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Preliminary communication

ROUSSIN'S RED SALT, $[(\mu\text{-S})_2Fe_2(NO)_4]^{2-}$; SOME CHEMISTRY AND AN INTERESTING COMPARISON WITH $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$

DIETMAR SEYFERTH and MICHAEL K. GALLAGHER
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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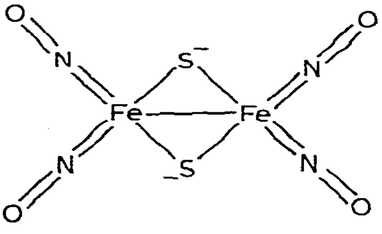
Summary

Reactions of Roussin's red salt in THF with monofunctional electrophiles have given products of type $(\mu\text{-RS})_2Fe_2(NO)_4$, with R = CH_3, C_2H_5, $CH_2{=}CHCH_2$, $PhCH_2$, Me_3Sn, Ph_3Sn, Ph_3Pb, PhHg and $\eta^5\text{-}C_5H_5Fe(CO)_2$, all of which are more or less air-sensitive, especially in solution. Similar reactions attempted with difunctional electrophiles, L_nMX_2, were unsuccessful except in the case of $(Ph_3P)_2PtCl_2$ which gave a monomeric product, $(Ph_3P)_2PtS_2Fe_2(NO)_4$ of as yet unknown structure. A comparison is made between the reactivity of $[(\mu\text{-S})_2Fe_2(NO)_4]^{2-}$ and $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$.

Roussin's "red salt" was first reported in 1858 [1], but it was only in 1882 that Pavel [2], by means of careful purification and analysis, correctly determined the composition of the potassium salt as "$Fe(NO)_2SK+2H_2O$" and suggested the dimeric constitution "$Fe(NO)_2S,Fe(NO)_2,K_2S$". The potassium salt was found to react with ethyl iodide to give a red, crystalline diethyl derivative, $(C_2H_5S)_2Fe_2(NO)_4$, whose dimeric constitution was confirmed by Hofmann and Wiede [3] and whose structure finally was elucidated by means of X-ray crystallography in 1958 (Fig. 1) [4]. Although the structure of the



(I)

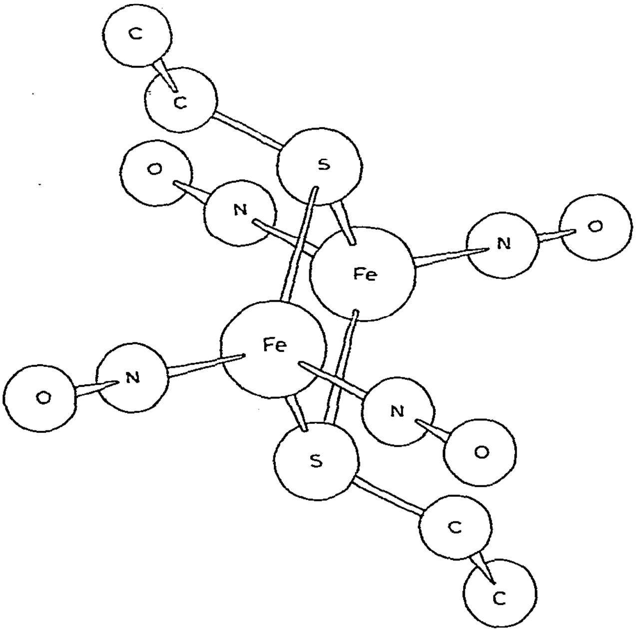


Fig. 1. The molecular structure of $(\mu\text{-}C_2H_5S)_2Fe_2(NO)_4$ [4].

anion of Roussin's red salt has not been established, it has been assumed, quite reasonably, that its structure is quite similar to that of its diethyl derivative, i.e., that it too has a planar S_2Fe_2 ring with tetrahedral geometry about the iron atoms, I. Curiously, the chemistry of this interesting dianion has received little attention, despite the fact that it has been known now for over 120 years and has been mentioned in many popular inorganic textbooks [5].

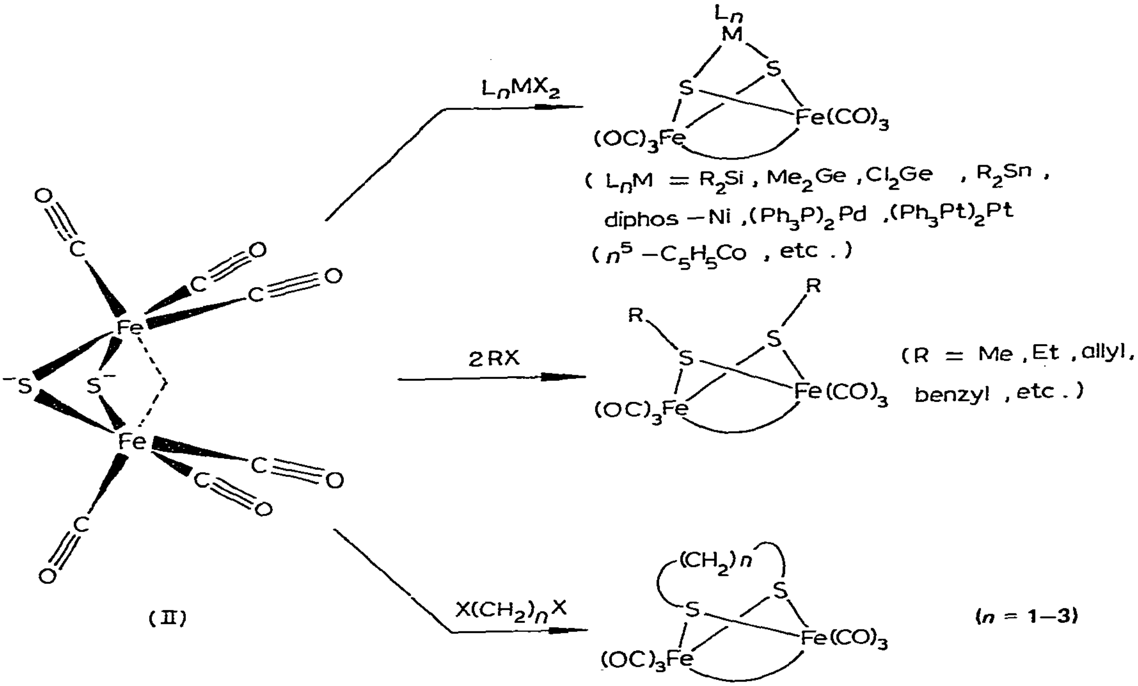
In recent research we have found that reductive cleavage of the S—S bond of μ-dithio-bis(tricarbonyliron) by metal hydrides gives a reactive, sulfur-centered dianion, II (eq. 1) [6—8]. Dianion II reacts readily with organic

$$(\mu\text{-}S_2)Fe_2(CO)_6 + 2MH \rightarrow \underset{(II)}{[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}} + 2M^+ + H_2 \qquad (1)$$

(MH = KH, $LiBEt_3H$, $LiAl(OBu\text{-}t)_3H$, $KB(s\text{-}Bu)_3H$)

halides, α,ω-dihalides and various main group and transition metal dihalides (Scheme 1). Although the structure of a salt of dianion II has not yet been determined, an X-ray diffraction study of the diethyl derivative, $(\mu\text{-}C_2H_5S)_2$-$Fe_2(CO)_6$, has been reported by Dahl and Wei (Fig. 2) [9].

A comparison of the structures of $(\mu\text{-}C_2H_5S)_2Fe_2(NO)_4$ and $(\mu\text{-}C_2H_5S)_2$-$Fe_2(CO)_6$ is of interest. In the nitrosyl complex, as mentioned, the iron atoms are tetrahedrally coordinated (excluding a possible iron—iron bond) and a planar S_2Fe_2 ring results. The Fe···Fe distance is 2.72 Å. More important for the purposes of this discussion, the S····S non-bonded distance is 3.63 Å. In contrast, in the hexacarbonyl complex the iron atoms are octahedrally coordinated and the S_2Fe_2 ring is puckered. In this case the bent Fe—Fe bond



SCHEME 1

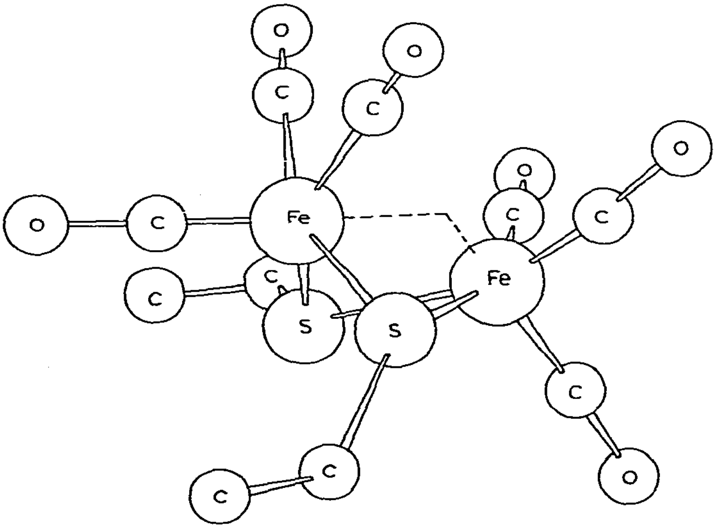


Fig. 2. The molecular structure of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ [9].

indicated by the dotted lines in Fig. 2 is included as a coordination position. The Fe···Fe distance in $(\mu\text{-}S_2)Fe_2(CO)_6$ is 2.54 Å and the S····S non-bonded distance is 2.93 Å. If one assumes that the structures of the two dianions, I and II, contain $S_2Fe_2L_n$ units not markedly different from those found in the respective diethyl esters, then one might expect their chemistries to be quite different. Both would be expected to react with sterically unencumbered electrophiles such as primary halides. On the other hand, dianion I should be able to react with more hindered electrophiles, while dianion II, with closer sulfur atoms and more substituents on the iron atoms, might be expected to be less reactive. The closer sulfur atoms in dianion II should facilitate reactions with difunctional reagents to form products in which an organic group, a metalloid or a metal atom has bridged the two sulfur atoms. In view of these considerations, we have undertaken a study of the chemistry of Roussin's red salt in parallel with our investigations of $(\mu\text{-}S_2)Fe_2(CO)_6$, $(\mu\text{-}Se_2)Fe_2(CO)_6$ and the di- and monoanions which may be prepared from them [6—8,10,11]. As Scheme 1 shows, dianion II does indeed react readily with alkyl halides and with difunctional reagents. However, all attempts to isolate stable products from the reaction of dianion II with Me_3SnCl and Ph_3SnCl were unsuccessful.

Roussin's red salt was prepared by the method of Pavel [2] (see also ref. [12]) from Roussin's "black ammonium salt" [1,2,12] and isolated as a hydrate, $Na_2[(\mu\text{-}S)_2Fe_2(NO)_4]\cdot 8H_2O$. It dissolves in THF to give a deep red solution. Such solutions were allowed to react at room temperature (under nitrogen with stirring) with an excess of various organic halides*. In each case sodium halide precipitated and an orange-red solution resulted. Column chromatography (silicic acid) gave the expected product in high yield. Prepared in this manner were $(\mu\text{-}RS)_2Fe_2(NO)_4$, R = CH_3 (91%), C_2H_5 (89%), $CH_2{=}CHCH_2$ (91%) and $PhCH_2$ (93%). Reactions of Roussin's red salt with organometallic monohalides also proceeded well. The reaction of dianion I with a slight excess of trimethyltin bromide gave air-sensitive red-purple crystals of $(\mu\text{-}Me_3SnS)_2Fe_2(NO)_4$ in 60% yield. Prepared in similar fashion were red-purple $(\mu\text{-}Ph_3SnS)_2Fe_2(NO)_4$ (78%), dark red-purple $(\mu\text{-}Ph_3PbS)_2\text{-}Fe_2(NO)_4$ (99%) and red $(\mu\text{-}PhHgS)_2Fe_2(NO)_4$ (33%). A reaction of Roussin's red salt with two molar equivalents of $[\eta^5\text{-}C_5H_5Fe(CO)_2THF]^+BF_4^-$ [13] in THF (room temperature for 15 h) gave, after column chromatography (silicic acid, CH_2Cl_2), the tetranuclear iron complex $(\mu\text{-}\eta^5\text{-}C_5H_5Fe(CO)_2S)_2Fe_2(NO)_4$, isolated as the purple-black 1:1 CH_2Cl_2 solvate in quantitative yield. Characteristic properties of the products are summarized in Table 1.

We assume that the Fe_2S_2 geometry in all of these products is much the same as it was found to be in $(\mu\text{-}C_2H_5S)_2Fe_2(NO)_4$ [4]. However, we have been able to prepare a bis(triphenylphosphine)platinum(II) derivative of Roussin's red salt by the reaction of the latter with an equimolar quantity of *cis*-$(Ph_3P)_2PtCl_2$ in THF. Column chromatography (silicic acid/CH_2Cl_2) gave black, crystalline $(Ph_3P)_2PtS_2Fe_2(NO)_4$, m.p. 198—201°C, in 95% yield**. The molecular weight of the product, determined by field desorption mass spectroscopy (m/e = 1015 with respect to ^{195}Pt) and vapor pressure osmometry in dichloromethane (1010 observed vs. 1015.49 calcd.) corresponded to that of the monomer. In view of the long non-bonded S····S distance in $(\mu\text{-}C_2H_5S)_2\text{-}Fe_2(NO)_4$, we suggest that formation of this apparently monomeric $(Ph_3P)_2Pt^{II}$ derivative may occur with some puckering of the Fe_2S_2 ring which serves to bring the sulfur atoms closer to each other. We hope that an X-ray diffraction

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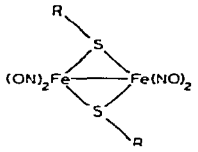
*These and all other reactions of Roussin's red salt and all subsequent operations were carried out under nitrogen using Schlenk techniques or in a Vacuum Atmospheres glove box. It should be noted that all $(\mu RS)_2Fe_2(NO)_4$ complexes, and especially the $(\mu\text{-}R_nMS)_2Fe_2(NO)_4$ complexes, are more or less sensitive to air in the solid state, much more so when in solution.

**Anal. Found: C, 42.43; H, 2.76; N, 5.45%. Calcd. for $C_{36}H_{30}O_4N_4S_2P_2Fe_2Pt$: C, 42.58; H, 2.98; N, 5.52%; ν(NO) 1735, 1690 cm^{-1}.

TABLE 1

$(\mu\text{-RS})_2Fe_2(NO)_4$ COMPLEXES PREPARED[a]



R =	Color	M.p. (°C)	ν(NO) (cm^{-1})
CH_3	red-black	92—93	1778, 1755 (in CH_2Cl_2)
C_2H_5 (known compound)	red-black	78.5—80 (lit. [12] 78)	1778, 1750 (in $CHCl_3$)
$CH_2{=}CHCH_2$	red-black	57—58	1782, 1754 (in $CDCl_3$)
$C_6H_5CH_2$	red-purple	148—150	1781, 1753 (in $CDCl_3$)
Me_3Sn	red-purple	182—185	1765, 1735 (in $CDCl_3$)
Ph_3Sn	red-purple	187—189	1760, 1732 (in CD_2Cl_2)
Ph_3Pb	red-purple	180 (dec)	1758, 1723 (in $CHCl_3$)
PhHg	red	195—200 (dec)	1770, 1740 (in $CHCl_3$)
η^5-$C_5H_5Fe(CO)_2$ (1:1 CH_2Cl_2 solvate)	black-purple	165—168 (dec)	1745, 1720 (in CD_2Cl_2)

[a] All compounds gave satisfactory results (±0.4%) for C, H and N on combustion analysis. The proton NMR spectra and the IR spectra of all compounds were in agreement with the presence of the indicated organic groups. For all compounds the molecular ion was observed in the mass spectrum (either electron impact at 70 eV or field desorption at 20 eV).

study of the platinum derivative will answer this interesting structural question.

Attempts to prepare analogous monomeric derivatives by reactions of Roussin's red salt with main group and other transition metal dihalides have thus far been unsuccessful. We report our preliminary results because the expected differences in the chemistries of $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$ and $[(\mu\text{-S})_2Fe_2NO)_4]$ have indeed been observed in the laboratory. Our work on the chemistry of Roussin's red salt and related metal-nitrosyl complexes is continuing. We note that W. Beck and his coworkers also have carried out some studies of reactions of Roussin's red salt [14]. Most notably, they have prepared the anhydrous tetraphenylarsonium salt and have converted this to the bridged mercapto complex, $(\mu\text{-HS})_2Fe_2(NO)_4$.

Acknowledgements

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References

1 L. Roussin, Compt. Rend. Acad. Sci. Paris, 46 (1858) 224; Liebigs Ann. Chem., 107 (1858) 120; Ann. Chim. Phys., [3] 52 (1858) 258.

2 O. Pavel, Ber., 15 (1882) 2600.

3 K.A. Hofmann and O.F. Wiede, Z. Anorg. Chem., 9 (1895) 295.

4 J.T. Thomas, J.H. Robertson and E.G. Cox, Acta Cryst., 11 (1958) 599.

5 (a) H.E. Roscoe and C. Schorlemmer, A Treatise on Chemistry, 5th edition, Vol. II, Macmillan and Co., London, 1913, pp. 1242—1243; (b) J.N. Friend (Ed.), A Text-Book of Inorganic Chemistry, Vol. IX, Part II, Charles Griffin & Co., London, 1925, pp. 178—182; (c) P.C.L. Thorne and E.R. Roberts, Fritz Ephraim Inorganic Chemistry, 4th edition, Oliver and Boyd, Edinburgh, 1943, pp. 679—680; (d) N.V. Sidgwick, The Chemical Elements and Their Compounds, Vol. II, Oxford University Press, 1950, pp. 1373—1374; (e) H.J. Emeléus and J.S. Anderson, Modern Aspects of Inorganic Chemistry, 2nd edition, Routledge & Kegan Paul Ltd., London, 1952, p. 416; (f) F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 4th edition, John Wiley & Sons, New York, 1980, p. 764.

6 D. Seyferth and R.H. Henderson, J. Amer. Chem. Soc., 101 (1979) 508.

7 D. Seyferth, R.S. Henderson and L.-C. Song, J. Organometal. Chem., 192 (1980) C1.

8 D. Seyferth, L.-C. Song and R.S. Henderson, J. Amer. Chem. Soc., 103 (1981), in press.

9 L.F. Dahl and C.F. Wei, Inorg. Chem., 2 (1963) 328.

10 D. Seyferth, R.S. Henderson and M.K. Gallagher, J. Organometal. Chem., 193 (1980) C75.

11 D. Seyferth and R.S. Henderson, J. Organometal. Chem., 204 (1981) 333.

12 F. Seel in G. Brauer (Ed.), Handbook of Preparative Inorganic Chemistry, 2nd ed., Vol. 2, Academic Press, New York, 1965, pp. 1763—1764.

13 D.L. Reger and C. Coleman, J. Organometal. Chem., 131 (1977) 153.

14 W. Beck, private communication, May 1981; W. Beck, R. Grenz, F. Götzfried and E. Vilsmaier, Chem. Ber., in press.