$$\sigma_z = N^2+2N\sum_j p_j(q_j)_z \cos(\mathbf{r}_j.\mathbf{h}) + \sum_j\sum_k p_jp_k(q_j)_z(q_k)_z\cos[(\mathbf{r}_j-\mathbf{r}_k).\mathbf{h}]\,, \quad (86)$$

or

$$\sigma_z^{1/2} = |F_z| = N+\sum_j p_j(q_j)_z\cos(\mathbf{r}_j.\mathbf{h})\,, \quad (87)$$

with $(q_j)_z$ being the z component of $\mathbf{q}_j$ relative to the new set of axes:

$$(q_j)_z = -(q_j)_{x'}\sin\theta+(q_j)_{z'}\cos\theta\,. \quad (88)$$

In all of the previous discussion in this paper, we may then make the formal substitution

$$M|q| = \sum_j p_j(q_j)_z\cos(\mathbf{r}_j.\mathbf{h})\,. \quad (89)$$

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The Structure of Roussin's Black Salt, $CsFe_4S_3(NO)_7.H_2O$

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The structure of the Roussinate ion, $Fe_4S_3(NO)_7^-$, has been determined from the Cs^+ and K^+ salts. The unit-cell parameters of the Cs^+ salt are

$$a = 9{\cdot}5_9,\ b = 9{\cdot}7_8,\ c = 10{\cdot}1_2\ \text{Å},\ \ \alpha = 112{\cdot}8°,\ \beta = 103{\cdot}5°,\ \gamma = 96{\cdot}5°;$$

and the space group is $P\bar{1}$. The isolated ion has approximately C_{3v} symmetry, with a tetrahedral arrangement of Fe, and 3 S above the centers of three faces. All FeNO groups are roughly linear, and no NO bridges occur. Average distances are Fe_I(apex) $\cdots$ Fe_{II} = 2·70 Å, $Fe_{II}\cdots Fe_{II}$ = 3·57 Å, Fe–S = 2·23 Å, $Fe_I{\equiv}N$ = 1·57 Å, $Fe_{II}{=}N$ = 1·67 Å, N=O = 1·20 Å. Our preferred electronic structure has 4 non-bonding electrons on each Fe, and one electron pair in a highly delocalized molecular orbital among the 4 Fe atoms, thus accounting for the diamagnetism and the high absorption coefficient.

Introduction

A prerequisite to any valence theory of the black Roussinate ion $Fe_4S_3(NO)_7^-$ is its structure determination, reported here. The chemical evidence for various proposed structures has been summarized by Addison & Lewis (1955), who list Seel's (1942) proposal based on the FeS structure and on Manchot & Linckh's (1926) early proposal of the $\{[(NO)_2FeS]_3Fe(NO)\}^-$ formula; but Addison & Lewis, as well as earlier authors, have proposed similar structures in which NO bridges occur. None of the electronic interpretations of these proposed structures have accounted for the observed diamagnetism (Cambi & Szegö, 1931). It seems probable that the electronic interactions giving rise to this diamagnetism are sufficiently weak to account also for the intense transitions to low-lying electronic levels which are indicated by the high extinction coefficient of this ion. A preliminary discussion of the valence structure is therefore included as a part of this structure determination by the X-ray diffraction method.

Experimental procedure

The K salt and Na salt were prepared from $NaNO_2$, KHS ($KOH+H_2S$) and $FeSO_4$ by the method of Pawel (1882). The Cs salt was obtained by the addition of Cs_2SO_4 to a solution of the Na salt.

A crystal of the Cs salt having dimensions 0·15 × 0·15 × 0·05 mm. was photographed with Mo $K\alpha$ radiation at a precession angle of 25° in the Bucessera. Although the linear absorption coefficient is 62 cm.$^{-1}$, no corrections for absorption or extinction were made. The 1443 observed reflections were obtained from the $h0l$; $h1l$; $h2l$; $h3l$; $h4l$; $0kl$; $1kl$; $2kl$; $3kl$; $4kl$; $2h,\bar{h},l$; $2h+1,\bar{h},l$; $h,\bar{h},l$; $h-1,\bar{h},l$; $h,\bar{2}\bar{h},l$; $h,2h,l$; hhl, $h+1,h,l$; and $h+2,h,l$ reciprocal lattice planes. For the K salt, a total of 200 $h0l$ and $0kl$ reflections were estimated.

The crystals were triclinic with cell parameters

$$a = 9{\cdot}5_9,\quad b = 9{\cdot}7_8,\quad c = 10{\cdot}1_2\ \text{Å},$$
$$\alpha = 112{\cdot}8^\circ,\quad \beta = 103{\cdot}5^\circ,\quad \gamma = 96{\cdot}5^\circ$$

and $V = 835$ Å^3 for the Cs salt, and

$$a = 9{\cdot}5_1,\quad b = 9{\cdot}9_2,\quad c = 10{\cdot}2_2\ \text{Å}\,,$$
$$\alpha = 117{\cdot}4^\circ,\quad \beta = 102{\cdot}6^\circ,\quad \gamma = 101{\cdot}0^\circ$$

and $V = 802$ Å^3. Densities of $2{\cdot}4_7$ g.cm.$^{-3}$ for the K salt and $2{\cdot}7_2$ g.cm.$^{-3}$ for the Cs salt were measured by flotation methods, and indicate that there are two formula weights (2·02 and 2·04, respectively) in the unit cell.

The intensities were corrected for Lorentz and polarization factors (Waser, 1951), and placed on a common scale with the use of reflections common to two or more photographs. The usual method of Wilson was used to obtain preliminary scale and temperature factors; the intensity distribution clearly suggested that the space group is $P\bar{1}$, not $P1$.

Structure determination

A three dimensional Patterson function was then interpreted in terms of the expected peak heights in $P\bar{1}$: Cs · · · Cs, 34; Cs · · · Fe, 32; Cs · · · S, 20; Fe · · · Fe (not related by $\bar{1}$), 15; and Fe · · · S, 9. The observed vectors of height 19 or greater are shown in Table 1.

Table 1. *Vectors originating from* Cs

	u	v	w	height		u	v	w	height
a	0·10	0·675	0·038	36	I	0·775	0·925	0·01	27
b	0·275	0·34	0·10	45	II	0·475	0·65	0·10	20
c	0·525	0·425	0·10	39	III	0	0·05	0·125	22
d	0·525	0·275	0·16	35	IV	0·15	0·925	0·15	29
e	0·35	0·60	0·225	36	V	0·525	0·675	0·20	26
f	0·375	0	0·125	39	VI	0·66	0·35	0·225	25
g	0·05	0·26	0·125	32	VII	0·825	0·64	0·26	26
h	0·45	0·275	0·25	44	VIII	0·90	0·34	0	30
i	0·05	0·725	0·25	40	IX	0·46	0·775	0·40	29
j	0·725	0·60	0·35	35	X	0·50	0	0·50	2(29·5)
k	0·875	0·89	0·375	34	XI	0·10	0·96	0·34	24
l	0·975	0·56	0·40	38	XII	0·35	0·075	0·35	23
m	0·225	0·675	0·40	42	XIII	0·225	0·088	0	26
n	0·375	0·30	0·45	34	XIV	0·75	0·01	0·25	19
o	0·75	0·10	0·50	46					

In order to find the Cs · · · Cs vectors, the Patterson projections along [010] and [100] of the K salt were compared with this three-dimensional map of the Cs salt. A unique interpretation was found which resulted in the identification shown in Table 2.

Maxima of the expected height were also found for all of the Fe · · · Fe and Fe · · · S vectors.

Atomic coordinates for Cs, Fe and S, derived from these vectors, were surprisingly close to our final values listed below. These coordinates were refined by three cycles of least squares from $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0{\cdot}34$ to $R = 0{\cdot}26$ for 230 of the strongest innermost reflections. Values of $r = \Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4$ fell from 0·55 to 0·18. Then four least-squares refinements of Cs, Fe and S atoms were carried out using about 1400 observed reflections, during which the values of R–r fell from 0·38–2·14 to 0·29–0·60.

The N and O atoms were located, without any chemical assumptions, from a three-dimensional difference electron density map from which Cs, Fe and S were subtracted. A summary of this map, and identification of peaks is shown in Table 3. A comparison of the coordinates of the first eight peaks of Table 3 with our final coordinates indicates that refinement of these heavy atoms was not complete at this stage. Moreover, all of these peaks were broadened in the region of the Cs, Fe or S positions.

Refinement was then continued with 1395 of the observed reflections. A total of 48 of the very outermost reflections were omitted in order to conserve computing time, which was 34 minutes per cycle. After seven cycles of three-dimensional least squares, refinement values of $R = 0{\cdot}193$ and $r = 0{\cdot}118$ were obtained. Isotropic temperature factors for Cs ($B = 2{\cdot}9$ Å^2), Fe (2·6 to 2·9 Å^2), S (3·0 Å^2), O (3·4 to 4·3 Å^2) and N (2·1 to 3·1 Å^2) were then replaced by anisotropic temperature factors for Cs, Fe and S. The final four cycles of refinement gave $R = 0{\cdot}144$ and $r = 0{\cdot}076$. It is felt that this final refinement is due chiefly to changes of the scale and isotropic temperature factors, and not to the anisotropy introduced at this point. Further refinement of the scale and temperature factors may still be possible, but the distance parameter shifts were already well within our standard deviations before this final anisotropic refinement was

Table 2. *Identification of peaks in Table* 1

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	*m*	*n*	*o*
Cs · · · Cs	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—
Cs–Fe	—	—	1	—	1	—	—	1	1	1	1	1	—	—	1
Cs · · · S	—	1	—	—	—	—	—	—	—	—	—	—	1	—	—
Fe · · · Fe	1	1	—	—	—	1	—	—	—	—	—	—	1	1	—
Fe–S	—	—	—	—	—	—	2	1	1	—	—	—	—	—	2

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Cs · · · Cs	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cs · · · Fe	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cs · · · S	—	—	—	—	1	1	1	—	—	—	1	—	—	—
Fe · · · Fe	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Fe · · · S	2	—	—	3	—	—	—	—	3	—	—	1	1	—

Table 3. *Summary of three dimensional difference map*

x	y	z	Height	Identification
0·26	0·18	0·04	34	Cs shift
0·75	0·525	0·138	21	Fe_1 shift
0·58	0·73	0·25	24	Fe_2 shift
0·70	0·35	0·325	19	Fe_3 shift
0·96	0·69	0·425	19	Fe_4 shift
0·515	0·49	0·15	17	S_1 shift
0·89	0·79	0·275	12	S_2 shift
0·925	0·45	0·30	20	S_3 shift
0·163	0·550	0·125	17	O_1
0·200	0·500	0·000	24	N_1
0·395	0·863	0·158	19	O_2
0·475	0·800	0·200	20	N_2
0·613	0·088	0·200	18	O_3
0·663	0·208	0·238	25	N_3
0·288	0·850	0·415	21	O_4
0·163	0·825	0·415	22	N_4
0·413	0·163	0·413	20	O_5
0·400	0·213	0·525	21	N_5
0·700	0·540	0·625	17	O_6
0·700	0·500	0·500	24	N_6
0·033	0·138	0·275	18	O_7
0·040	0·200	0·413	24	N_7
0·050	0·813	0·025	18	H_2O
0·238	0·200	0·263	14	False
0·843	0·145	0·088	13	False

Table 4. *Summary of agreement between F_o and F_c*

Class	R
hkl	0·144
$0kl$	0·13
$h0l$	0·19
$hk0$	0·17
h odd	0·14
k odd	0·14
l odd	0·14
$h+k$ odd	0·14
$h+l$ odd	0·14
$k+l$ odd	0·15
$h+k+l$ odd	0·14

made. Our final agreement for various classes of planes is shown in Table 4, and final distance parameters Table 5.

Standard deviations in atomic coordinates, computed from diagonal terms only, are 0·004 Å for Cs, 0·007 Å for Fe, 0·014 Å for S, 0·035 Å for O and 0·040 Å for N. These values lead to standard derivations of 0·01 Å for Fe · · · Fe, 0·02 Å for S · · · S, $0{\cdot}01_5$ Å for Fe · · · S, 0·04 Å for Fe · · · N and 0·06 Å for N · · · O distances.

Results and discussion

A drawing of the Roussinate ion is shown in Fig. 1, and projections of the structure along [001] and [010] are shown in Figs. 2 and 3. Bond distances are summarized in Table 6. All other distances in the crystal seem to be normal. The H_2O molecule appears not to form hydrogen bonds, since no contacts are less than 3 Å.

Table 5. *Final atomic coordinates*

Atom	$\pm x$	$\pm y$	$\pm z$
Cs	0·263	0·140	0·075
Fe_1	0·780	0·565	0·165
Fe_2	0·603	0·739	0·294
Fe_3	0·712	0·412	0·322
Fe_4	0·985	0·749	0·427
S_1	0·561	0·481	0·172
S_2	0·824	0·818	0·275
S_3	0·931	0·492	0·305
O_1	0·177	0·551	0·118
O_2	0·396	0·855	0·141
O_3	0·636	0·090	0·210
O_4	0·285	0·846	0·439
O_5	0·419	0·165	0·406
O_6	0·695	0·532	0·618
O_7	0·028	0·140	0·280
H_2O	0·056	0·822	0·012
N_1	0·213	0·497	0·001
N_2	0·476	0·796	0·189
N_3	0·673	0·217	0·233
N_4	0·154	0·811	0·420
N_5	0·403	0·208	0·534
N_6	0·706	0·491	0·498
N_7	0·041	0·199	0·411

Table 6. *Summary of bond distances within the* $Fe_4S_3(NO)_7^-$ *ion* (Fe_1 = Apex)

Fe_1–Fe_2	2·736 Å	Fe_1–N_1	1·57 Å
Fe_1–Fe_3	2·691	Fe_2–N_2	1·71
Fe_1–Fe_4	2·702	Fe_2–N_5	1·63
Fe_2–Fe_3	3·558	Fe_3–N_3	1·73
Fe_2–Fe_4	3·567	Fe_3–N_6	1·66
Fe_3–Fe_4	3·594	Fe_4–N_4	1·70
Fe_1–S_1	2·192	Fe_4–N_7	1·61
Fe_1–S_2	2·236	N_1–O_1	1·25
Fe_1–S_3	2·157	N_2–O_2	1·13
Fe_2–S_1	2·289	N_3–O_3	1·17
Fe_2–S_2	2·247	N_4–O_4	1·21
Fe_3–S_1	2·197	N_5–O_5	1·26
Fe_3–S_3	2·226	N_6–O_6	1·17
Fe_4–S_2	2·258	N_7–O_7	1·21
Fe_4–S_3	2·274		
S_1–S_2	3·549		
S_1–S_3	3·462		
S_2–S_3	3·551		

Our results compare favorably with those of Thomas, Robertson & Cox (1958) who determined the structure of the red salt ethyl ester $Fe_2S_2(NO)_4(C_2H_5)_2$. Distances obtained by them are Fe · · · Fe = 2·72 Å, Fe · · · S = 2·26 Å, Fe · · · N = 1·66 Å and N · · · O = 1·17 Å. The SFeS angle is 106° in the red salt ester and 106° in the black salt ion. Our Fe · · · S distance of 2·23 Å compares favorably with the distances of 2·26 Å in pyrite (Parker & Whitehouse, 1932) and 2·23 to 2·25 Å in marcasite (Buerger, 1937).

A comparison of our results with the radii of 0·70 Å for N–, 0·60 Å for N=, 1·04 Å for S– and 1·23 Å for Fe– given by Pauling (1940) allows us to place some of the bonding electrons. The N=O distance of 1·20 Å is the expected double bond distance (Dulmage, Meyers & Lipscomb, 1951). The Fe–S distance of 2·23 Å indicates a single bond, and is, quite reasonably, about 0·04 Å shorter than the distance predicted for the slightly less strongly bound d^2sp^3 Fe from which the radius was determined. The Fe=N distance of 1·67 Å (excluding the apex $Fe_1{\equiv}N_1$ distance of

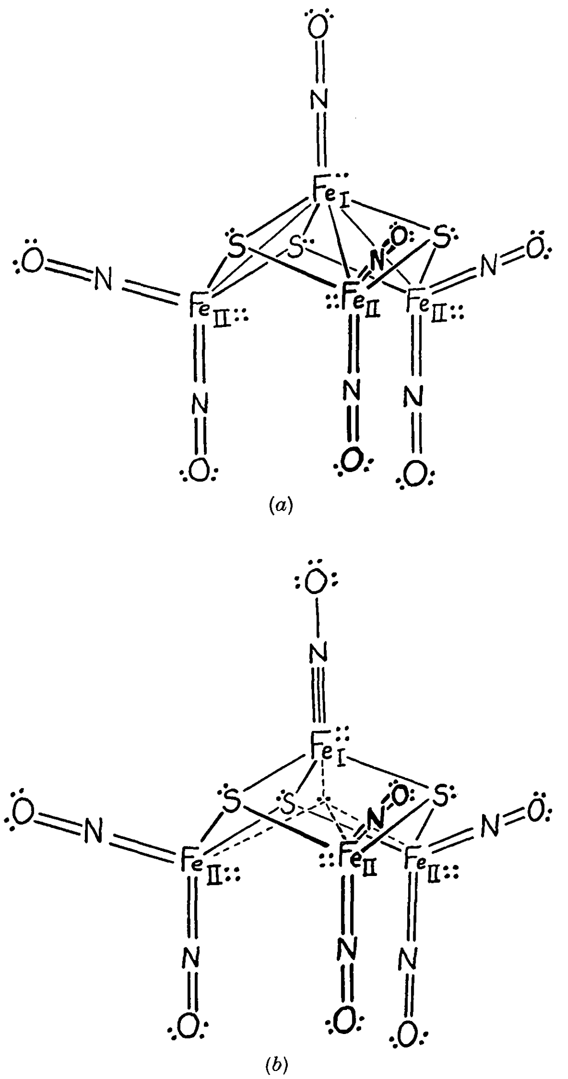

Fig. 1. (*a*) A classical valence structure for the Fe$_4$S$_3$(NO)$_7^-$ ion. All orbitals are filled in agreement with the diamagnetism, but bonding around Fe$_{\rm I}$ is not satisfactory. (*b*) A preferred valence structure for the Fe$_4$S$_3$(NO)$_7^-$ ion. The dotted lines indicate a four-center molecular orbital among the four Fe atoms which is weakly bonding. Resonance of the type Fe$\equiv$N–O$^-$ will improve the charge distribution.

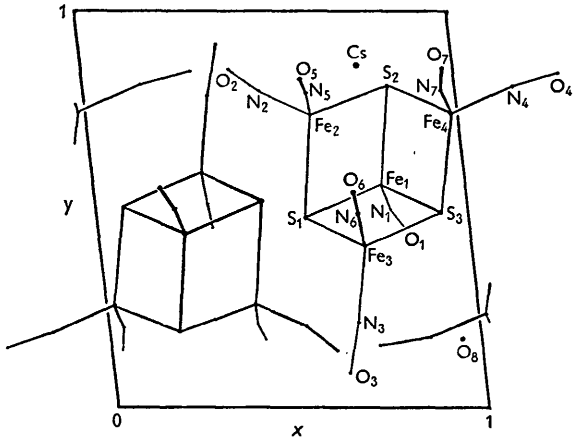

Fig. 2. Projection of the structure along the *c* axis.

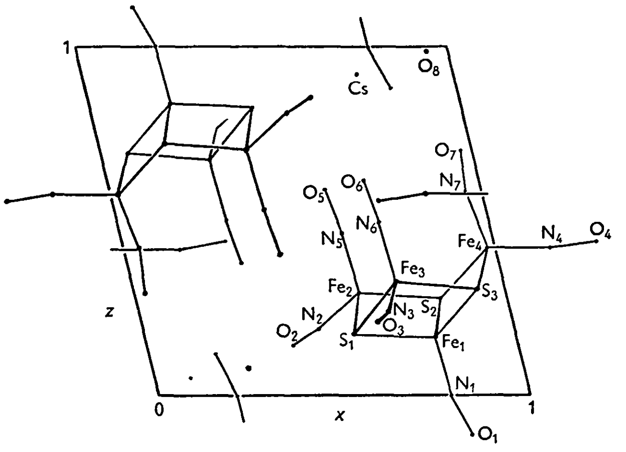

Fig. 3. Projection of the structure along the *b* axis.

1·57 Å) is 0·26 Å shorter than the Fe–N single bond distance, and is regarded here as a double bond. The Fe$_{\rm I}$–Fe$_{\rm II}$ distance of 2·70 Å is significantly longer than the single bond distance of 2·46 Å for d^2sp^3 Fe and use of Pauling's equation, $d = d_1 - 0{\cdot}6 \log n$, for bond order suggests that it is a bit less than half of a bond. Presumably this interaction is sufficiently strong to give bonding levels so that the electrons are all paired up, and low-lying excited levels so that the absorption spectrum lies in the visible region. Hence in Fig. 1(*a*) we have drawn bonds from Fe$_{\rm I}$ to Fe$_{\rm II}$ (Johansson & Lipscomb, 1958). It is possible to show that this valency scheme fills all of the electronic levels, thus accounting for the observed diamagnetism (Cambi & Szegö, 1931). Assume that all of the nine $4s3d^54p^3$ orbitals are used. Fe$_{\rm I}$ forms 8 bonds and hence can accommodate one non-bonding pair, while Fe$_{\rm II}$ forms 7 bonds and hence can accommodate two non-bonding pairs. Then, counting the 4 non-bonding electrons on each O and two on each S, the ion has a total of 48 non-bonding electrons, which together with the 80 bonding electrons give an excess of just one electron over the 127 positive charges from the closed shell O^{+6}, N^{+5}, Fe^{+8} and S^{+6} configurations. Moreover, O, N and S have octets and Fe has 18 electrons beyond the argon core just as classical valence theory would suggest from many examples. These electrons fill 4 orbitals on each of O, N and S and 9 orbitals on Fe, and leave the ion with a single negative charge. The use of this idea, that the effective atomic number of Fe is 18, places too high formal charges on Fe (-2 on Fe$_{\rm I}$ and -3 on Fe$_{\rm II}$), and hence delocalization of these electrons by resonance with structures involving O$^-$ is required; but it is surprising how well this concept works in complex situations, even though more complete discussions do not always agree in all of the details.

A more detailed discussion (Fig. 1(*b*)) gives us an alternative to the above assumptions of localized bonds. Because of the low symmetry C_1 for Fe_{II} and C_{3v} for Fe_{I}, the fivefold degeneracy of the *d* levels is split completely in Fe_{II}; and splits in Fe_{I} into axially symmetric (*A*) orbitals, *s*, p_z and d_{z^2}, of different energies; into separate doubly degenerate pairs, p_x, p_y and d_{xy}, d_{yz} of symmetry E_1 at 90° angles in x, y; and into a doubly degenerate pair d_{xy} and $d_{x^2-z^2}$ of symmetry E_1' at 45° angles in x, y. We shall assume that the bonding situation about Fe_{II} is very similar to that of Fe in the $Fe_2S_2(NO)_4^{-2}$ ion (Fig. 4). Without making use of orbitals of higher energy than those normally considered in the valence shell, the pair of E_1' levels is oriented so that it bonds weakly to the 3 S, the 3 Fe_{II} or the apex NO group. No satisfactory structures seem to be possible in which these E_1' orbitals are vacant, and hence we fill them with two non-bonding electron pairs. Already, then, this more detailed picture differs from the results described above in which only one electron pair on Fe_{I} is non-bonding. In order to avoid an inordinately high formal charge on Fe_{I}, it seems reasonable to assume that the $Fe_{I}{\equiv}N{-}O^-$ predominates over the $Fe{=}N{=}O$ electronic structure. This conclusion is indicated by the $Fe_{I} \cdots N$ distance of 1·57 Å and the $N \cdots O$ distance of 1·25 Å at the apex which are different in the expected directions, though perhaps not significantly so in view of the standard deviations, from the average over the other six groups for which $Fe \cdots N$ is 1·67 Å and $N \cdots O$ is 1·20 Å. Hence a triple bond to N, two non-bonding pairs in the E_1' orbitals, and three single bonds to the 3 S atoms account for all but one of the Fe_{I} orbitals. Thus we have used, respectively, orbitals of symmetry $A+E_1$, E_1' and $A+E_1$, thereby leaving one orbital of symmetry *A* to interact with the three Fe_{II} orbitals. The remaining electron pair can now be placed into the one low-lying electronic level formed from these four Fe orbitals. This electron pair is strongly delocalized and has low-lying excited levels. To us, this more detailed valence discussion accounts for the diamagnetism and the intense absorption in a more satisfactory way than the more classical and more localized valence structure derived above.

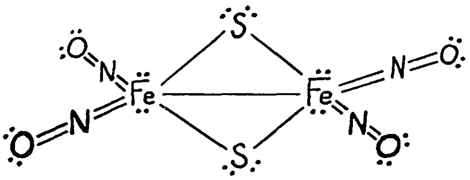

Fig. 4. The structure of the $Fe_2S_2(NO)_4^{-2}$ ion as suggested by the result of study of the red salt ester by Thomas, Robertson & Cox (1958). The bonding about Fe is similar to the bonding about Fe_{II} in the $Fe_4S_3(NO)_7^-$ ion.

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