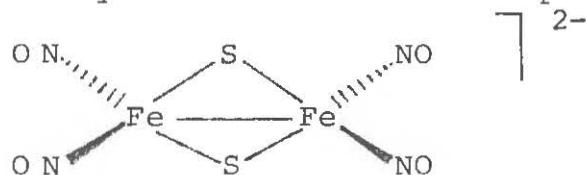


"Roussin's Red Salt Revisited:  
Metal Nitrosyl Dimers and Clusters"

Timothy D. Weatherill      Final Seminar

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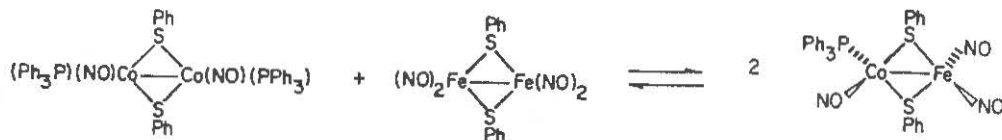
Since its preparation in 1858, "Roussin's Red Salt,"  $M_2Fe_2(\mu-S)_2(NO)_4$  ( $M = Na^+, K^+$ ) [1], has elicited little interest from the inorganic community despite the intense activity in the areas of metal nitrosyls and iron-sulfur compounds.



While our initial investigations into the chemistry of Roussin's Red Salt began as a simple query of the reactivity of this compound towards electrophiles [2], our findings prompted us to investigate the synthesis of metal nitrosyl dimers in general, later evolving into a study of metal nitrosyl clusters.

Metathetical replacement of the bridging iodo ligands in  $Fe_2(\mu-I)_2(NO)_4$  [3] with  $Na_2E$  ( $E = S, Se, Te$ ) was found to be an efficient route to the corresponding Red Salts. Anhydrous solutions of  $Fe_2(\mu-E)_2(NO)_4^{2-}$  could be generated and derivatized with a variety of alkylating or metalating agents. Similarly, the compound  $[Co(NO)_2I]_x$  [3] was found to be a versatile starting material for the esters  $Co_2(\mu-ER)_2(NO)_4$ .

The  $Co_2(\mu-ER)_2(NO)_4$  dimers possess two additional electrons compared to the 34 electron  $Fe_2(\mu-ER)_2(NO)_4$  species; these electrons are assumed to occupy an orbital which is mainly metal-metal anti-bonding. [4] Relative kinetic stabilities of these dimers were studied from the perspective of reactivity. "Mixed esters" of the type  $M_2(\mu-SR)(\mu-SR')(NO)_4$  could be isolated for the formally M-M bonded 34e dimers whereas the 36e mixed esters prove to be too labile to isolate. Extension of the mixed ester synthesis led to the preparation of a mixed-metal dimer:

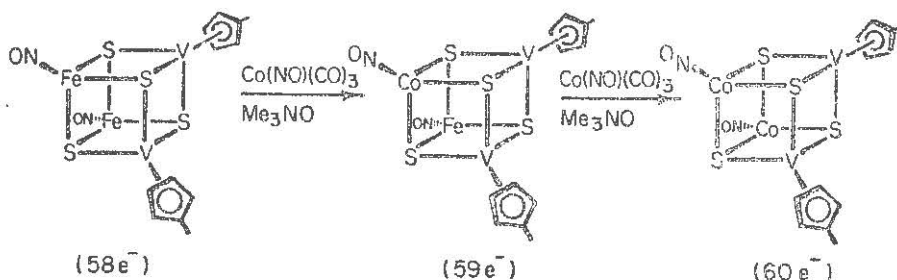


A study of the temperature dependence of the  $K_{eq}$  for this process indicated that the reaction is mildly endothermic, the driving force being a favorable entropy term.

Our studies on metal nitrosyl sulfides were extended to the synthesis of mixed-metal sulfide clusters. The compound  $(MeCp)_2V_2S_4$  exhibits rich and varied coordination chemistry and has been used

to prepare a number of clusters containing both early and late transition metals [5]. In this way complexes of the type  $(\text{MeCp})_2\text{V}_2\text{S}_4 \cdot \text{ML}_n$  were prepared for  $\text{ML}_n = \text{Fe}(\text{NO})_2$ ,  $\text{CoCp}$ ,  $\text{Ir}(\text{PPh}_3)\text{Cl}$ , and  $[\text{Ni}(\text{MeCp})_2\text{V}_2\text{S}_4]$ .

A series of novel, electron deficient cubanes  $(\text{MeCp})_2\text{M}_2\text{S}_4\text{M}'_2 - (\text{NO})_2$  ( $\text{M} = \text{V}, \text{Mo}$ ;  $\text{M}' = \text{Fe}, \text{Co}, \text{Ni}$ ) have been prepared [6]. The  $\text{V}_2\text{S}_4\text{Fe}_2$  cubane undergoes transmetalation with  $\text{Co}(\text{CO})_3\text{NO}$  to produce the hybrid species  $(\text{MeCp})_2\text{V}_2\text{S}_4\text{CoFe}(\text{NO})_2$ :



Other probable cubanes obtained from  $(\text{MeCp})_2\text{V}_2\text{S}_4$  include  $(\text{MeCp})_2 - \text{V}_2\text{S}_4\text{Cr}_2\text{Cp}_2$  and  $(\text{MeCp})_2\text{V}_2\text{S}_4\text{Cu}_2(\text{PPh}_3)_2$ . The structural data for  $\text{V}_2\text{S}_4\text{Fe}_2$ ,  $\text{V}_2\text{S}_4\text{Co}_2$ , and  $\text{V}_2\text{S}_4\text{Ni}_2$  cubanes together with the results of electrochemical and magnetic studies will be discussed.

## References

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