Inorg. Chem. **1992**, *31*, 3497-3499

Preparations and Structures of a Zinc(II) Dimer and Zinc(II)/Nickel(II) Pentanuclear Derivatives of *N,N'*-Bis(mercaptoethyl)-1,5-diazacyclooctane: [(BME-DACO)Zn]$_2$ and {[(BME-DACO)Ni]$_3$[ZnCl]$_2$}{BF$_4$}$_2$

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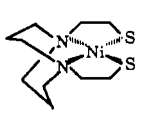
The macrocyclic ligand *N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane, H$_2$BME-DACO, has been demonstrated competent to complex transition metals, generating in monomeric form the square planar (BME-DACO)Ni^{II} (**1**).[1] By further use of available lone pairs on sulfur, homo- and heteropolynuclear complexes are generated. Reported thus far is the dimer of Fe^{II} in which one sulfur from each metal bridges to the second, generating a symmetrical 2 Fe–2 S core, [(BME-DACO)Fe]$_2$ (**2**).[2] Structures **3**, [(BME-DACO)Ni(μ-Cl)FeCl]$_2$,[2] and **4**, [(BME-DACO)Ni]$_2$Ni^{2+},[3] are exemplary of the use of **1** as a bidentate ligand, generating, in the cases shown, staircase or steplike structures. Note that the propensity for Fe^{II} to be pentacoordinate governs the overall nuclearity of both **2** and **3**, and the tendency of Ni^{II} to be square planar results in the trinuclear structure **4**.



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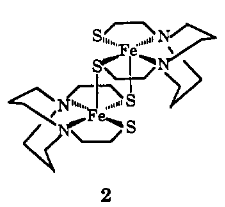

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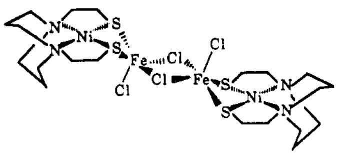

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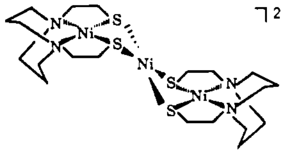

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In all known structures of derivatives of the BME-DACO ligand, the N$_2$S$_2$ binding sites are oriented in a square or quasi-square plane as the steric constraints for this ligand dictate. The greatest deviation from square planarity is in the form of an 18.2° tetrahedral twist, observed for the oxygenated derivative [*N*-(mercaptoethyl)-*N'*-(sulfinoethyl)diazacyclooctanato]nickel(II), (MESE-DACO)Ni (**5**).[3] The geometry of complexes obtained from the tetrahedral preference of zinc[4] thus pose an interesting problem for the BME-DACO ligand, and we proceeded to prepare zinc derivatives as well as an unprecedented NiZn heterometallic, making use of (BME-DACO)Ni^{II} as a metallothiolate ligand.

Under anaerobic conditions, the ligand H$_2$BME-DACO (3.50 g, 15 mmol)[1] dissolved in 50 mL of dry toluene was added to anhydrous zinc acetylacetonate (3.95 g, 15 mmol) in 100 mL of toluene without stirring. On standing overnight, the product crystallized out of solution as colorless crystals of [(BME-DACO)-Zn]$_2$ (**6**) (3.50 g, 78% yield).[5] Crystals suitable for X-ray analysis were obtained on recrystallization from a hot 50:50 mixture of methanol and acetonitrile.[6]

The reaction of the (BME-DACO)Ni^{II} complex with zinc chloride gave the same product regardless of stoichiometry; the following procedure, carried out under a N$_2$ atmosphere, optimized the yield. Addition of anhydrous ZnCl$_2$ (0.031 g, 0.22 mmol) in 10 mL of dry MeOH to a purple solution of (BME-DACO)Ni^{II} (0.10 g, 0.34 mmol)[1] in 20 mL of MeOH immediately shifted the solution color to bright red. A pink solid precipitated upon adding 150 mL of anhydrous ether. Ion exchange was required to obtain X-ray-quality crystals. Thus (BME-DACO)Ni^{II} and NaBF$_4$ were dissolved in 30 mL of dry methanol in a test tube and a THF solution of ZnCl$_2$ was carefully layered in by syringe. The product, analyzing as {[(BME-DACO)Ni]$_3$Zn$_2$Cl$_2$}{BF$_4$}$_2$ (**7**),[5] crystallized from this solution as red crystals.[6]

Figures 1 and 2 contain the molecular structures of **6** and **7**, respectively. Compound **6** is a dimer of (BME-DACO)Zn and is directly analogous to [(BME-DACO)Fe]$_2$ (**2**) described above.[2] That is, the Zn ions are pentacoordinate in an approximate square pyramidal geometry; thiolate sulfurs from adjacent (BME-DACO)Zn units occupy the apical sites of the SqPy resulting in a dimer with a 2 Zn–2 S core. In both **6** and **2** the M--S$_{\mathrm{terminal}}$ bond distance is significantly shorter than the M--S$_{\mathrm{bridge}}$. The Zn–S$_{\mathrm{apical}}$ distance of 2.394 (1) Å is intermediate between the Zn–S bond distances in the (quite distorted) square plane (Zn–S(1) = 2.327 (1) and Zn–S(2) = 2.494 (1) Å). The Zn–Zn distance is 3.34 (1) Å. Interestingly, the iron complex of *N,N'*-bis(2-mercaptoethyl)-dimethyl-1,3-propanediamine, BME-Me$_2$PDA, a ligand containing only half the rigidity of the DACO framework, also results in a dimeric complex with a 2 Fe–2 S core,[7] roughly similar to **2**. With Zn however, the flexibility of BME-Me$_2$PDA permits (distorted) tetrahedral coordination resulting in a tetranuclear species with two ZnCl$_2$ units bridging into two (BME-Me$_2$PDA)Zn units.[8]

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(1) Mills, D. K.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1990**, *29*, 4364. Details of the BME-DACO ligand preparation are to be published (Mills, D. K.; Darensbourg, M. Y. *Inorg. Syn.*, submitted for publication) and are available on request from the authors.

(2) Mills, D. K.; Hsiao, Y. M.; Farmer, P. J.; Atnip, E. V.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 1421.

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(4) Tetrahedral zinc complexes with N$_2$S$_2$ donor sets are known. See for example: (*a*) Corwin, D. T., Jr.; Koch, S. A. *Inorg. Chem.* **1988**, *27*, 493. (b) Harrowfield, J. McB.; Pakawatchi, C.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 825. (c) Mawby, A.; Irving, H. M. N. H. *J. Inorg. Nucl. Chem.* **1972**, *34*, 109. (d) Greene, D. L.; McCormick, B. J.; Pierpont, C. G. *Inorg. Chem.* **1973**, *12*, 2148. An octahedral complex with N$_2$S$_4$ donors is also known: Bell, N. A.; Johnson, E.; March, L. A.; Marsden, S. D.; Nowell, I. W.; Walker, Y. *Inorg. Chim. Acta* **1989**, *156*, 205.

(5) Elemental analyses (Galbraith Laboratories) are as follows. (a) Calcd (found) for Zn$_2$C$_{20}$H$_{40}$N$_4$S$_4$: C, 40.35 (40.61); H, 6.72 (6.58); N, 9.41 (9.58). Mp (with dec) > 300 °C. (b) Calcd (found) for Ni$_3$Zn$_2$Cl$_2$B$_2$F$_8$C$_{30}$H$_{60}$N$_6$S$_6$: C, 28.83 (28.95); H, 4.80 (4.88); N, 6.73 (6.60). Mp (with dec) > 300 °C. ^{1}H NMR for Zn$_2$C$_{20}$H$_{40}$N$_4$S$_4$ in pyridine-d_5 at 100 °C: δ (ppm) = 3.14 (multiplet, 4 H), 2.98 (triplet, J = 5 Hz, 4 H), 2.87 (triplet, J = 5 Hz, 4 H), 2.37 (complex multiplet, 6 H), 1.79 (multiplet, 2 H).

(6) X-ray diffraction data were collected at 296 K for [(BME-DACO)Zn]$_2$ and {[(BME-DACO)Ni]$_3$Zn$_2$Cl$_2$}{BF$_4$}$_2$ and the structures solved by standard procedures with semiempirical absorption corrections applied. Crystallographic data are given as a, b, c; β, space group, Z, 2θ range, unique observed reflections, semiempirical absorption corrections $T_{\max}$, $T_{\min}$ and R (R_w). [(BME-DACO)Zn]$_2$: 8.926 (2), 12.785 (2), 11.199 (2) Å; 101.13 (2)°, $P2_1/n$, 2, 4.0°/50.0°, 2018 ($F > 4.0\sigma(F)$), 0.839, 0.624, 0.0303 (0.0450). {[(BME-DACO)Ni]$_3$Zn$_2$Cl$_2$}{BF$_4$}$_2$: 16.571 (3), 16.571 (3), 16.571 (3) Å; 90.00°, $P2_13$, 4, 4.0°/50.0°, 1775 ($F > 4.0\sigma(F)$), 0.995, 0.957, 0.0667 (0.0828). Absolute configuration of **7**: η = 0.77 (13) (Rodgers, D. *Acta Crystallogr.* **1981**, *A37*, 734).

(7) Karlin, K. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6951.

(8) Hu, W. J.; Barton, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1973**, *95*, 1170.

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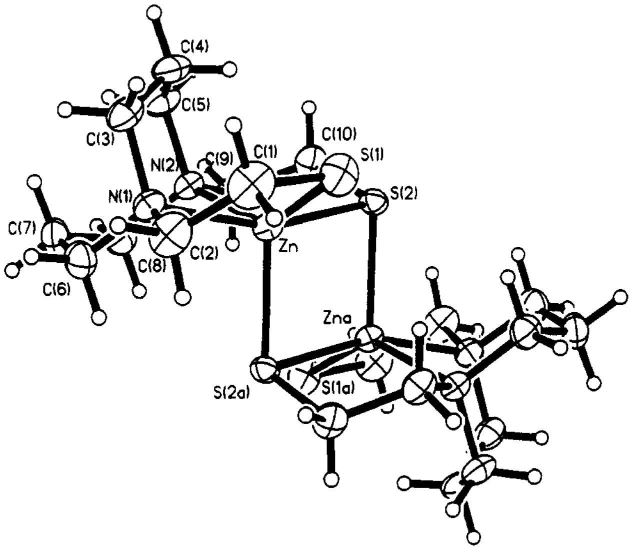

Figure 1. Thermal ellipsoid plot (50% probability) of [(BME-DACO)Zn]$_2$. Selected bond lengths (Å): Zn–S(1), 2.327 (1); Zn–S(2A), 2.394 (1); Zn–S(2), 2.494 (1); Zn–N(1), 2.231 (2); Zn–N(2), 2.255 (2); S(2)–Zn(A), 2.394 (1). Selected bond angles (deg): S(2)–Zn–N(1), 159.3 (1); S(1)–Zn–N(2), 140.7 (1); S(1)–Zn–S(2), 97.6 (1); N(1)–Zn–N(2), 80.9 (1); S(1)–Zn–N(1), 85.1 (1); S(2)–Zn–N(2), 84.2 (1); S(2)–Zn–S(2A), 93.8 (1); S(1)–Zn–S(2A), 119.1 (1); N(1)–Zn–S(2A), 102.8 (1); N(2)–Zn–S(2A), 99.8 (1); Zn–S(2)–Zn(A), 86.2 (1).

Only one-third of the molecular cation **7** is unique in the cubic space group $P2_13$. The Zn and Cl atoms are positioned on the 3-fold axis, while the nickel is located on a general position. The 3-fold crystallographic axis is coincident with the 3-fold axis of the Zn tetrahedra. The unique structure shown in Figure 2 demonstrates that three square planar **1** units, with bond angles and distances largely unchanged from the free complex **1**,[1] serve as bidentate bridging ligands to two zinc chlorides. Stripped of ligands, the nuclearity is thus expressed as a trigonal bipyramid of metal ions, with three nickels in the equatorial plane and two zincs in the axial position, resulting in a Zn--Zn distance of 4.35 (1) Å, Zn--Ni distances of 3.69 (1) and 3.64 (1) Å, and Ni-Ni distances of 5.11 (1) Å. The closest nonbonded Ni–S distances are 3.89 (1) and 4.03 (1) Å. The average S–Zn–S angles are 112°, and the average S–Zn–Cl angles are 106°. In **6** and **7**, the DACO framework is in the usual boat/chair configuration with respect to Ni and the ethylene sulfide units eclipse each other across the N_2S_2 square plane.

The service of (BME-DACO)Ni^{II} as both a bidentate ligand to a single metal as well as a bidentate bridging ligand to two metal centers results in the slight structural differences presented in Figure 3. In **4**, for example,[3] the ∠S–Ni–S bite of the metallothiolate chelate is 82.8 (1)°, whereas in **7** ∠S–Ni–S opens to 88.1 (2)°. The angle between the normals to the best NiN$_2$S$_2$ plane and the S(1)–Zn(1)–Zn(2)–S(2) plane (mean deviation from that Zn$_2$S$_2$ plane is calculated at 0.03 Å) is 103.4°, significantly the same as that observed when **1** serves as a bidentate ligand. In **4**, the folding angle (or angle between the normals to the planes) between the NiS$_4$ square plane and the best plane calculated for an NiN$_2$S$_2$ unit (mean deviation = 0.061 Å) is 103.5°. Nevertheless the directional difference in sulfur lone pairs and the differences in nickel–nickel distances (2.685 (1) Å in **4**; 5.11 (1) Å in **7**) are of consequence to the Ni$^{II/I}$ reduction potentials in such polymetallics; vide infra.

Both **6** and **7** are air-stable in the solid state, although prolonged exposure discolors the white **6** solid. The zinc dimer **6** is largely insoluble in all solvents excepting pyridine (in which the ^{1}H NMR spectrum is best interpreted as a pyridine-complexed monomer).[5] It is reactive with alkylating agents such as MeI, producing as yet incompletely characterized thioether derivatives. Zinc is displaced by nickel on reaction of **6** with Ni(acac)$_2$ in 50:50 MeOH/CH$_3$CN, producing mixtures of **1** and **4** as well as Zn(acac)$_2$.

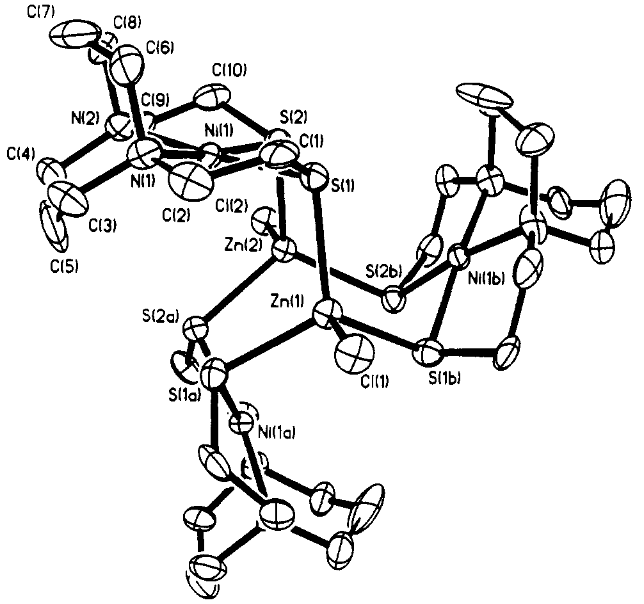

Figure 2. Thermal ellipsoid plot (50% probability) of {[(BME-DACO)Ni]$_3$Zn$_2$Cl$_2$}{BF$_4$}$_2$. Hydrogen atoms are omitted for clarity. Selected distances (Å): Cl(1)–Zn(1), 2.268 (8); Cl(2)–Zn(2), 2.270 (9); Zn(1)–S(1), 2.361 (5); Zn(2)–S(2), 2.348 (5); Ni(1)–S(1), 2.183 (5); Ni(1)–S(2), 2.189 (5); Ni(1)–N(1), 2.01 (1); Ni(1)–N(2), 2.01 (1). Selected bond angles (deg): Cl(1)–Zn(1)–S(1), 106.8 (1); Cl(2)–Zn(2)–S(2), 105.6 (1); S(1)–Ni(1)–S(2), 88.1 (2); S(1)–Ni(1)–N(1), 90.6 (5); S(2)–Ni(1)–N(2), 90.6 (5); N(1)–Ni(1)–N(2), 90.0 (6); Ni(1)–S(1)–Zn(1), 106.5 (2); Ni(1)–S(2)–Zn(2), 108.7 (2); Zn(1)–S(1)–C(1), 100.7 (7); Zn(2)–S(2)–C(10), 100.7 (7).

Salts of the heterometallic **7** dissolve in water with deaggregation, yielding the purple, diamagnetic **1**, characterizable by NMR and vis-UV spectroscopy. In MeOH, a mixture of **7** and **1** exists, whereas, in CH$_3$CN, spectral and electrochemical probes suggest **7** is an intact species. The vis-UV spectrum of **7** in CH$_3$CN solution shows an intense charge-transfer band below 300 nm with a barely discernible shoulder at 350 nm and only one band in the visible (λ_{max} = 528 nm, ϵ = 508 M^{-1} cm^{-1}). In contrast, **1** has two visible absorptions, 602 and 500 nm.[1] The ^{1}H NMR measurements of **7** in CH$_3$CN find broad signals indicative of paramagnetism which are consistent with Ni^{II} in higher coordination environments. [The decrease in thiolate-sulfur donor ability when involved in bridge bonding may enhance specific solvent or anion interaction at nickel.]

The cyclic voltammogram response of **7** in dry acetonitrile (0.1 M [Bu$_4$N][PF$_6$]) also indicates the nickel thiolate sulfurs are charged neutralized; i.e., the irreversible oxidation of +0.50 mV, which is characteristic of **1**,[1] is replaced by two reversible reductions at $E_{1/2}$ = −1.03 and −1.25 V and an irreversible wave at −1.45 V, referenced to Ag$^+$/AgCl.[9] These reductions, assumed to be sequential Ni$^{II/I}$ processes, are sufficiently close to suggest that individual **1** units are little coupled to each other.[10,11] In contrast, the trinuclear species **4**, with close Ni--Ni intramolecular distances, has $E_{1/2}$ = −0.66 (rev) and −1.60 V (irrev); i.e., a $\Delta E_{1/2}$ value of ca. 1 V, suggesting delocalization of the added electron.[9-11]

Although there are several Zn/Ni heterometallics reported in the literature,[12] to our knowledge, this is the first which utilizes thiolate as a bridging ligand. The most obvious outcome of this work is the demonstration of the remarkable scope of the (BME-

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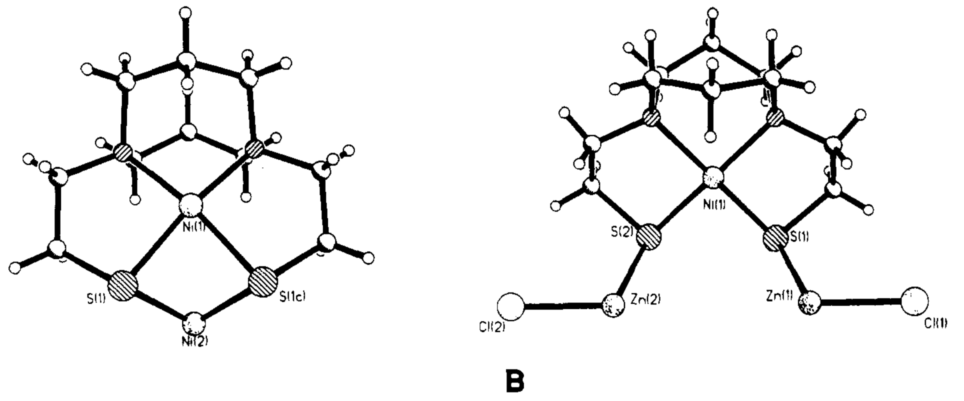

Figure 3. Comparison of the (BME-DACO)Ni^{II} unit as a bidentate ligand to Ni^{2+} in [(BME-DACO)Ni]$_2$Ni^{2+} (A) and as a bidentate bridging ligand to two Zn^{2+} ions in {[(BME-DACO)Ni]$_3$Zn$_2$Cl$_2$}$^{2+}$ (B).

DACO)M complexes in the generation of polynuclear structures.[13,14] A full description of the spectral (vis-UV and EPR) and electrochemical properties of these species in even- and odd-electron forms is in preparation.[9]

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Supplementary Material Available: Table IS, listing experimental crystallographic data, Tables IIIS, VIS, and VIIS, listing complete bond lengths and angles, Tables IIS and VS, listing atomic coordinates and equivalent isotropic displacement parameters, Tables IVS and VIIIS, listing anisotropic displacement parameters, and Figures 1S–4S, showing alternative views and packing diagrams of [(BME-DACO)Zn]$_2$ and of {[(BME-DACO)Ni]$_3$Zn$_2$Cl$_2$}[BF$_4$]$_2$ (12 pages). Ordering information is given on any current masthead page.

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(13) Although we have not demonstrated the simple monodentate binding ability of the (BME-DACO)Ni^{II} unit, the report of Blinn and Treichel et al.[14] on an analogous system suggests that conditions could be found to prepare complexes using only one sulfur donor site.

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