the rate of back electron transfer relative to that in solution (column 6). Adsorption effects of ionic species at the polar aluminosilicate surface and/or the electrostatic field within the zeolite supercage[17,18] could be the contributory factors in the marked retardation of the electron-transfer rate. Indeed from the magnitude of the latter, we estimate the CT ion pair to be stabilized within the zeolite supercage over that in solution by roughly 8 kcal mol^{-1}.[19,20] The chemical consequences accompanying the dramatically prolonged lifetimes of CT ion pairs enabled by zeolite supercages will be reported at a later time.

Acknowledgment. We thank the National Science Foundation, Robert A. Welch Foundation, and Texas Advanced Research Program for financial support.

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Applications of the N_2S_2 Ligand, *N,N′*-Bis(mercaptoethyl)-1,5-diazacyclooctane, toward the Formation of Bi- and Heterometallics: $[(BME\text{-}DACO)Fe]_2$ and $[(BME\text{-}DACO)NiFeCl_2]_2$

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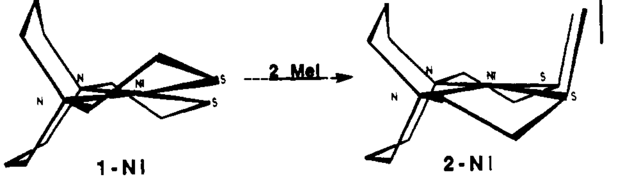
Recently we reported the synthesis of a new macrocyclic ligand based on a derivative of diazacyclooctane, *N,N′*-bis(mercaptoethyl)-1,5-diazacyclooctane, H_2BME-DACO.[1] The X-ray crystal structures of the complexes (BME-DACO)Ni^{II} (**1**-Ni) and [(Me$_2$BME-DACO)Ni^{II}][I]$_2$ (**2**-Ni) were the first determined for



the N_2S_2 Busch-type[2] complexes as monomers, a success presumably due to the control of aggregation provided by steric bulk of the ligand. The structures evidenced the well-known conformational requirements of the DACO ring,[3] resulting in a sterically protected hydrophobic pocket, especially for the **2**-Ni complex, where dialkylation occurred on the same side of the square plane.[1] This methylated derivative (and others alkylated with C_2H_5I, $C_6H_5CH_2Br$, *i*-C_3H_7I, and $BrCH_2CH_2CH_2Br$)[4] results from the reactivity of the metal-bound thiolate sulfur atoms of **1**-Ni analogous to that of the Busch-type $(H_2NCH_2CH_2S)_2Ni^{II}$ complexes.[5] In fact, the sulfurs in such complexes are potential binding sites for an additional metal as illustrated by $[(H_2NCH_2CH_2S)_4Ni_3](I)_2$.[2] Structural studies by Dahl and Wei showed the trimetallic to consist of three linked square planes: two NiN_2S_2 planes separated by a NiS_4 plane at torsional angles of 109°.[6]

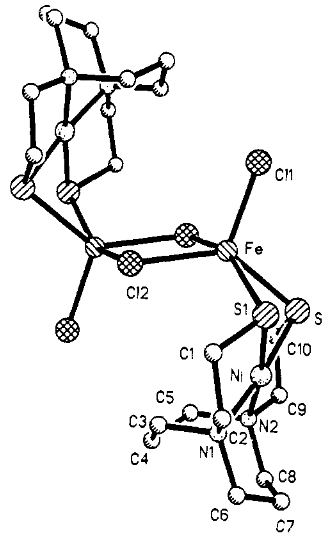


Figure 1. Molecular structure of $[(BME\text{-}DACO)NiFeCl_2]_2$ (**1**-Ni_2Fe_2). Selected bond lengths (Å): Fe–Cl(1), 2.286 (3); Fe–Cl(2), 2.422 (3); Fe–Cl(2A), 2.547 (3); Fe–S(1), 2.552 (3); Fe–S(2), 2.462 (3); Ni–S(1), 2.172 (3); Ni–S(2), 2.165 (3); Ni–N(1), 1.974 (8); Ni–N(2), 1.966 (9). Selected bond angles (deg): S(1)–Fe–Cl(2A), 153.6 (1); Cl(2)–Fe–S(2), 134.3 (1); Cl(1)–Fe–Cl(2A), 99.4 (1); Cl(1)–Fe–Cl(2), 111.9 (1); Cl(1)–Fe–S(1), 106.2 (1); Cl(1)–Fe–S(2), 113.7 (1); S(1)–Fe–S(2), 72.2 (1); Cl(2)–Fe–S(1), 93.1 (1); Cl(2)–Fe–Cl(2A), 82.9 (1); S(2)–Fe–Cl(2A), 91.9 (1); S(1)–Ni–S(2), 85.9 (1); N(1)–Ni–N(2), 91.0 (3); S(2)–Ni–N(2), 91.0 (2); S(1)–Ni–N(1), 91.3 (3); Ni–S(1)–Fe, 81.6 (1); Ni–S(2)–Fe, 83.9 (1); Fe–Cl(2)–Fe(A), 97.1 (1).

We are applying the ability of **1**-Ni to serve as a complex ligand toward the preparation of Ni and Fe heterometallics in biological-type ligation settings appropriate to provide redox and magnetic behavior for comparison to nickel-containing hydrogenases.[7] To our knowledge $[(BME\text{-}DACO)Ni(\mu\text{-}Cl)FeCl]_2$ (**1**-Ni_2Fe_2) is the first Ni/Fe heterometallic complex with classical (as opposed to organometallic) donor atoms and represents a new type of heterotetrametallic, containing two square-planar nickel(II) and two pseudo-square-pyramidal iron(II) ions. Square-pyramidal iron is also seen in $[(BME\text{-}DACO)Fe]_2$ (**1**-Fe_2) in which the iron(II) centers are simultaneously bound to two BME-DACO ligands, resulting in a 2Fe–2S core, analogous to the dimeric iron complex of dimethyl-*N,N′*-bis(2-mercaptoethyl)-1,3-propanediamine, BME-Me$_2$PDA.[8]

Reaction of **1**-Ni in CH_3CN with anhydrous $FeCl_2$ in either 2:1 or 1:1 molar equivalents results in formation of a thermally

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and air stable red-brown crystalline product (>70% yield) of empirical formula $NiFeCl_2C_{10}H_{20}N_2S_2$.[9] The complex is insoluble in THF, acetone, and hydrocarbons and forms slightly air sensitive solutions in water and methanol. Crystals suitable for X-ray analysis were obtained either directly from the preparation described above or on recrystallization (methanol/hexane/ether layer diffusion). A μ_{eff} of 3.49 μ_B per iron was calculated from solid-state magnetic susceptibility measurements at 25 °C.[10] The vis–UV spectrum in CH_3OH solution measures intense bands at λ_{max} ($\epsilon \times 10^{-3}$) = 570 (sh), 486 (0.55), 410 (1.8), and 310 (2.0) nm. The reactivity of the complex with [n-Bu_4N][PF_6] or [Et_4N][BPh_4] electrolytes in CH_3CN, which results in an intractable black product, has thus far thwarted attempts to record the cyclic voltammogram.

As seen in Figure 1, the molecular structure[11] of **1**-Ni_2Fe_2 contains two square-planar **1**-Ni units, with bond angles and distances largely unperturbed from the free complex.[1] The thiolate sulfurs of **1**-Ni along with two bridging chlorides form a basal plane of pseudo-square-pyramidal[12,13] FeS_2Cl_3, from which the Fe is displaced toward the apical chloride ligand by 0.754 Å. The $Fe_2(\mu\text{-}Cl)_2$ unit is perfectly planar. A similar $(X_{ap})_2Fe_2(\mu\text{-}X)_2$ unit was observed for the dimeric complex $[Cp_2Mo(\mu\text{-}H)_2Fe(Br_{ap})(\mu\text{-}Br)]_2$ in ref 14. In contrast, the $Cp_2Mo(\mu\text{-}S\text{-}n\text{-}Bu)_2FeCl_2$ binuclear complex has a T_d $Fe^{II}(\mu\text{-}SR)_2Cl_2$ coordination.[15]

The angularity of the Fe–S–Ni (average 83°) of **1**-Ni_2Fe_2 leads to a Ni···Fe distance of 3.100 (1) Å, well beyond known Ni–Fe single bond lengths reported at 2.40–2.44 Å.[16] In the Busch–Jicha trimetallic complex, i.e., $[(H_2NCH_2CH_2S)_2Ni]_2Ni^{2+}$, the even more acute Ni–S–Ni angles of 77.5° enforce Ni···Ni(central) distances of 2.733 (7) Å, suggesting some partial Ni···Ni interaction.[6] The Fe–Fe distance in **1**-Ni_2Fe_2 is 3.725 (1) Å, again implying no metal–metal interaction.

The [(BME-DACO)Fe]$_2$ (**1**-Fe_2) complex is prepared in gram quantities by reacting toluene solutions of $Fe(acac)_3$ and H_2BME-DACO in an Fe to ligand ratio of 1:3. (Excess ligand is used for the reduction of Fe(III) to Fe(II) and yields cleaner product.)[8] On standing under N_2 for 2 days, the air-stable red-brown product separated out as large, well-formed crystals in ca. 90% yield based on $Fe(acac)_3$. **1**-Fe_2 is sparingly soluble in CH_3OH at 22 °C, yielding an orange solution that becomes intensely dark red-brown upon further dissolution at 60 °C. The vis–UV spectra at these two temperatures are the same: a well-defined intense band at λ_{max} ($\epsilon \times 10^{-3}$) = 310 (12.57) nm is observed along with weaker broad bands at 410 (4.50) and 480 (3.79) (CH_3OH solution). The solid-state magnetic susceptibility of **1**-Fe_2 at 25 °C yielded a μ_{eff} of 3.73 μ_B per iron.[10] Cyclic voltammetry, measured in CH_3CN with 0.1 M [n-Bu_4N][PF_6] as supporting electrolyte, shows a quasi-reversible cathodic wave at −0.40 V (vs Ag/AgCl).

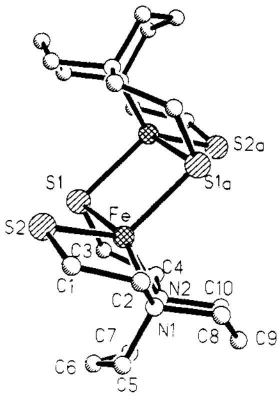

Figure 2. Molecular structure of [(BME-DACO)Fe]$_2$ (**1**-Fe_2). Selected bond lengths (Å): Fe–S(1), 2.421 (1); Fe–S(1A), 2.417 (1); Fe–S(2), 2.346 (1); Fe–N(1), 2.249 (3); Fe–N(2), 2.261 (3); S(1)–Fe(A), 2.417 (1). Selected bond angles (deg): S(1)–Fe–N(1), 157.7 (1); S(2)–Fe–N(2), 140.5 (1); S(1)–Fe–S(2), 97.9 (1); N(1)–Fe–N(2), 81.1 (1); S(2)–Fe–N(1), 83.0 (1); S(1)–Fe–N(2), 84.5 (1); S(1)–Fe–S(1A), 96.6 (1); S(2)–Fe–S(1A), 116.6 (1); N(1)–Fe–S(1A), 102.9 (1); N(2)–Fe–S(1A), 102.1 (1); Fe–S(1)–Fe(A), 83.4 (1).

Iron is best described as existing in a pseudo-square-pyramidal coordination environment in [(BME-DACO)Fe]$_2$ (**1**-Fe_2) with τ = 0.28.[12] The apical site is occupied by a sulfur from a second (BME-DACO)Fe giving rise to a 2Fe–2S core (Figure 2). There is little significant difference in the Fe–S distances within the FeS_2N_2 basal plane and the Fe–S_{apical}. The Fe is displaced out of the best least-squares basal plane (mean deviation of S and N from N_2S_2 plane, 0.189 Å) by 0.59 Å, and the Fe–Fe distance is 3.218 (1) Å, as compared to 3.371 Å in the Lippard et al. analogue, [(BME-Me_2PDA)Fe]$_2$.[8] In fact, Fe–S and Fe–N distances are by and large consistent in the Lippard complexes, [(BME-Me_2PDA)Fe]$_2$ and the ethylenediamine derivative [(BME-Me_2EDA)Fe]$_2$, and in **1**-Fe_2, despite the fact that the coordination geometry of iron in [(BME-Me_2PDA)Fe]$_2$ is TBP.[8]

The ethylene linkages between N and S eclipse each other across the NiN_2S_2 square plane for all structures in which the sulfur is trivalent, i.e., **2**-Ni and **1**-Ni_2Fe_2 and also in **1**-Fe_2. The DACO framework of both **1**-Ni_2Fe_2 and **1**-Fe_2 shows the characteristic chair/boat configurations seen for **1**-Ni and **2**-Ni.[1]

The **1**-Ni complex reacts with anhydrous $NiBr_2$ to yield an intensely dark red solution, which is a Busch–Jicha[5]-type Ni_3 complex,[4] and analogous to [(BME-Me_2PDA)Ni]$_2Ni^{2+}$.[17,18] Attempts to derive molecular models of a trimetallic such as $(\mathbf{1}\text{-Ni})_2FeCl^+$, i.e., without the $[Fe(\mu\text{-}Cl)]_2$ core and alternating Fe–Cl_{term} units of **1**-Ni_2Fe_2, resulted in ring carbon to chloride contacts that were impossibly short without severe distortions of the metallochelate ligand, distortions that cannot take place given the steric restrictions of the cyclooctane ring. This suggests that the preference that Fe(II) shows for pentacoordination in such complexes actually promotes the formation of the tetrametallics.

Reactivity studies of **1**-Fe_2 and **1**-Ni_2Fe_2 complex are underway. The effects of steric demands of such chelates on reactivity was earlier demonstrated in the [(BME-Me_2PDA)Fe]$_2$ complex, which was shown to be incapable of binding CO whereas the ethylene diamine analogue [(BME-Me_2EDA)Fe]$_2$ formed an isolable CO adduct.[8] We find no evidence for a stable CO adduct of **1**-Fe_2 under the same conditions that are successful for [(BME-Me_2EDA)Fe]$_2$ or under more forcing conditions. The stability of the Fe_2S_2 core is evident in attempts to disrupt it with other

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(9) Elemental analysis (Galbraith Laboratories): (a) Anal. Calcd for $NiFeCl_2C_{10}H_{20}N_2S_2$ (Found): C, 28.75 (29.59); H, 4.82 (4.98); N, 6.70 (6.68). mp 315–330 °C (dec). (b) Anal. Calcd for $FeC_{10}H_{20}N_2S_2$ (Found): C, 41.67 (41.98); H, 6.99 (7.19); N, 9.72 (9.63). mp >350 °C.

(10) The μ_{eff} values for the title complexes are consistent with antiferromagnetically coupled high-spin Fe(II). Ginsberg, A. P.; Lines, M. E.; Karlin, K. D.; Lippard, S. J.; DiSalvo, F. J. *J. Am. Chem. Soc.* **1976**, *98*, 6958.

(11) X-ray diffraction data were collected at 23 °C on a Nicolet R3m/V diffractometer. Structures were solved by standard procedures; empirical absorption corrections were applied. Crystallographic data are given as a, b, c; β; space group, Z, 2θ range, unique observed reflections, $R(R_w)$ (%). [(BME-DACO)Ni(μ-Cl)FeCl]$_2$: 11.603 (4), 8.789 (3), 14.804 (5) Å; 99.97 (3)°, $P2_1/n$, 2, 4.0°/50.0°, 1891 ($I > 2\sigma(I)$), 6.38 (6.70). [(BME-DACO)Fe]$_2$: 9.007 (2), 12.747 (3), 11.187 (3) Å; 101.14 (2)°, $P2_1/n$, 4, 4.0°/50.0°, 2004 ($I > 1.3\sigma(I)$), 3.24 (3.49).

(12) The designation, pseudo-SP, derives from application of the τ test of Addison et al.,[13] which must be used with caution for this mixed-ligand case because of the differences in the Fe–Cl and Fe–S bond lengths. The τ test was applied by using the largest angle of S1–Fe–Cl2a (153.6°) as α and the next largest angle of Cl2–Fe–S2 (134.3°) as β yielding τ, $(\alpha - \beta)/60$, of 0.32, where a $\tau = 0$ would define a perfect SP, and a $\tau = 1$, a regular TBP.

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S-donor ligands such as SMe^-. Addition of MeI to **1**-Fe_2 produced extremely air sensitive, paramagnetic solutions, in contrast to the monomeric **1**-Ni complex, which yielded stable S-alkylated **2**-Ni.[1] The extent and sites of alkylation, iron, thiolate sulfur, or bridging sulfur, are under investigation.[4] In the presence of SPh^-, MeI cleaves the **1**-Ni_2Fe_2 dimer resulting in **2**-Ni and thiolato iron complexes, while MeI alone does not add to the complex. We are pursuing as well the intriguing possibility for heterobimetallic interactions, Fe···L···Ni, with small molecule donors and **1**-Ni_2Fe_2.

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Supplementary Material Available: Atom positional parameters for [(BME-DACO)Ni(μ-Cl)$FeCl]_2$ and [(BME-DACO)$Fe]_2$ (1 page). Ordering information is given on any current masthead page.

High Enantioselectivity in the Intramolecular Cyclopropanation of Allyl Diazoacetates Using a Novel Rhodium(II) Catalyst

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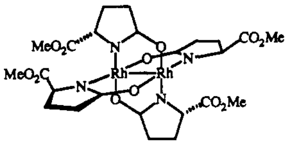
Interest in the synthesis and chemistry of the cyclopropane subunit may be attributed to a number of factors including its occurrence in natural products,[1] its biological significance,[2] its ability to function as a probe of reaction mechanisms,[3] and its utility as an intermediate in the preparation of complex molecules via vinylcyclopropane and homo-Cope rearrangements.[4] Given its important position, it is surprising that few general methods have been developed for preparing optically active cyclopropanes.[5] Although the metal-catalyzed decomposition of diazo carbonyl compounds in the presence of alkenes to give cyclopropanes is well-known in carbenoid chemistry,[6] few chiral catalysts have been designed that achieve high levels of enantioselectivity in these transformations.[7-15] Of those, only the chiral salicylaldimine copper(II) catalysts described by Aratani[7] and the chiral (semicorrinato)copper(II) catalysts designed by Pfaltz,[8] or their bisoxazoline analogues reported by Masamune,[9] appear to be capable of attaining high enantiomeric excesses in intermolecular cyclopropanations. In the course of several ongoing synthetic investigations, we required efficient access to optically pure, trisubstituted cyclopropanes. In order to address this need, we discovered a new class of catalysts for effecting enantioselective carbenoid transformations[16] whose suitability in intramolecular cyclopropanations of allylic diazoacetates is extraordinary.

The common strategic element found in approaches to designing catalysts for inducing enantioselective carbenoid transformations has consisted of attaching chiral ligands to a central metal atom.[7-15] To this end, we screened a series of dirhodium(II) amide complexes that were synthesized by ligand substitution.[17] Thus, dirhodium(II) tetrakis[methyl 2-pyrrolidone-5(*S*)-carboxylate] [Rh_2(5*S*-MEPY)$_4$ (**1**)] and dirhodium(II) tetrakis[methyl 2-pyrrolidone-5(*R*)-carboxylate] [Rh_2(5*R*-MEPY)$_4$ (**2**)] were conveniently prepared by ligand exchange with rhodium(II) acetate and the corresponding (5*S*)- or 5(*R*)-methyl pyroglutamate.[18] Like rhodium(II) acetamide[17] and rhodium(II) trifluoroacetamide,[19] these compounds possess four bridging amide ligands that are positioned so that each rhodium is sterically and electronically equivalent, and the two nitrogen donor atoms on each rhodium are in a cis arrangement.[20]



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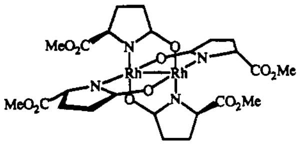

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