–S–O angles found here are significantly less than tetrahedral, while the O–S–O angles are correspondingly greater.

In the cation, the two independent P–N distances are 1.584(4) and 1.587(4) Å, and the P–N–P angle is 134.5(1)°.

The crystal structure determination shows clearly the dinuclear character of the anion: the structure determination, and the elemental analysis of the $[N(PPh_3)_2]^+$ salt, show that the charge associated with the dinuclear anion is 2-, rather than 6-.[12] The near-linearity of the Fe–N–O fragments indicates that the nitrosyl ligands are bound formally as NO^+: this in turn indicates that the iron atoms are formally Fe^{-I}, d^9.

N.M.R. and I.r. Spectra.—The ^{15}N n.m.r. spectrum of $[N(PPh_3)_2]_2[Fe_2(S_2O_3)_2(^{15}NO)_4]$, labelled with ^{15}N at 99% isotopic enrichment, consists of a sharp singlet, in both $CDCl_3$ and CD_2Cl_2 solution. The spectrum in $CDCl_3$ was unchanged between +30 and −60 °C. This spectrum is thus unlike the ^{15}N spectra of $[Fe_2(SR)_2(^{15}NO)_4]$ (R = alkyl) which exhibit a singlet, assigned to the *trans*, C_{2h}, conformer, and a pair of doublets forming an AX system, assigned to the *cis*, C_{2v}, conformer.[7,9] The spectrum of the $[Fe_2(S_2O_3)_2(^{15}NO)_4]^{2-}$ ion is thus indicative of the presence solely of the *trans* conformer, as found in the solid state. Since the barriers to *trans* $\rightleftharpoons$ *cis* conversion in $[Fe_2(SR)_2(NO)_4]$ are[24] typically 60—80 kJ mol^{-1} for R = alkyl, it is unlikely that the barrier in $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ is so low that interconversion which is fast on the n.m.r. time-scale occurs even at −60 °C.

The ^{15}N chemical shift shows[25–27] that the near-linearity of the Fe–N–O fragments found in the solid state is preserved in solution; the formal oxidation state of the iron is thus Fe^{-I} in solution also.

Solutions containing $[Fe_2(S_2O_3)_2(^{15}NO)_4]^{2-}$ have long-term stability when kept under a N_2 atmosphere, but upon exposure to air the ^{15}N n.m.r. spectrum shows ready conversion into $[Fe_4S_3(^{15}NO)_7]^-$, together with $[^{15}NO_2]^-$ and $[^{15}NO_3]^-$.

In dichloromethane solution, the $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ anion exhibits the expected two NO stretching vibrations (of B_u and A_u symmetry in C_{2h}) at 1 787 and 1 757 cm^{-1} for the unlabelled ion, and at 1 748 and 1 718 cm^{-1} for the ^{15}NO complex. These wavenumbers differ somewhat from the values, 1 801 and 1 734 cm^{-1}, recorded[12] in a Nujol mull for a potassium salt described as $K_3[Fe(S_2O_3)(NO)_2]\cdot H_2O$.

EHMO Calculations.—Calculation of the net atomic charges at the experimental geometry of the anion $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ shows that the mean charge on the oxygen atoms of the thiosulphato ligand is −0.88. This, and the calculated close proximity of such oxygen atoms in the C_{2v} *cis* conformer (calculated assuming planarity of the Fe_2S_2 ring and a geometry at bridging sulphur identical to that in the C_{2h} *trans* conformer), may explain the occurrence of only the C_{2h} form in solution.

The electronic structure of dimers $M_2X_2(NO)_4$, containing the monoatomic bridging ligands X = Cl or I, have been comprehensively discussed by Summerville and Hoffmann,[21] on the basis of EHMO calculations. We have made similar calculations on $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$, which contains of course a polyatomic bridging ligand: apart from our inclusion of *d*-orbitals on the sulphur atoms, and the necessary reduction in symmetry from the D_{2h} of $M_2X_2(NO)_4$ to the C_{2h} of $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$, our results are broadly in accord with those reported by Summerville and Hoffmann, and consequently we make only a few additional remarks here.

At the experimental geometry (angle Fe–S–Fe 74.3°) and for a wide range of Fe–S–Fe angles on either side of the experimental value, the h.o.m.o.–l.u.m.o. gap exceeds 1 eV: hence,[21] diamagnetism is expected even though each iron centre is formally d^9, Fe^{-I}. Diamagnetism does not, in itself, require the existence of a metal–metal bond,[21] although the 18-electron rule formalism does require such a bond. In fact, we calculate that the Fe–Fe overlap population is no more than 0.06 at the experimental geometry: even when the Fe–S–Fe angle is set at 68.8°, corresponding to an Fe–Fe distance of 2.539 Å (identical to that in iron metal[28]), this overlap only rises to 0.11. The evidence, from these calculations, for the existence of an iron–iron bond in $[Fe_2(S_2O_3)_2(NO)_4]^{2-}$ is not strong.

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