Volume 31
Number 2
January 22, 1992

Inorganic Chemistry

Communications

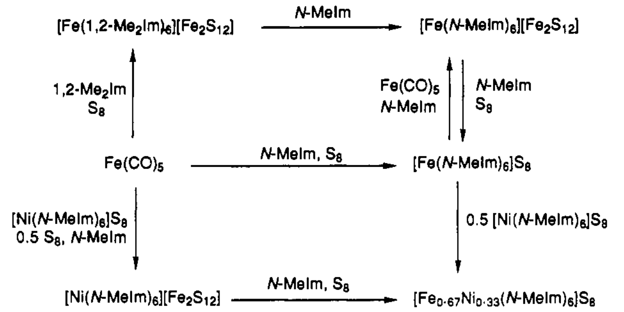
N-Methylimidazole-Promoted Reactions of Iron and Nickel Carbonyls with Chalcogens: Interconversions of Iron Polysulfide Complexes and the Structure of $[FeSe_8(CO)_2]^{2-}$

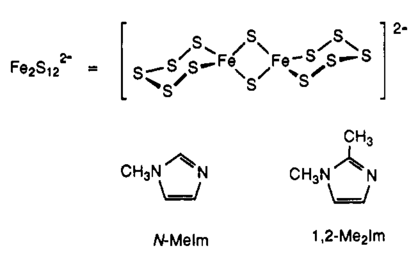
We have recently shown that *N*-alkylimidazole solvents promote the direct reactions of metal powders with elemental sulfur and selenium to give polychalcogenide complexes.[1,2] This methodology exploits the ability of these heterocycles to compete with polychalcogenide ligands for coordination sites on metal ions. As described in this paper, *N*-alkylimidazole solvents also enhance the reactivity of metal carbonyls toward elemental sulfur and selenium.[3] This preparative innovation has allowed us to probe the interconversion chemistry of iron polysulfides.[4]

Portionwise addition of 3.91 g (15.2 mmol) of S_8 to a solution of 2.98 g (2 mL, 15.21 mmol) of $Fe(CO)_5$ in 30 mL of *N*-MeIm resulted in rapid evolution of CO, which in one case was collected and characterized by its IR spectrum. No visible reaction occurred until after the sulfur was added to the solution of the iron carbonyl in the *N*-MeIm. After 10 min under flowing nitrogen, the dark red reaction mixture was diluted with 80 mL of toluene to give 11.68 g of red microcrystalline $[Fe(N\text{-MeIm})_6]S_8$ (95% yield).[5] Analogous reactions occur with $Ni(CO)_4$ (25 °C, 6 h, 97% yield) and $Mn_2(CO)_{10}$ (90 °C, 12 h, 72% yield). These octasulfide salts were previously obtained by the relatively slower reaction (hours at 60 °C) of the respective metal powders with an *N*-MeIm solution of sulfur.[2]

The high reactivity of the metal carbonyl prompted an investigation of the effects of M:S stoichiometry (Scheme I). The addition of 0.5 equiv of S_8 (vs 1 equiv described above) to an *N*-MeIm solution of $Fe(CO)_5$ followed by ether precipitation affords the mixed-valence salt $[Fe(N\text{-MeIm})_6][Fe_2S_{12}]$.[6] Its IR spectrum in the range 1650–600 cm^{-1} matches that for other salts of $[Fe(N\text{-MeIm})_6]^{2+}$, while the optical spectrum of its DMF solution is very similar to that for $(PPh_4)_2Fe_2S_{12}$.[7] Addition of 2 equiv of PPh_4Br to a DMF solution of $[Fe(N\text{-MeIm})_6][Fe_2S_{12}]$ followed by Et_2O precipitation afforded black microcrystals of $(PPh_4)_2[Fe_2S_{12}]$ in high yield.[8]

Scheme I





The reaction of $Ni(CO)_4$ with 0.5 mol of S_8 gave only a ~50% yield of $[Ni(N\text{-MeIm})_6]S_8$. Apparently, $Ni(CO)_4$ is less reactive than $Fe(CO)_5$ toward S_8^{2-}. This difference in reactivity was utilized in a synthesis of a heterometallic polysulfide salt. Treatment of an *N*-MeIm solution of $Fe(CO)_5$ with $[Ni(N\text{-MeIm})_6]S_8$ and 0.5 mol of S_8 gave $[Ni(N\text{-MeIm})_6][Fe_2S_{12}]$. The formulation of the heterometallic salt was supported by optical spectroscopy, as well as by microanalysis and the optical and IR spectra of the mixed DMF–*N*-MeIm complex obtained by reprecipitation of this salt from DMF and ether.[9] Thermogravimetric analysis of $[Ni(N\text{-MeIm})_6][Fe_2S_{12}]$ showed 75.8% (theory 74.5%) weight loss by 600 °C, consistent with the formation of $Fe_{0.67}Ni_{0.33}S$.

The addition of 1.5 equiv of S_8 to a brown *N*-MeIm solution of $[Fe(N\text{-MeIm})_6][Fe_2S_{12}]$ produced a red color indicative of $[Fe(N\text{-MeIm})_6]S_8$, which was isolated in virtually quantitative yield. These results illustrate three effects that may prove generally applicable to transition-metal polychalcogenide chemistry:

---

(1) Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043. Dev, S.; Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6385.

(2) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 2514.

(3) The reactions of metal carbonyls with elemental sulfur and selenium have been studied for many years: Hieber, W.; Geisenberger, O. *Z. Anorg. Allg. Chem.* **1950**, *262*, 15. Markó, L. In *The Organometallic Chemistry of Iron*; Koerner von Gustorf, E. A., Fischler, I., Grevels, W. H., Eds.; Academic Press: New York, 1978; Vol. 2.

(4) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223. Kanatzidis, M. G. *Chem. Mater.* **1990**, *2*, 337.

(5) These $[M(N\text{-MeIm})_6]S_8$ compounds were identified by microanalysis and by comparisons of their IR spectra with those of samples prepared from metal powders.[2]

(6) Anal. Calcd for $Fe(C_4H_6N_2)_6][Fe_2S_{12}]$: C, 27.59; H, 3.47; N, 1608. Found: C, 28.08; H, 3.71; N, 16.10.

(7) Coucouvanis, D.; Swenson, D.; Stremple, P.; Baenziger, N. C. *J. Am. Chem. Soc.* **1979**, *101*, 3392. Müller, A.; Schladerbeck, N. H.; Krickemeyer, E.; Bögge, H.; Schmitz, K. Z. *Z. Anorg. Allg. Chem.* **1989**, *570*, 7. Müller, A.; Schladerbeck, N. *Chimia* **1985**, *39*, 23.

(8) Lower S:$Fe(CO)_5$ and S:Fe stoichiometries afford soluble products which have not been identified.

(9) Anal. Calcd for $[Ni(N\text{-MeIm})_3(DMF)_3][Fe_2S_{12}]$: C, 24.71; H, 3.85; N, 12.34. Found: C, 25.05; H, 3.65; N, 12.44. UV–vis, λ_{max} (DMF solution): 370, 446, 602 nm. ν_{CO}(KBr) = 1657 cm^{-1}.

0020-1669/92/1331-0153$03.00/0

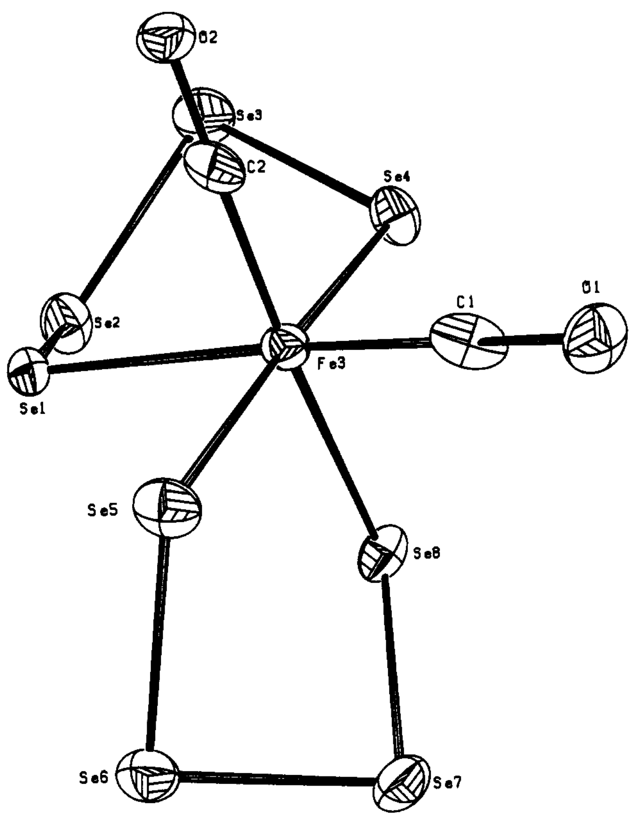


Figure 1. Structure of the anion of $[\mathrm{Fe}(N\text{-MeIm})_6]^{2+}[\mathrm{Fe}(\mathrm{Se}_4)_2(\mathrm{CO})_2]^{2-}$, with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å): Fe–N range = 2.17–2.21 (2); Se–Se range = 2.331–2.349 (3); Fe–Se1 = 2.450 (3); Fe–Se5 = 2.419 (3); Fe–Se8 = 2.439 (3); Fe–C1 = 1.75 (2); Fe–C2 = 1.73 (2). Selected bond angles (deg): Se5–Fe–Se8 = 99.7 (1); Se1–Fe–Se4 = 97.7 (1); C1–Fe–C2 = 94.4 (10).

1. High S:M ratios favor the *cleavage* of metal–sulfur bonds in polysulfido complexes. This is due to the fact that the basicity of S_x^{2-} is inversely proportional to x.[10]
2. Elemental sulfur is selectively Lewis acidic toward the sulfur anions. This occurs even in preference to a large excess of highly basic *N*-MeIm.
3. Polysulfido ligands are less capable of stabilizing high oxidation states than sulfide (S^{2-}). This is illustrated by the reduction of $\mathrm{Fe^{III}}$ (in $\mathrm{Fe_2S_{12}}^{2-}$) to $\mathrm{Fe^{II}}$ (in $[\mathrm{Fe}(N\text{-MeIm})_6]\mathrm{S}_8$). This conversion is reminiscent of the metal-centered reduction of $\mathrm{Mo^{VI}S_4}^{2-}$ by S_8.[11]

The nature of the donor solvent influences the thioanion generated via our donor-solvent-promoted reactions of $\mathrm{Fe(CO)_5}$ (and, more slowly, via those of Fe powder). This was demonstrated using 1,2-$\mathrm{Me_2Im}$, whose coordinating power suffers because of nonbonded interactions between the 2-methyl group and adjacent ligands within an octahedral coordination sphere.[12] The reaction (50 °C, 6 h) of S_8 with a 1,2-$\mathrm{Me_2Im}$ solution of $\mathrm{Fe(CO)_5}$ gave, after ether precipitation, exclusively $[\mathrm{Fe}(1,2\text{-}\mathrm{Me_2Im})_6][\mathrm{Fe_2S_{12}}]$,[13] *despite the presence of excess sulfur.* Reactivity studies relate $[\mathrm{Fe}(1,2\text{-}\mathrm{Me_2Im})_6][\mathrm{Fe_2S_{12}}]$ to all other iron compounds described herein (Scheme I).

The stability of DMF solutions of $[\mathrm{Fe}(N\text{-MeIm})_6]\mathrm{Y}$ (Y = $[\mathrm{Fe_2S_{12}}]^{2-}$, $\mathrm{S_8}^{2-}$) contrasts with our finding that attempted dissolution of $[\mathrm{Ni}(N\text{-MeIm})_6]\mathrm{S}_8$ in DMF results in immediate deposition of NiS.[2] The stability of DMF solutions of $[\mathrm{FeL_6}]$(thioanion) suggests two lines for further research, synthesis of polysulfide salts of other iron cations by ligand exchange at the cation and the dissolution of iron metal in DMF/S_8.

The reactions of metal carbonyls (Mn, Fe, Ni) with *N*-MeIm suspensions of gray selenium also proceed well. The *N*-MeIm/$\mathrm{Fe(CO)_5}$/Se reaction (25 °C, 12 h; toluene precipitation) afforded brown microcrystals of $[\mathrm{Fe}(N\text{-MeIm})_6]^{2+}[\mathrm{Fe}(\mathrm{Se}_4)_2(\mathrm{CO})_2]^{2-}$ in 94% yield (eq 1).[14] X-ray crystallography[15] showed that this salt

$$2\mathrm{Fe(CO)_5} + 8\mathrm{Se} \rightarrow [\mathrm{Fe}(N\text{-MeIm})_6][\mathrm{Fe(CO)_2(Se_4)_2}] + 8\mathrm{CO} \tag{1}$$

consists of pseudooctahedral $[\mathrm{Fe}(N\text{-MeIm})_6]^{2+}$ and $[\mathrm{Fe}(\mathrm{Se}_4)_2(\mathrm{CO})_2]^{2-}$ centers (Figure 1). The unit cell contains two different but similar centrosymmetric dications. The anion adopts a cis geometry with two $\mathrm{FeSe_4}$ rings. Although substituted iron polychalcogenides are rare, the dianion closely resembles $[\mathrm{Ru}(\mathrm{Se}_4)_2(\mathrm{CO})_2]^{2-}$, obtained from the reaction of $\mathrm{K_2Se_5}$ and $\mathrm{Ru_3(CO)_{12}}$.[16] This similarity highlights the relationship between the reactions *N*-MeIm/$\mathrm{M(CO)}_n$/Se and $\mathrm{M(CO)}_n/\mathrm{E}_n^{2-}$.[17] The *N*-MeIm/$\mathrm{M(CO)}_n$/X reaction generates its own gegenion in the form of the very stable $[\mathrm{M}(N\text{-MeIm})_6]^{2+}$.

On the basis of these results, it is clear that strong donor solvents provide a powerful means to explore reactivity networks for metal polychalcogenide complexes.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE-87-11460. We thank Shifang Luo and Partha Paul for assistance. T.B.R. thanks the John S. Guggenheim Memorial Foundation for support during part of this project.

Supplementary Material Available: Tables of bond distances and angles, thermal parameters, and atomic coordinates and ORTEP diagrams of the cations (7 pages); a listing of structure factors (19 pages). Ordering information is given on any current masthead page.

School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

Thomas B. Rauchfuss*
Somanath Dev
Scott R. Wilson

Received July 24, 1991

---

[10] This effect has also been observed for the conversion of $[\mathrm{Mn}(N\text{-MeIm})_6][\mathrm{Mn_2S_{11}}]$ to $[\mathrm{Mn}(N\text{-MeIm})_6]\mathrm{S}_8$: Ramli, E. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1990.

[11] Coucouvanis, D.; Toupadakis, A.; Lane, J. D.; Koo, S. M.; Kim, C. G.; Hadjikyriacou *J. Am. Chem. Soc.* **1991**, *113*, 5271. Stiefel, E. I.; Halbert, T. R.; Coyle, C. L.; Wei, L.; Pan, W.-H.; Ho, T. C.; Chianelli, R. R.; Daage, M. *Polyhedron* **1989**, *8*, 1625.

[12] Collman, J. P.; Halbert, T. R.; Suslick, K. S. In *Metal Ion Activation of Dioxygen*; Spiro, T. G., Ed.; Wiley: New York, 1980.

[13] Anal. Calcd for $\mathrm{C_{30}H_{48}Fe_3N_{12}S_{12}}$: C, 31.92; H, 4.29; N, 14.88. Found (preparation from Fe powder in parentheses): C, 31.67 (32.08); H, 4.40 (4.39); N, 14.77 (15.30).

[14] Anal. Calcd for $\mathrm{C_{26}H_{36}N_{12}Fe_2O_2Se_8}$: C, 24.17; H, 2.81; N, 13.00; Se, 48.88. Found: C, 24.13; H, 2.81; N, 12.80; Se, 49.26. Its IR spectrum (KBr) shows ν_{CO} bands at 1958 and 1911 cm^{-1}. The molar conductance of its *N*-MeIm solution (5.22×10^{-4} M) is 49.80 Ω^{-1} cm^{-2} mol^{-1}.

[15] Crystal grown from *N*-MeIm and THF: $\mathrm{C_{26}H_{36}N_{12}Fe_2O_2Se_8}$, $P\bar{1}$, a = 9.651 (3) Å, b = 10.877 (4) Å, c = 19.697 (5) Å, α = 89.80 (2)°, β = 88.62 (2)°, γ = 83.33 (3)°, V = 2053 (2)Å^3. With Mo Kα radiation, 6257 reflections were collected at −78 °C, of which 2845 were observed ($I > 2.58\sigma(I)$). The data were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods (SHELX-86) and refined to final R = 0.056 and R_w = 0.062.

[16] Draganjac, M.; Dhingra, S.; Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* **1990**, *29*, 590.

[17] See: O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971. O'Neal, S. C.; Kolis, J. W. *Inorg. Chem.* **1989**, *28*, 2780. Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195. Eichorn, B. W.; Haushalter, R. C.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 728.

Stability and Structure of $\mathrm{C_{12}B_{24}N_{24}}$: A Hybrid Analogue of Buckminsterfullerene

The 60-vertex, truncated icosahedral cluster system known as buckminsterfullerene ("buckyball", $\mathrm{C_{60}}$), has attracted increased attention following recent reports of its laboratory-scale synthesis.[1] Such large clusters provide a bridge between atomic and ma-

---

[1] (a) Howard, J. B.; McKinnon, J. T.; Makarovsky, Y.; Lafleur, A. L.; Johnson, M. E. *Nature* **1991**, *352*, 139. (b) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (c) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

0020-1669/92/1331-0154$03.00/0