The Construction of $(N_2S_2)Ni-Pd$ Clusters: A Slant-Chair, a Basket and a C_4-Paddlewheel Structure

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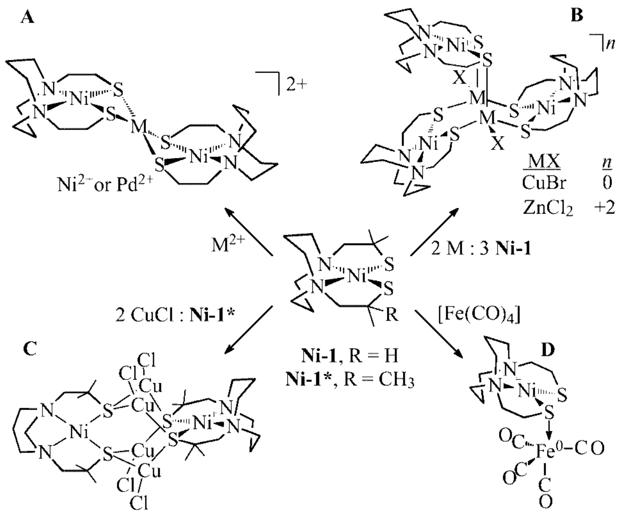
In pursuit of an analogy between bidentate diphosphane ligands and *cis*-dithiolato nickel complexes, the easily prepared [bis(mercaptoethane)diazacycloheptane]nickel complex, **Ni-1′**, has been treated with Pd^{II} and Ni^{II} sources. With the latter, trinickel species are observed with typical slant-chair structures; for palladium(II) chloride, a basket-type structure is realized in which the floor of the basket is a PdS_4 unit and the sides are N_2S_2 units. One chloride atom is held within the basket at a Pd···Cl distance of 3.26 Å. With $Pd(NO_3)_2$ as a palladium source, a hexanuclear aggregate in the form of a C_4-paddlewheel structure is obtained. In this structure, the N_2S_2Ni complex serves as a bidentate ligand which bridges two Pd^{2+} cations at a distance of 3.132 Å.

Introduction

The scope of polyheterometallic cluster complexes with thiolates as bridging ligands traverses the periodic table,[1,2] and there is extensive literature of N_2S_2Ni complexes as metallothiolate ligands to nickel and palladium.[2–7] The most common composition is a trimetallic cluster complex with a slant-chair structure made of two square-planar N_2S_2Ni complexes, which flank a central planar S_4Ni unit. This form (**A**, Scheme 1) is highlighted by [bis(mercaptoethane)diazacyclooctane]nickel, [(bme-daco)Ni^{II}], or **Ni-1**, and is known to readily capture excess Ni^{II} or Pd^{II} metal ions.[8,9] A 2:3 ratio of $ZnCl_2$ or CuBr to **Ni-1** results in a C_3-paddlewheel cluster with three **Ni-1** units performing as bidentate-bridging ligands, placing either Zn^{II} or Cu^{I} atoms in tetrahedral S_3X coordination geometry (**B**, Scheme 1).[10,11] With an excess of $Cu^{I}Cl$, an adamantane-like Ni_2Cu_4 cluster **C** results; four CuCl units bridge two (bme*-daco)Ni^{II} moieties [**Ni-1***, bme*-daco = *N*,*N′*-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane], engaging all available lone pairs on all sulfurs for coordinating to the soft Cu^{I} metal centers.[12] At the other extreme, the **Ni-1** moiety uses a single lone pair and binds as a monodentate ligand to iron(0) in [(**Ni-1**)$Fe(CO)_4$], D.[13]



Scheme 1

The success of **Ni-1** and **Ni-1*** as metallothiolate ligands to other metals may be ascribed to the strong chelate effect of bme- and bme*-daco to Ni^{II}, as well as the generally excellent crystallinity and typical air stability of its derivatives. These features are attributed to the optimal 90° bite angles of the N−Ni−N and S−Ni−S moieties within the square-planar **Ni-1** and **Ni-1*** complexes, as well as the fused six-membered nickel-diazacyclohexane rings which adopt classic and stable chair-boat configurations.[14] Points of modification have thus far been limited to the attachment of different pendant arms to the diazacycle framework.[15–17] The readily procured seven-membered ring diazacycloheptane may be substituted for the daco ligand, generating [(bme-dach)Ni] or **Ni-1′**, whose S-based reactivity towards electrophiles such as O_2 and RX differs subtly as compared to **Ni-1**.[18] Electronic effects arising from disparities in Ni−S orbital overlap account for the differences observed. The use of **Ni-1′** as a metallothiolate ligand has not yet been explored.

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It is increasingly apparent that N_2S_2Ni complexes behave toward other metals as ligands with donor abilities which are similar to phosphane ligands.[11,13,19,20] Steric and electronic modifications should lead to a class of ligands whose properties might be controlled similarly to the exceedingly versatile and technically important phosphane ligands. We report on the preparation of Ni−Pd polymetallic complexes based on **Ni-1′** as a metallothiolate ligand.

Results and Discussion

Consistent with reactions of **Ni-1** that led to structural type **A** (Scheme 1), metallation of **Ni-1′** with palladium(II) chloride produced a trimetallic species, which was discovered to be (**Ni-1′**)$_2$PdCl$_2$. X-ray diffraction studies revealed a molecular structure which is unlike any so far reported for such formulations. Rather than the slant-chair arrangement of the three d^8 square-planar conformations, the N_2S_2Ni planes emanate from the same side of the S_4Pd plane with dihedral angles of 132−134°, and Pd−Ni and Ni−Ni distances of 3.13 and 5.97 Å, respectively. As shown in Figure 1, the basket-like structure shows the 2-carbon N−N linker in both **Ni-1′** units facing inward towards an entrained chloride ion, which is located 3.26 Å above the Pd^{II} metal center. Although this distance is about 0.4 Å longer than expected for a Pd−Cl bond in square-pyramidal coordination,[21] conductivity measurements (vide infra) indicate that ion association is maintained in solution. The extended crystal packing diagram shows the second chloride ion to be located at interstitial positions throughout the crystal lattice.

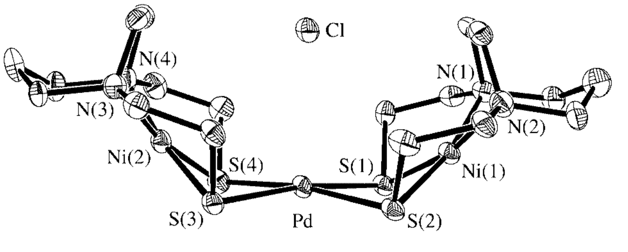


Figure 1. Molecular structure of cationic portion of [(**Ni-1′**)$_2$PdCl]$^+$[Cl]$^-$, thermal ellipsoids at 50 % probability; selected averaged distances (Å) and angles (°): Pd−S 2.369(3), Pd−Ni 3.100(2), Pd···Cl 3.262(3), Ni−N 1.957(8), Ni−S 2.190(3); S(2)−Pd−S(1) 81.02(8), S(2)−Pd−S(3) 97.43(8), S(1)−Pd−S(4) 98.80(8), S(3)−Pd−S(4) 81.74(8), N−Ni−S 92.6(2), S−Ni−S 89.7(1), N−Ni−N 83.1(3)

While the N- and S-atom mean deviations from the best N_2S_2 and S_4 planes of [(**Ni-1′**)$_2$PdCl][Cl] are no more than 0.014 Å, the palladium atom is displaced by 0.157 Å from the S_4 plane towards the chloride ion (Table 1). The Ni^{II} cations are displaced, by 0.224 and 0.167 Å out of the S(1)−S(2)−N(1)−N(2) and N(3)−N(4)−S(3)−S(4) planes, respectively. This moves the nickel ions away from the chloride ion and into a less sterically encumbered position with respect to the hydrocarbon N to S and N to N linkages (Figure 1). The S−Ni−S angles are approximately 90°, and the bite angle imposed by the S−Ni−S metallothiolate ligand on the Pd metal center, i.e. the S−Pd−S angle, is considerably less, mean 81.4°.

Although the Ni:Pd ratio in the complex, which is derived from treating **Ni-1′** and Pd(NO$_3$)$_2$ in a 2:1 ratio, is the same as that of the chloride analogue, the composition of the isolated complex is a discrete hexanuclear cluster cation [(**Ni-1′**)$_4$Pd$_2$]$^{4+}$ with four nitrate counterions within the crystal lattice. The form of the Ni_4Pd_2 cluster (Figure 2) is that of a C_4-paddlewheel structure, which contains a Pd−Pd axis and four **Ni-1′** paddles in which S−Ni−S units

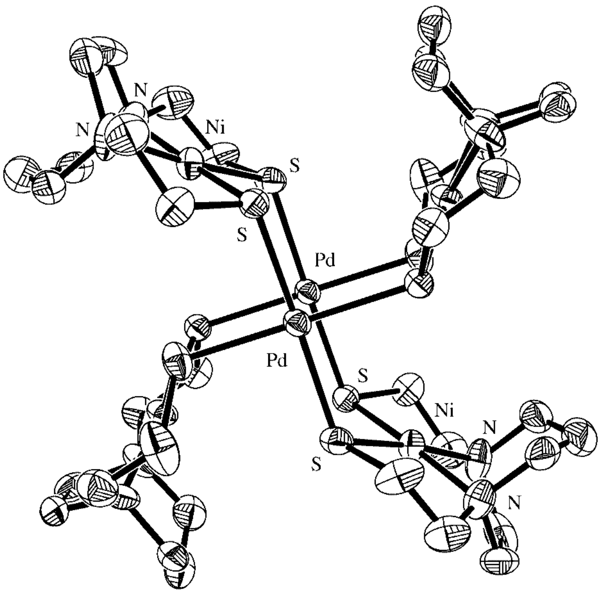


Figure 2. Molecular structure of cationic portion of [(**Ni-1′**)$_4$Pd$_2$][NO$_3$]$_4$, thermal ellipsoids at 50 % probability; selected averaged distances (Å) and angles (°): Pd−S 2.334(2), Pd···Pd 3.132(1), Ni···Ni 4.872, Ni−N 1.940(6), Ni−S 2.157(2); S−Pd−S 89.99(6), N−Ni−S 90.8(2), S−Ni−S 95.68(7), N−Ni−N 82.6(3), Pd−S−Ni 114.42(7)

Table 1. Folding angles of N_2S_2 and the S_4 planes, metal displacement from both of the planes, and M−Ni distances

Complex	Folding angles of N_2S_2 and S_4 planes (°)	Ni displacement out of N_2S_2 plane (Å)	Metal displacement out of S_4 plane (Å)	M···Ni (Å)
[(**Ni-1**)$_2$Ni][Br]$_2$	103.1	0.17	0.0	2.685
[(**Ni-1′**)$_2$NiCl][Cl]	95.2, 138.9	0.194, 0.053	0.520	2.679, 3.053
[(**Ni-1′**)$_2$Ni][Br]$_2$	121.7	0.186	0.0	2.847
[(**Ni-1′**)$_2$PdCl][Cl]	132.3, 134.0	0.167, 0.224	0.1568	3.071, 3.129
[(**Ni-1′**)$_4$Pd$_2$][NO$_3$]$_4$	−	0.066, 0.073	0.033	−

span the palladium atoms that are 3.13 Å apart. In addition to the two rather perfect S_4Pd and four N_2S_2Ni square planes, two other planes are comprised of S_4Pd_2 units. The nitrate counterions appear to have directional long-range interactions with O−Ni and O−Pd average distances of 3.42 and 3.55 Å, respectively. This is not the first structure of its kind.[6,22] A similar C_4-paddlewheel structure, which comprise bis(aminoethanethiolate)nickel $[(H_2NCH_2CH_2S)_2$-Ni or $aet_2Ni]$ as a metallothiolate ligand to palladium, has been reported with parallel S_4Pd planes separated by 3.02 Å.[6] The isostructural compound $[(aet_2Pd)_4Pd_2]^{4+}[Br_4]^{4-}$ has a Pd···Pd distance of 3.19 Å.[6]

A recently reported hexanickel complex was derived from the aggregation of two $Ni(BF_4)_2$ moieties with four N_2S_2Ni complexes based on the $[^{-}S(CH_2)_2N(Me)(CH_2)_3N(Me)(CH_2)_2S^{-}]$ ligand.[22] The flexibility of this open-chain ligand generated torsionally distorted or twisted NiS_4 units, in contrast to the highly regular structural features of the cationic complex $[(\mathbf{Ni\text{-}1'})_4Pd_2]^{4+}$.

In order to determine the interplay of the mesocycle and counterion effects on the basket, the paddlewheel, and the slant-chair structural forms of the Ni−Pd polymetallic complexes, **Ni-1** was exposed to $Pd(NO_3)_2$ under the reaction conditions which produced the C_4-paddlewheel structure. However, the slant-chair trimetallic molecular structure was evident in the isolated crystalline material; it had no significant differences in metric parameters from those found for the chloride salt of $[(\mathbf{Ni\text{-}1})_2Pd]^{2+}$ (Scheme 1).[9]

Likewise, the **Ni-1′** moiety was treated with $NiCl_2$, which resulted in a trimetallic complex of composition $[(\mathbf{Ni\text{-}1'})_2NiCl][Cl]$. As shown in Figure 3, this trimetallic complex does not adopt the basket form of the palladium analogue $[(\mathbf{Ni\text{-}1'})_2PdCl][Cl]$, but is rather a modified slant-chair structure with a chloride ion strongly bound to a the pentacoordinate square-pyramidal nickel central atom of the S_4NiCl unit. The Ni−Cl distance is 2.304 Å, and Ni is displaced by 0.52 Å from the S_4 plane towards the apical chloride ligand. The Ni−S distances in the pentacoordinate $ClNiS_4$ unit are on average 0.27 Å longer than the Ni−S distances in the four-coordinate nickel atom within the N_2S_2Ni plane. The orientation of the chloride ligand generates distinctly different environments for Ni(3) and Ni(1). Ni(3) is displaced from its N_2S_2 ligand plane by 0.194 Å and shifts away from the chloride ligand; Ni(1) lies within the N_2S_2 plane (displacement of 0.053 Å). The closest Cl···Ni(1) and Cl···Ni(3) distances are 4.712 Å and 3.539 Å, respectively. Another consequence of this asymmetric structure is the difference in S−Ni−S angles of the N_2S_2Ni sites: the terminal S−Ni−S angles are 5° smaller than the parent N_2S_2Ni complex [90.5° and 90.46° for S(2)−Ni(3)−S(2a) and S(1)−Ni(1)−S(1a), respectively]. The central nickel atom (NiS_4) has bite angles to the N_2S_2Ni ligands of 79.2° and 77.7°.

Two other structures were determined as references for counterion interactions. The trimetallic complex prepared from the reaction of **Ni-1′** with $NiBr_2$ showed the common slant-chair arrangement, with no anion interaction with the central S_4Ni unit (Figure 4). However, the product of combining $PdBr_2$ and **Ni-1′** produced another hexanuclear, Ni_4Pd_2 C_4-paddlewheel complex with four bromide anions, as in the nitrate salt.

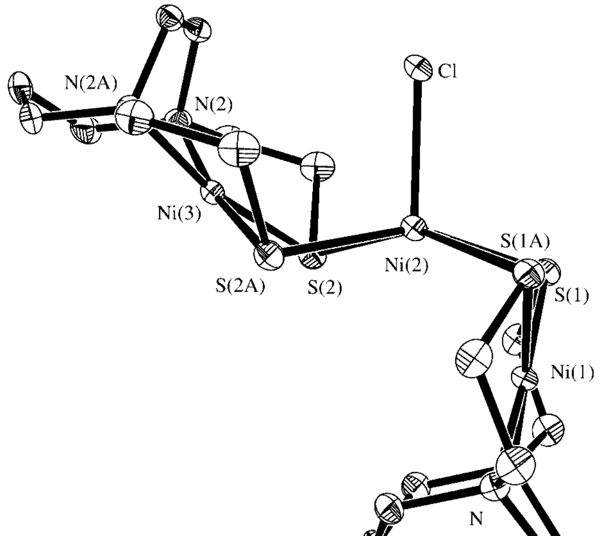


Figure 3. Molecular structure of the cationic portion of $[(\mathbf{Ni\text{-}1'})_2NiCl]^{+}Cl^{-}$, thermal ellipsoids at 50% probability; selected averaged distances (Å) and angles (°): Ni−N 1.930(4), (N_2S_2)Ni−S 2.155(1), (S_4)Ni−S 2.420(1), Ni(2)−Cl 2.304(2), Ni(1)···Ni(2) 2.679, Ni(2)···Ni(3) 3.053; N−Ni−N 83.2(3), N−Ni−S 92.63(1), S(1)−Ni(1)−S(1A) 90.46(8), S(2)−Ni(2)−S(2A) 79.20(7), S(2)−Ni(2)−S(1) 96.21(5), Cl(1)−Ni(2)−S(2) 100.59(5), Cl(1)−Ni(2)−S(1) 104.23(5)

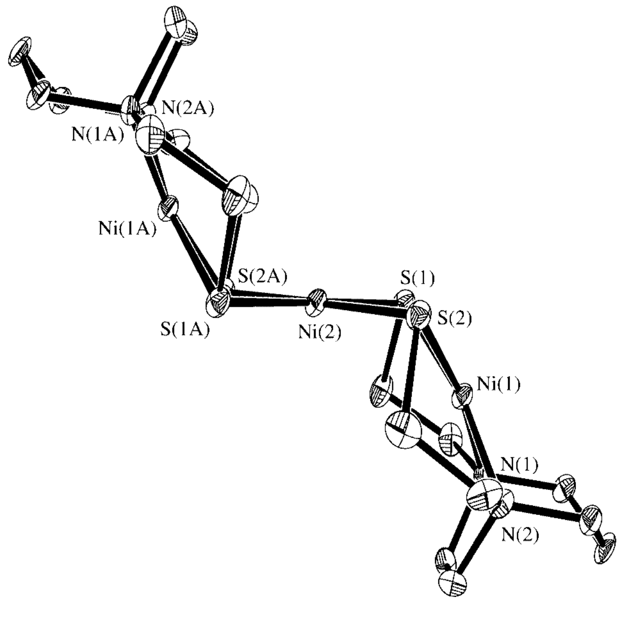


Figure 4. Molecular structure of the cationic portion of $[(\mathbf{Ni\text{-}1'})_2Ni](Br_2)$, thermal ellipsoids at 50 % probability; selected averaged distances (Å) and angles (°): Ni−N 1.924(6), Ni(1)−S 2.149(2), Ni(2)−S 2.211(2), Ni(1)···Ni(2) 2.847(1); N−Ni−N 83.6(2), N−Ni−S 92.9(2), S(2)−Ni(1)−S(1) 88.72(7), S(2)−Ni(2)−S(1) 85.63(6), S(2)−Ni(2)−S(1A) 94.37(6)

Solution Characterization

The colors, electronic spectral, and electrochemical features of the heterometallic complexes are ascribed to a combination of the central NiS_4 or PdS_4 units and the S-modified (bme-dach)Ni moieties. The basket and the C_4-paddlewheel palladium structures are paprika-red in color and have similar electronic spectral features. The intense L→M charge-transfer band of tan-colored **Ni-1′** at 280 nm is red-shifted on formation of the Pd derivatives to approximately 320 nm, and a broad band of lower intensity covers the 370−480 nm range. The latter has been assigned to PdS_4 coordination.[7] In contrast the trinickel slant-chair species are an intense red-black. The absorptions of the CT bands that tail off into the range of 400−500 nm have ε values of approximately 2000 $Lmol^{-1}cm^{-1}$. These values are again consistent with previous assignments to a NiS_4 chromophore.[7]

The results of molar conductivity measurements determined on CH_3OH solutions at 25 °C are listed in Table 2. The molar conductance values for the trinickel species are well within the range of three ions in CH_3OH (reported as 160−220 $cm^{-1}mol^{-1}\Omega^{-1}$),[23] indicating ion dissociation and a di-uni-uni electrolyte system. In contrast, for the [(**Ni-1′**)$_2$PdCl]Cl "basket" compound, a lower value of $\Lambda_M = 83$ $cm^{-1}mol^{-1}\Omega^{-1}$ is indicative of a uni-uni electrolyte which has a range in CH_3OH of 80−115 $cm^{-1}mol^{-1}\Omega^{-1}$.[23] From this, we conclude that the Pd−Cl interaction implied for the entrained chloride in the solid-state molecular structure remains intact in CH_3OH. The C_4-paddlewheel structure has a value of $\Lambda_M = 136$ $cm^{-1}mol^{-1}\Omega^{-1}$, which is between the two- and three-ion range in CH_3OH, and indicates that at least some of the long-range nitrate associations with the 4+ cation that was observed in the solid-state structure are maintained in solution, generating [{(**Ni-1′**)$_4$Pd$_2$}(NO$_3$)$_2$]$^{2+}$ and two free nitrate ions.

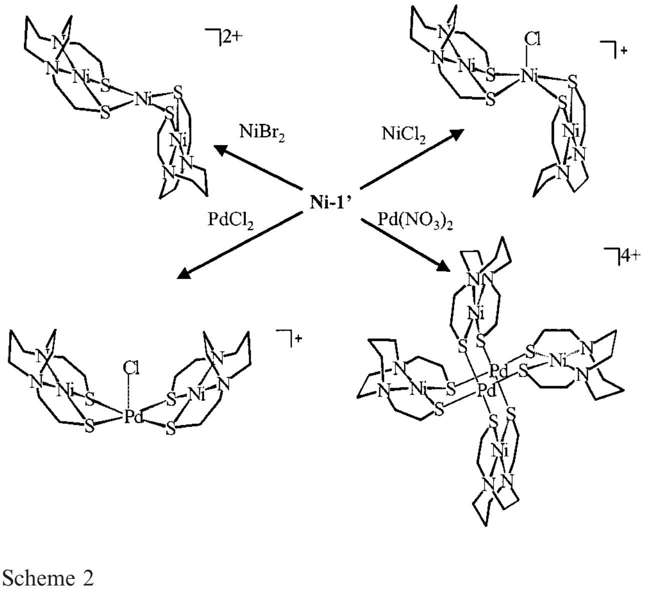
Table 2. Molar conductivities in MeOH at 25 °C

Compound	Λ_M at 10^{-3} M ($cm^{-1}mol^{-1}\Omega^{-1}$)
[(**Ni-1**)$_2$Ni][Br]$_2$	191
[(**Ni-1′**)$_2$NiCl][Cl]	168
[(**Ni-1′**)$_2$Ni][Br]$_2$	166
[(**Ni-1′**)$_2$PdCl][Cl]	83
[(**Ni-1′**)$_4$Pd$_2$][NO$_3$]$_4$	136

Electron-spray ionization mass spectral results for the new cluster compounds were consistent with the solid-state formulations, including observation of a group of signals centered at 1508 m/z with correct isotopomer ratios computed for the intact hexanuclear cluster complex with three nitrates attached, [{(**Ni-1′**)$_4$Pd$_2$}$^{4+}$(NO$_3$)$_3$]$^+$. The dicationic complex [(**Ni-1′**)$_2$M]$^{2+}$ is a prominent species in this and all other compounds studied.

Conclusion

The graphical summary of the polymetallics based on **Ni-1′** (Scheme 2) shows the N_2S_2Ni metallothiolate ligand maintains its structural integrity whether it serves as a bidentate bridging ligand spanning two metal centers or as a that bidentate ligand to a single metal center. As can be seen in Figure 5, when **Ni-1′** is a bidentate ligand to a single metal center, the S−Ni−S angle is smaller then in its parent complex, but as a bridging bidentate ligand there is no change. Both binding modes generate stable complexes which are related to diphosphane derivatives. Analogy of **Ni-1′** in its bidentate bridging capability is towards the diphenylphosphinomethane (dppm) ligand, whose small bite angle is well-known to facilitate the formation of "A-frame" bimetallic clusters. The structure of a heptanuclear Ni_3Cu_4



Scheme 2

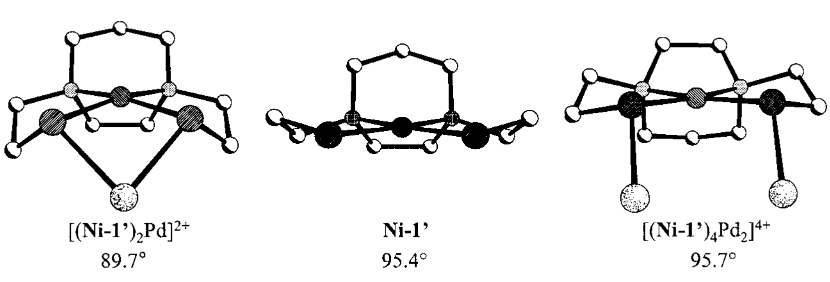


Figure 5. Comparison of the N_2S_2Ni unit as a bidentate ligand, its parent complex, and as a bidentate bridging ligand; values given are S−Ni−S angles

cluster with a mixed set of dppm and aet$_2$Ni ligands support this analogy.[24] Nevertheless, dppm has also been used in the preparation of mononuclear [M(dppm)][BF$_4$]$_2$ salts, M = Pd, Ni;[25] these cations are analogous to our trimetallic cations.

The minor structural change from the eight-membered daco ring to the seven-membered dach framework for N_2S_2 ligand complexes resulted in structural diversity heretofore not observed in the polymetallic species. Notably, in contrast to the daco analogue, the loss of one methylene unit in the dach framework resulted in a different folding pattern as evidenced by the basket case, a different nuclearity as seen in the paddlewheel structure, and an enhanced capability to bind counterions as noted in the chloride-bound slant-chair structure. These differences appear to derive from a lesser steric requirement of the dach mesocyclic framework.

Experimental Section

General Remarks: Where anaerobic conditions were required, standard Schlenk techniques with argon and an argon glovebox were used. Solvents were dried and distilled using standard methods.[26] (bme-daco)Ni,[27] (bme-dach)Ni,[18] and [(bme-daco)$_2$Ni$_3$]-[Cl$_2$] [8] were synthesized according to published procedures. Anhydrous nickel(II) bromide (Strem), nickel(II) chloride hexahydrate (J.T. Baker), palladium(II) nitrate hydrate (Strem), and palladium(II) chloride (Johnson Matthey) were used as received. UV/Vis spectra were recorded on a Hewlett−Packard 8453 diode array spectrometer using quartz cells (1.00 cm path length). Elemental analyses were performed by Canadian Microanalytical Services Ltd., Delta, British Columbia, Canada. Electrospray Ionization mass spectra were recorded using a MDS-Series QStar Pulsar with a spray voltage of 5 KeV at the Laboratory for Biological Mass Spectroscopy at Texas A&M University. Conductance measurements were made using an Orion 160 conductivity meter.

[{(bme-dach)Ni}$_2$PdCl]$^+$[Cl]$^-$: Palladium chloride (0.087 g, 0.49 mmol) was refluxed under argon in CH_3CN (25 mL) until dissolved and then added to (bme-dach)Ni (0.272 g, 0.982 mmol) in CH_3CN (15 mL) to produce an orange-red precipitate. The solid was collected, redissolved in a minimum of CH_3OH, filtered and dried in vacuo. Yield: 0.336 g, 94 %. Single crystals of X-ray quality were grown from slow diffusion of diethyl ether into an CH_3CN solution. UV/Vis (CH_3OH) λ_{max} in nm (ε): 230 (22 500), 266 (19 000), 308 (20 000), 386 (6600), 420 (5700). $C_{18}H_{36}Cl_2N_4Ni_2PdS_4$ (731.5): calcd. C 29.56, N 7.66, H 4.96; found C 27.7, N 7.05, H 5.32. Mass spectrum (*m*/*z*): 330 [{(bme-dach)Ni}$_2$Pd]$^{2+}$; 696 [{(bme-dach)Ni}$_2$PdCl]$^+$.

[{(bme-dach)Ni}$_4$Pd$_2$][NO$_3$]$_4$: (bme-dach)Ni (0.116 g, 0.419 mmol) was made into a slurry with CH_3CN (25 mL). Palladium nitrate hydrate (0.049 g, 0.212 mmol) was dissolved in CH_3CN (25 mL) and transferred by cannula to the (bme-dach)Ni solution which immediately began to turn orange red. After about 10 minutes, the reaction mixture was filtered in air leaving some unchanged (bme-dach)Ni, which was washed with CH_3CN. The solution was layered with *n*-hexane and put in the refrigerator to give dark red blocks of product. Yield: 0.105 g, 64 %. UV-Vis (CH_3OH), λ_{max} in nm (ε): 230 (53 000), 266 (39 000), 308 (43 000), 386 (15 000), 420 (12 000). $C_{36}H_{72}N_{12}Ni_4O_{12}Pd_2S_8$ (1569.2): calcd. C 27.55, N 10.71, H 4.62; found C 27.36, N 10.77, H 4.73. Mass spectrum (*m*/*z*): 330 [{(bme-dach)Ni}$_2$Pd]$^{2+}$; 722 [{(bme-dach)Ni}$_2$(PdNO$_3$)]$^+$, 1507 [{(bme-dach)Ni}$_4${Pd$_2$(NO$_3$)$_3$}]$^+$, 461 [{(bme-dach)Ni}$_4$(Pd$_2$NO$_3$)]$^{3+}$.

[{(bme-daco)Ni}$_2$Pd][NO$_3$]$_2$: (bme-daco)Ni (0.230 g, 0.791 mmol) was dissolved in CH_3CN (15 mL). The yellow-brown sample of palladium nitrate hydrate (0.091 g, 0.394 mmol) was dissolved in CH_3CN (15 mL) and transferred by cannula to the purple (bme-daco)Ni solution which immediately began to turn dark red, forming a precipitate. The reaction mixture was stirred overnight and then placed in an ice-water bath. The precipitate was collected on a Büchner funnel and washed with ice cold CH_3CN. Yield: 0.178 g, 58 %. Single crystals of X-ray quality were grown from slow diffusion of diethyl ether vapor into a CH_3OH solution in the refrigerator. UV-Vis (CH_3OH), λ_{max} in nm (ε): 286 (17 700), 250 (16 000), 328 (13 000), 408 (4000), 524 (3000). $C_{20}H_{40}N_6Ni_2PdO_6S_4$ (812.6): calcd. C 29.56, N 10.34, H 4.96; found C 29.18, N 10.10, H 4.98. Mass spectrum (*m*/*z*): 343 [{(bme-daco)Ni}$_2$Pd]$^{2+}$.

[(bme-dach)$_2$Ni$_3$][Br]$_2$: A slurry containing $NiBr_2$ (0.374 g, 1.71 mmol) in 50 mL of distilled CH_3OH was added to a slurry of (bme-dach)Ni (0.535 g, 1.93 mmol) in CH_3OH (20 mL). The development of a dark red color was immediate. The solution was stirred overnight. The solvent was removed, the residue dissolved in CH_3CN, and filtered through a medium porosity frit under air. The solvent was removed in vacuo yielding a dark red solid. Yield: 0.084 g, 11%. Single crystals of X-ray quality were grown from slow evaporation of a CH_3OH solution. UV-Vis (CH_3OH), λ_{max} in nm (ε): 482 (1880), 406 (2520), 278 (16 600), 227 (19 700). $C_{18}H_{36}Br_2N_4Ni_3S_4$ (772.7): calcd. C 27.98, N 7.25, H 4.70; found C 26.83, N 7.00, H 4.73. Mass spectrum (*m*/*z*): 306 [(bme-dach)$_2$Ni$_3$]$^{2+}$; 693 [(bme-dach)$_2$Ni$_3$]$^{2+}$Br$^-$.

[(bme-dach)$_2$Ni$_3$Cl]$^+$[Cl]$^-$: [(bme-dach)$_2$Ni$_3$Cl]$^+$Cl$^-$ was synthesized in a similar fashion to [(bme-dach)$_2$Ni$_3$][Br]$_2$, using $NiCl_2{\cdot}6H_2O$ as an exogenous nickel source. Yield: 0.150 g, 60 %. $C_{18}H_{36}Cl_2N_4Ni_3S_4$ (683.8): calcd. C 29.67, N 8.19, H 5.31; found C 31.62, N 7.65, H 5.29. Mass spectrum (*m*/*z*): 306 [(bme-dach)$_2$Ni$_3$]$^{2+}$; 647 [(bme-dach)$_2$Ni$_3$Cl]$^+$.

X-ray Crystallographic Study: Low temperature X-ray diffraction data were collected on a Bruker SMART CCD-based diffractometer (Mo-K_α radiation, λ = 0.71073 Å) and covered a hemisphere of space upon combining three sets of exposures. The space groups were determined based on systematic absences and intensity statistics using the SMART[28] program for data collection and cell refinement. Raw data frame integration was performed with SAINT+.[29] Other programs used include SHELXS-86 (Sheldrick)[30] for structure solution, SHELXL-97 (Sheldrick)[31] for structure refinement and SHELXTL-Plus, version 5.1 or later (Bruker),[32] for molecular graphics and preparation of material for publication. The structures were solved by direct methods. Anisotropic displacement parameters were determined for all non-hydrogen atoms. Hydrogen atoms were added at idealized positions and refined with fixed isotropic displacement parameters equal to 1.2 (1.5 for methyl protons) times the isotropic displacement parameters of the atoms to which they were attached. Collection and refinement summaries are shown in Table 3. SADABS[31] and Wingx[33] were used on the palladium clusters. CCDC-215014 [{(**Ni-1′**)$_2$Ni}Br$_2$], CCDC-215016 [{(**Ni-1′**)$_2$NiCl}Cl], CCDC-215015 [{(**Ni-1′**)$_4$Pd$_2$}(NO$_3$)$_4$], and CCDC-215013 [{(**Ni-1′**)$_2$PdCl}Cl] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge

Table 3. Crystal data

	[(**Ni-1′**)$_2$Ni][Br$_2$]	[(**Ni-1′**)$_2$NiCl][Cl]	[(**Ni-1′**)$_4$Pd$_2$][NO$_3$]$_4$	[(**Ni-1′**)$_2$PdCl][Cl]
Formula	$C_{18}H_{36}Br_2N_4Ni_3S_4\cdot$ $2CH_3OH$	$C_{18}H_{36}Cl_2N_4Ni_3S_4\cdot$ CH_3OH	$C_{36}H_{72}N_{12}Ni_4O_{12}Pd_2S_8\cdot$ $2CH_3CN$	$C_{18}H_{36}Cl_2N_4Ni_2PdS_4\cdot$ CH_3CN
M_r (g/mol)	418.38	486.11	1651.28	772.52
T (K)	110(2)	110(2)	110(2)	110(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/m$	$P2_1/c$	$P\bar{1}$
Unit cell				
a (Å)	7.5116(17)	9.5873(17)	12.373(3)	10.545(5)
b (Å)	15.047(3)	13.537(2)	14.585(4)	12.032(6)
c (Å)	13.664(3)	10.8074(19)	16.331(4)	12.630(6)
α (°)	90	90	90	108.548(7)
β (°)	105.643(3)	90.670(3)	91.314(5)	94.331(8)
γ (°)	90	90	90	91.978(7)
V (Å^3)	1487.2(6)	1402.5(4)	2946.3(14)	1512.1(12)
Z	2	2	4	2
GooF	0.904	1.054	1.019	1.066
Reflections collected	9483	6260	21585	8104
Reflections observed	3518	2111	5136	5037
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0593, 0.1280	0.0407, 0.1155	0.0652, 0.1656	0.0677, 0.1643
$R1$, $wR2$ (all data)	0.1096, 0.1460	0.0441, 0.1177	0.0739, 0.1800	0.0994, 0.1889

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[1] D. W. Stephan, T. T. Nadasdi, *Coord. Chem. Rev.* **1996**, *147*, 147−208.
[2] A. R. Dias, M. H. Garcia, M. J. Villa de Brito, A. Galvão, *J. Organomet. Chem.* **2001**, *632*, 75−84.
[3] K. A. Jensen, *Z. Anorg. Chem.* **1936**, *227*, 25−31.
[4] D. C. Jicha, D. H. Busch, *Inorg. Chem.* **1962**, *1*, 872−877.
[5] D. Gibson, S. J. Lippard, *Inorg. Chem.* **1986**, *25*, 219−222.
[6] T. Konno, K. Yonenobu, J. Hidaka, K. Okamoto, *Inorg. Chem.* **1994**, *33*, 861−864.
[7] M. A. Turner, W. L. Driessen, J. Reedijk, *Inorg. Chem.* **1990**, *29*, 3331−3335.
[8] P. J. Farmer, T. Solouki, D. K. Mills, T. Soma, D. H. Russell, J. H. Reibenspies, M. Y. Darensbourg, *J. Am. Chem. Soc.* **1992**, *114*, 4601−4605.
[9] G. Musie, P. J. Farmer, T. Tuntulani, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **1996**, *35*, 2176−2183.
[10] T. Tuntulani, J. H. Reibenspies, P. J. Farmer, M. Y. Darensbourg, *Inorg. Chem.* **1992**, *31*, 3497−3499.
[11] M. L. Golden, M. V. Rampersad, J. H. Reibenspies, M. Y. Darensbourg, *Chem. Commun.* **2003**, 1824−1825.
[12] M. L. Miller, S. A. Ibrahim, M. L. Golden, M. Y. Darensbourg, *Inorg. Chem.* **2003**, *42*, 2999−3007.
[13] C-H. Lai, J. H. Reibenspies, M. Y. Darensbourg, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2390−2393.
[14] A. E. Martell, R. D. Hancock, *Metal Complexes in Aqueous Solutions*; Plenum Press: New York, **1996**, ch. 3.
[15] X-H. Bu, M. Du, L. Zhang, Z-L. Shang, R-H. Zhang, M. Shionoya, *J. Chem. Soc., Dalton Trans.* **2001**, 729−735.
[16] X-H. Bu, M. Du, L. Zhang, Z-L. Shang, R-H. Zhang, D.-Z. Liao, M. Shionoya, T. Clifford, *Inorg. Chem.* **2000**, *39*, 4190−4199.
[17] X-H. Bu, M. Du, L. Zhang, D-Z. Liao, J-K. Tang, R-H. Zhang, M. Shionoya, *J. Chem. Soc., Dalton Trans.* **2001**, 593−598.
[18] J. J. Smee, M. L. Miller, C. A. Grapperhaus, J. H. Reibenspies, M. Y. Darensbourg, *Inorg. Chem.* **2001**, *40*, 3601−3605.
[19] M. A. Reynolds, T. B. Rauchfuss, S. R. Wilson, *Organometallics* **2003**, *22*, 1619−1625.
[20] R. C. Linck, C. W. Spahn, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc.* **2003**, *125*, 8700−8701.
[21] R. Bartsch, S. Hietkamp, S. Morton, H. Peters, O. Stelzer, *Inorg. Chem.* **1983**, *22*, 3624−3632.
[22] A. J. Amoroso, S. S. M. Chung, D. J. E. Spencer, J. P. Danks, M. W. Glenny, A. J. Blake, P. A. Cooke, C. Wilson, M. Schroder, *Chem. Commun.* **2003**, 2020−2021.
[23] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81−122.
[24] H-W. Xu, Z-N. Chen, S. Ishizaka, N. Kitamura, J-G. Wu, *Chem. Commun.* **2002**, 1934−1935.
[25] A. Miedaner, R. C. Haltiwanger, D. L. DuBois, *Inorg. Chem.* **1991**, *30*, 417−427.
[26] A. J. Gordon, R. A. Ford, *The Chemist's Companion*; J. Wiley and Sons: New York **1972**.
[27] D. K. Mills, I. Font, P. J. Farmer, Y.-M. Hsiao, T. Tuntulani, R. M. Buonomo, D. C. Goodman, G. Musie, C. A. Grapperhaus, M. J. Maguire, C.-H. Lai, M. L. Hatley, J. J. Smee, J. A. Bellefeuille, M. Y. Darensbourg, *Inorganic Syntheses.* **1998**, *32*, 89−98.
[28] SMART 1000 CCD, Bruker Analytical X-ray Systems: Madison, WI, **1999**.
[29] SAINT-Plus, version 6.02 or later: Bruker, Madison, WI, **1999**.
[30] G. Sheldrick. SHELXS-86: *Program for Crystal Structure Solution*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, **1986**.
[31] G. Sheldrick. SHELXL-97: *Program for Crystal Structure Refinement*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, **1997**.
[32] SHELXTL, version 5.1 or later: Bruker, Madison, WI, **1998**.
[33] L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837−838.

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