

Dinuclear nickel complexes modeling the structure and function of the acetyl CoA synthase active site

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A dinuclear nickel complex with methyl and thiolate ligands, $\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{Me})(\text{SDmp})$ (**2**), has been synthesized as a dinuclear $\text{Ni}_d\text{-Ni}_p$ -site model of acetyl-CoA synthase (ACS) (dadt^{Et} is *N,N'*-diethyl-3,7-diazanonane-1,9-dithiolate; Dmp is 2,6-dimesitylphenyl). Complex **2** was prepared via 2 methods: (i) ligand substitution of a dinuclear $\text{Ni}(\text{II})\text{-Ni}(\text{II})$ cation complex $[\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{tmtu})_2](\text{OTf})_2$ (**1**) with MeMgBr and KSDmp (tmtu is tetramethylthiourea), (ii) methyl transfer from methylcobaloxime $\text{Co}(\text{dmgBF}_2)_2(\text{Me})(\text{Py})$ (**5**) to a $\text{Ni}(\text{II})\text{-Ni}(\text{O})$ complex such as $[\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{cod})]$ (**3**), generated in situ from $\text{Ni}(\text{dadt}^{\text{Et}})$ and $\text{Ni}(\text{cod})_2$, followed by addition of KSDmp (cod is 1,5-cyclooctadiene; dmgBF_2 is difluoroboryl-dimethylglyoximate). Method ii models the formation of $\text{Ni}_p\text{-Me}$ species proposed as a plausible intermediate in ACS catalysis. The reaction of **2** with excess CO affords the acetylthioester $\text{CH}_3\text{C}(\text{O})\text{SDmp}$ (**8**) with concomitant formation of $\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{CO})_2$ (**9**) and $\text{Ni}(\text{CO})_4$ plus $\text{Ni}(\text{dadt}^{\text{Et}})$. When complex **2** is treated with 1 equiv of CO in the presence of excess 1,5-cyclooctadiene, the formation of **9** and $\text{Ni}(\text{CO})_4$ is considerably suppressed, and instead the dinuclear $\text{Ni}(\text{II})\text{-Ni}(\text{O})$ complex is generated in situ, which further affords **2** upon successive treatment with $\text{Co}(\text{dmgBF}_2)_2(\text{Me})(\text{Py})$ (**5**) and KSDmp. These results suggest that (i) ACS catalysis could include the $\text{Ni}_d(\text{II})\text{-Ni}_p(\text{O})$ state as the active species, (ii) The $\text{Ni}_d(\text{II})\text{-Ni}_p(\text{O})$ species could first react with methylcobalamin to afford $\text{Ni}_d(\text{II})\text{-Ni}_p(\text{II})\text{-Me}$, and (iii) CO insertion into the $\text{Ni}_p\text{-Me}$ bond and the successive reductive elimination of acetyl-CoA occurs immediately when CoA is coordinated to the Ni_p site to form the active $\text{Ni}_d(\text{II})\text{-Ni}_p(\text{O})$ species.

acetylthioester formation | dinuclear nickel-site model | N2S2 ligand | nickel acyl complex

Acetyl-CoA synthase/CO dehydrogenase (ACS/CODH), a bifunctional metalloenzyme found in acetogenic, methanogenic, and sulfate-reducing bacteria, has the important function of fixing CO and CO_2 in the global carbon cycle (1–3). Whereas CODH catalyzes the reversible conversion of CO_2 to CO, ACS assembles acetyl-CoA from CO, CoA, and a methyl moiety that is derived from the methylcobalamin of the corrinoid iron-sulfur protein (CFeSP). Recently, the crystal structures of the ACS/CODH system from the bacteria *Moorella thermoacetica* and *Carboxydotherrmus hydrogenoformans* have been elucidated (4–6); the ACS active site denoted as the A-cluster contains a $[\text{Fe}_4\text{S}_4]$ cubane cluster and a $\text{Ni}_d\text{-Ni}_p$ dinuclear site as shown in Fig. 1, where the 2 nickels designated as Ni_d and Ni_p occupy distal and proximal positions, respectively, to the $[\text{Fe}_4\text{S}_4]$ cluster. The geometry around Ni_d is square planar, composed of 2 cysteine sulfurs and 2 carboxamide nitrogens of the tripeptide Cys-Gly-Cys from the protein backbone. Ni_p carries an unidentified ligand X and 3 bridging cysteine sulfurs, 2 from the aforementioned tripeptide, and 1 from the $[\text{Fe}_4\text{S}_4]$ cluster.

Biological investigations suggest that the oxidized state of the cluster A_{ox} should be formulated as $\{\text{Ni}_d^{2+}\text{-Ni}_p^{2+}\text{-}[\text{Fe}_4\text{S}_4]^{2+}\}$ (7–9). However, the electronic configuration of the active reduced state, probably reduced by 2 electrons from A_{ox} , which is proposed to be $\{\text{Ni}_d^{2+}\text{-Ni}_p^{1+}\text{-}[\text{Fe}_4\text{S}_4]^{1+}\}$, has not yet been firmly established (10–11). The order of the addition of the substrates,

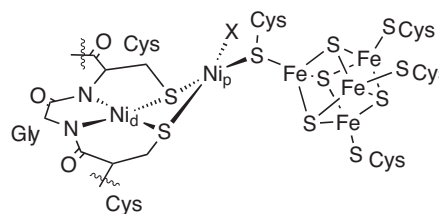


Fig. 1. Schematic view of the ACS active site.

Me, CO, and CoA, to the active site is also controversial, and several mechanisms have been proposed on the basis of biological and computational studies (12–14). On the other hand, synthetic studies that probe the reaction mechanisms are limited in number, although various thiolato-bridged dinuclear nickel complexes have been reported as A-cluster models (15–23).

Proposed ACS mechanisms commonly involve the following steps: (i) methyl transfer from methylcobalamin to the reduced $\text{Ni}_p(\text{O})$ [or $\text{Ni}_p(\text{I})$] site, (ii) CO insertion into the $\text{Ni}_p\text{-Me}$ bond, and (iii) formation of acetyl-CoA via the reductive elimination at the Ni_p site (1–3, 7–14). These reactions had been studied by using mononuclear nickel complexes. CO insertion into the $\text{Ni}\text{-Me}$ bonds of $\text{Ni}(\text{NS}_3^{\text{R}})\text{Me}$ [NS_3^{R} is $\text{N}(\text{CH}_2\text{CH}_2\text{SR})_3$; R is *i*-Pr, *t*-Bu], investigated by Stavropoulos et al. (24), resulted in the formation of acetylthioesters $\text{CH}_3\text{C}(\text{O})\text{SR}$ and $\text{Ni}(\text{O})$ species in high yield upon treatment with CO. Likewise, the reaction of $[\text{Ni}(\text{bpy})(\text{SR})(\text{Me})]$ with >3 equiv of CO was found to yield $[\text{Ni}(\text{bpy})(\text{CO})_2]$ and acetylthioesters (25). Before these reports, Kim et al. (26) had shown that the reaction of $\text{Ni}(\text{dppe})(\text{SAr})(\text{Me})$ with CO generated $\text{CH}_3\text{C}(\text{O})\text{SAr}$. Recently, Rampersad et al. (27) demonstrated the acetylthioester formation in the reaction of $\text{Ni}\text{-Pd}$ dinuclear complex, $\text{Ni}(\text{bme-daco})\text{Pd}(\text{CO})(\text{COMe})$, with NaSMe . Eckert et al. (28) reported the methyl-transfer reaction from methylcobaloxime to $(\text{triphos})\text{Ni}^0(\text{PPh}_3)$ to give $[(\text{triphos})\text{NiMe}]^{2+}$. They have also reported that the dinuclear nickel methyl complex $[\text{Ni}(\text{phma})\text{Ni}(\text{Me})(\text{dppe})]^-$ reacts with CO to give $[\text{Ni}(\text{phma-CO-Me})]^-$ and $(\text{dppe})\text{Ni}(\text{CO})_2$, in which acetylation occurs at the thiolato sulfur of the phma ligand (29).

We report herein ACS model studies using a series of thiolato-bridged dinuclear nickel complexes in the $\text{Ni}(\text{II})\text{-Ni}(\text{II})$ and $\text{Ni}(\text{II})\text{-Ni}(\text{O})$ states, including a key $\text{Ni}(\text{II})\text{-Ni}(\text{II})$ dinuclear complex carrying a methyl and a thiolate, $\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{Me})(\text{S-}$

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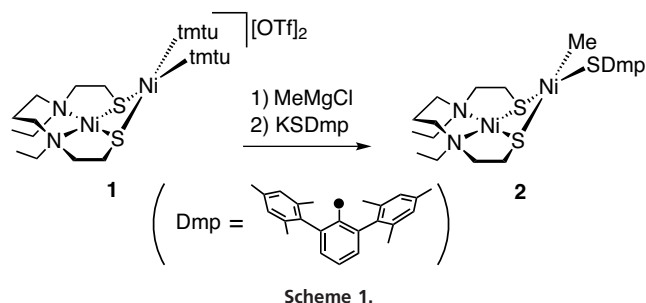
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Dmp) (**2**). Although the diaminedithiolate dadt^{Et} ligand applied to this model study would have different electronic properties from the diamidodithiolate Cys-Gly-Cys ligand of A-cluster in ACS, the results herein would provide a clue to the reaction mechanism for the ACS catalysis.

Results and Discussion

Dinuclear Nickel Complex Having Methyl and Thiolato Ligands.

We have recently reported the synthesis of a series of thiolato-bridged dinuclear nickel complexes such as $\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{SAR})_2$ and $[\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{L})_2]^{2+}$ (L is tmtu, $t\text{BuNC}$; tmtu is tetramethylthiourea) (**30**, **31**). During these studies, we found that the tmtu-substituted dinuclear complex $[\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{tmtu})_2](\text{OTf})_2$ (**1**) reacted with MeMgCl and KSDmp stepwise in THF at -60°C to afford the dinuclear nickel complex $[\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{Me})(\text{SDmp})]$ (**2**) carrying a methyl and a thiolate in 76% yield as a reddish-purple powder (Scheme 1). Complex **2** is an intriguing entity modeling the dinuclear nickel site of the A-cluster. The Me and SDmp moieties closely resemble the substrates of the ACS mediating reaction, a methyl group and CoA, respectively. The ^1H NMR spectrum of **2** shows a singlet signal at -0.66 ppm that is attributable to the Ni–Me group (**25**, **26**, **29**).

The molecular structure of **2** was confirmed by X-ray crystallography. Complex **2** crystallized with 2 crystallographically independent molecules, **2A** and **2B**, and Fig. 2 shows their structures. The metric parameters of **2A** and **2B** are mostly similar. One of the structural differences between **2A** and **2B** derives from the geometry of dadt^{Et} ligand; the conformation of the Ni(1)–N(2)–C(6)–C(7)–S(2) ring and the orientation of 1 ethyl group differ between **2A** and **2B**. The other intriguing structural disparity is the folding of the 2 Ni-coordination planes along the $\mu\text{S}-\mu\text{S}$ vector, where the dihedral angle defined by the 2 Ni($\mu\text{-S}$) $_2$ planes is 119.4° for **2A** and 103.5° for **2B**. As a result, the Ni–Ni distance of **2A** [2.9029(3) Å] is markedly longer than that of **2B** [2.6935(3) Å]. This observation points to a soft nature of the potential energy curve for the folding motion. The Ni–Me bond lengths of **2A** and **2B** are comparable to that of $[\text{Ni}(\text{phma})\text{Ni}(\text{Me})(\text{dppe})]^-$ [1.966(2) Å] (**28**). Because of the strong *trans* influence of the methyl group, the Ni(2)–S(1) distances are elongated by 0.10 and 0.12 Å compared with the Ni(2)–S(2) distances.

The bond lengths and angles of **2A** and **2B** also compared well with the relevant structural parameters reported for the A-clusters of ACS $_{\text{Mt}}$ (from *Moorella thermoacetica*) and ACS $_{\text{Ch}}$ (from *Carboxydotherrmus hydrogenformans*) (**5**, **6**), as shown schematically in Fig. 3. Although the Cys-Gly-Cys tripeptide of the A-cluster must have different geometrical/electronic properties from the dadt^{Et} model ligand, the core structures of **2A** (and **2B**) and the A-cluster are very much alike. Like **2A**, **B**, the Ni(2)– μS bonds are longer than the Ni(1)– μS bonds, except for Ni(2)–S(2) of ACS $_{\text{Mt}}$, which is *trans* to the Ni(2)–S(3) bond. The dihedral angle between the Ni($\mu\text{-S}$) $_2$ planes is somewhat larger for the A-clusters. Of note are the elongated Ni(2)–S(1) distances

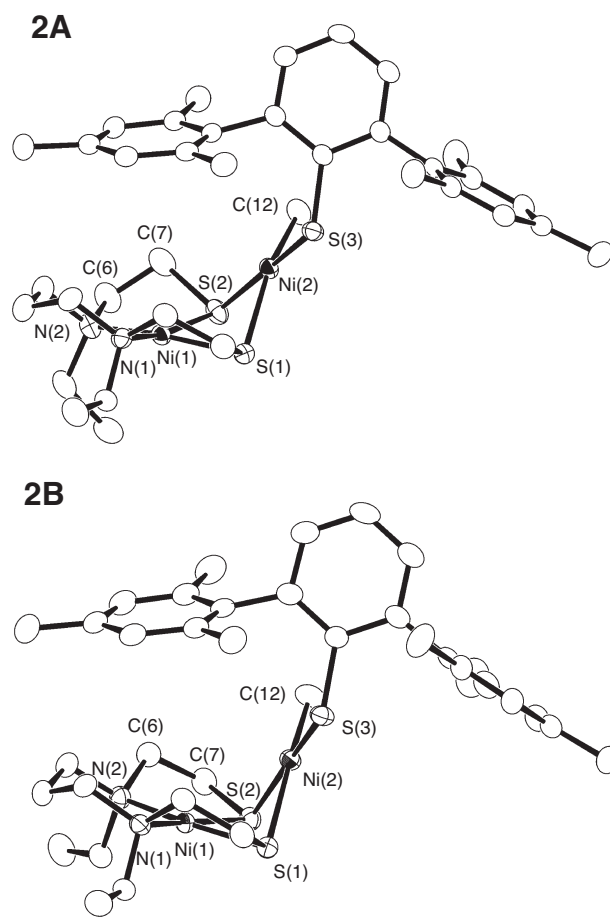


Fig. 2. ORTEP drawing of $\text{Ni}(\text{dadt}^{\text{Et}})\text{Ni}(\text{Me})(\text{SDmp})$ (**2A**, **2B**). Thermal ellipsoids are shown at 50% probability.

observed for both **2A**, **B**, and the A-clusters, compared with the Ni(2)–S(2) lengths. This elongation indicates that the unidentified ligand X of ACS has a strong *trans* influence, which may be as strong as a Me group.

Synthesis of 2 via a Ni_d(II)–Ni_p(0) Complex. A plausible mechanism of ACS catalysis includes the Ni_d(II)–Ni_p(0) state of the A-cluster as an active, reduced form (**1**, **3**, **9**). The formation of “[Ni(S₂N₂′)Ni(cod)]^{2−}” in situ from [Ni(S₂N₂′)]^{2−} and Ni(cod)₂ [S₂N₂′ is *N,N*′-ethylenebis(3-mercaptopropionamide)] has been proposed by Rauchfuss and coworkers (**16**), and here we report the synthesis of a similar Ni_d(II)–Ni_p(0) model by the reaction of Ni(dadt^{Et}) and Ni(cod)₂. When an acetonitrile solution of Ni(dadt^{Et}) was added to a toluene solution of Ni(cod)₂ at -20°C , the solution immediately turned dark purple. Although we have not yet isolated this species because of its thermal instability, the formation of the Ni(II)–Ni(0) complex such as Ni(dadt^{Et})Ni(cod) (**3**) was strongly indicated by a trapping reaction with fumaronitrile, affording Ni(dadt^{Et})Ni(η^2 -(*E*)-NCCH=CHCN) (**4**) in 77% yield (Scheme 2). The molecular structure of **4** was determined by X-ray crystallography [see supporting information (SI) Text]. To get further insights into the Ni(II)–Ni(0) complex formed in situ, we examined the reaction at low temperature and monitored by ^1H -NMR. Because the dissociation of 1,5-cyclooctadiene and the consumption of Ni(dadt^{Et}) and Ni(cod)₂ were confirmed, the formation of the Ni(II)–Ni(0) complex is indicated. However, the signals except for those of the dissociated 1,5-cyclooctadiene are considerably broad, and therefore the Ni(II)–Ni(0) complex has not

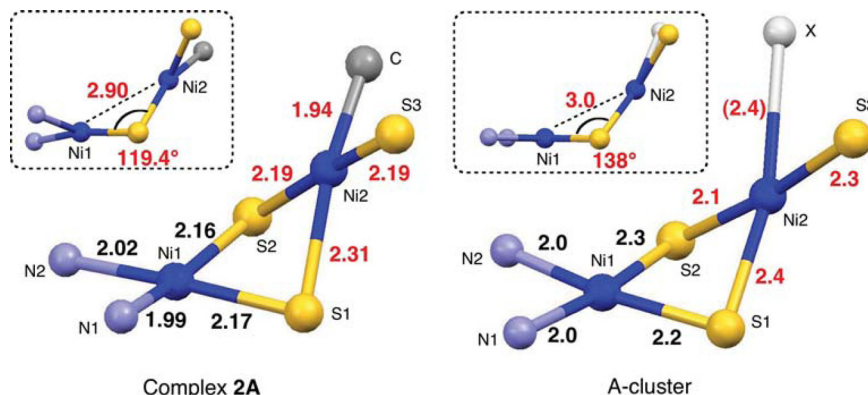


Fig. 3. Core structures of Ni(dadt^{Et})Ni(Me)(SDmp) (**2A**) and A-cluster in ACS_{Mt}. In square, a view of structure from the S1–S2 vector.

yet completely characterized. The broadness of the signals may suggest the fractional cod coordination to the Ni(0) site.

Modeling the methyl-transfer step from methylcobalamin to the Ni_p site, proposed for the ACS catalytic mechanism, the reaction of the Ni(II)–Ni(0) complex with methylcobaloxime Co(dmgBF₂)₂(Me)(Py) (**5**) was examined (28). Because of the thermal instability, the reaction of the Ni(II)–Ni(0) complex and **5** was conducted at –30 °C, although the reaction was rather sluggish at this temperature. After stirring the solution containing the Ni(II)–Ni(0) complex and **5** for 37 h, addition of KSDmp and workup gave **2** in 60% yield (Scheme 2). This result indicates that ACS catalysis could include the Ni_d(II)–Ni_p(0) state as an active state, reacting with methylcobalamin to afford the Ni_d(I–I)–Ni_p(II)–Me species.

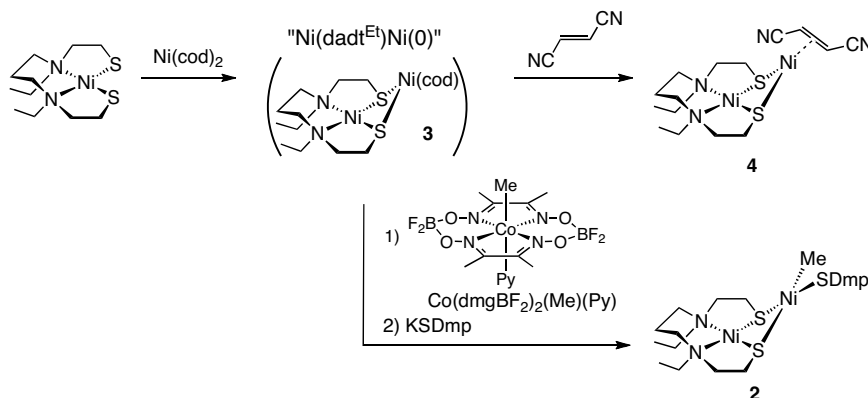
Methylation of Ni(0) can also be achieved by oxidative addition of MeI to the Ni(II)–Ni(0) complex, affording complex **2** upon successive treatment with KSDmp (Scheme 3). However, this route produces an inferior yield of <20%, probably because the MeI addition to the Ni(0) site competes with electrophilic addition of MeI to the μ-thiolates of the dadt^{Et} ligand as observed for analogous reactions of Ni(N₂S₂) complexes (32). The selective methylation of the Ni_p site in ACS could be due to the steric bulk of the methylcobalamin, which may hinder the nucleophilic methylation of the cystein sulfurs bridging the 2 nickel centers. Although the putative MeI adduct of the Ni(II)–Ni(0) complex, [Ni(dadt^{Et})Ni(Me)I], was not isolated, a similar reaction of the Ni(II)–Ni(0) complex with iodopentafluorobenzene confirms the oxidative addition process, giving the analogous adduct Ni(dadt^{Et})Ni(C₆F₅)I (**6**) in 24% yield. Complex **6** was further converted to Ni(dadt^{Et})Ni(C₆F₅)(SDmp) (**7**) via subsequent addition of KSDmp (Scheme 3). The molecular

structures of **6** and **7** were analyzed by X-ray crystallography (see *SI Text*).

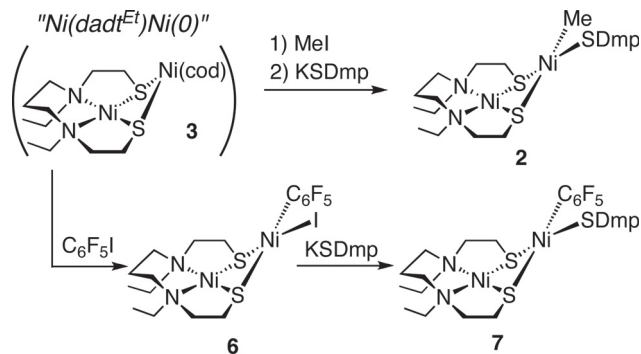
Acetylthioester Formation. To model the formation of acetyl-CoA at the ACS active site, we examined the reaction of **2** with CO. Treatment of **2** with an atmospheric pressure of CO in THF at room temperature resulted in an immediate color change from reddish purple to reddish brown. After removal of volatiles, the materials soluble to ether were subjected to silica gel column chromatography to afford the acetylthioester CH₃C(O)SDmp (**8**) in 89% yield. This result proves that the dinuclear nickel complex **2** can carry out a reaction similar to that of ACS. The residual reddish brown solid, insoluble to ether, was identified as Ni(dadt^{Et}), which was recovered in quantitative yield.

When CO gas was charged to a THF solution of **2** at –60 °C, it was noticed that the color first changed from reddish purple to a dark green before becoming reddish brown. After stirring the solution for 3 min at –60 °C, a dark-green solid was precipitated from the reaction mixture upon addition of hexane. The IR spectrum of the nearly colorless THF/hexane solution showed ν_{CO} bands at 2,044 and 1,710 cm^{–1}, which are attributable to Ni(CO)₄ and **8**, respectively. The dark-green precipitate was crystallized from acetonitrile/ether, and the resulting dark-green needles were subjected to X-ray structural analysis. The crystals were found to contain the dinuclear nickel dicarbonyl complex Ni(dadt^{Et})Ni(CO)₂ (**9**) and Ni(dadt^{Et}) in a 1:1 ratio (Scheme 4).

The formation of the acetylthioester, CH₃C(O)SDmp (**8**), probably proceeds via insertion of CO into the Ni–Me bond of **2** with successive reductive elimination. The latter step, where Ni(2) in Fig. 2 is reduced from Ni^{II} to Ni⁰, would be facilitated



Scheme 2.

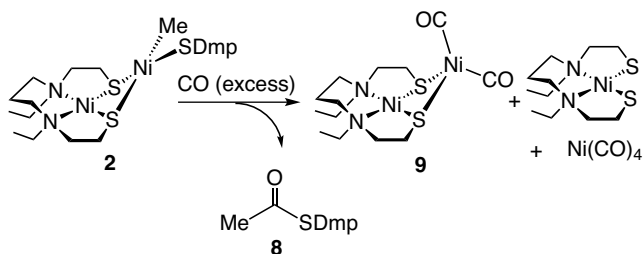


Scheme 3.

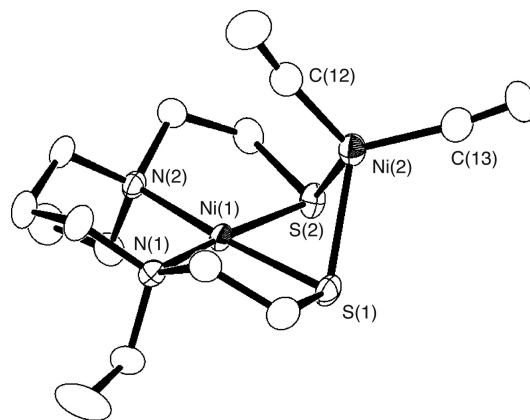
by coordination of CO at Ni(2), to generate **9** and Ni(CO)₄. In an attempt to detect the possible nickel(II) acetyl intermediate, we examined the reaction of **2** with 1 equiv of CO at -60°C . However, the detectable products were the same as those obtained from the reaction of **2** with atmospheric CO, i.e., CH₃C(O)SDmp (**8**), **9**, and Ni(dadt^{Et}), except for the presence of unreacted starting complex **2**. The result indicates that the reductive elimination of the acetylthioester facilitated by CO coordination is faster than the preceding CO insertion into the Ni–Me bond.

An ORTEP drawing of **9** is given in Fig. 4. The coordination geometries of Ni(1) and Ni(2) are square planar and tetrahedral, typical for Ni(II) and Ni(0) oxidation states, respectively. The long Ni(2)–μS bonds of 2.3847(8)–2.3577(8) Å corroborate the Ni(0) state for Ni(2), and the Ni(1)–μS bond lengths of 2.1866(7)–2.1956(6) Å are similar to those of the Ni(II)–Ni(II) dinuclear nickel models (15, 21, 30, 31). Interestingly, the dihedral angle of 97.6° between the 2 Ni(μ-S)₂ planes is notably smaller than those of Ni(II)–Ni(II) dinuclear nickel models (10, 18–23). It is also smaller than that (109.7°) of the closely related complex, [Et₄N]₂{Ni(S₂N₂')}{Ni(CO)₂}, reported by Linck et al. (16). The IR spectrum of the dark-green needles shows 2 ν_{CO} bands at 1,971 and 1,890 cm⁻¹, which are reasonable for a Ni(0) dicarbonyl such as **9**; the ν_{CO} bands of [Et₄N]₂{Ni(S₂N₂')}{Ni(CO)₂} were reported to appear at 1,948 and 1,866 cm⁻¹. This shift of ν_{CO} to lower wave numbers indicates greater back donation to CO for the negatively charged dinuclear complex.

To obtain further insight into the CO insertion into the Ni–Me bond, the dinuclear complex carrying an electron-withdrawing benzenethiolate, Ni(dadt^{Et})Ni(Me)(SC₆Cl₅) (**10**), was prepared in a similar fashion from **1**, MeMgCl, and KSC₆Cl₅ (25). When a dichloromethane solution of **10** was treated with atmospheric CO at room temperature, MeC(O)SC₆Cl₅ was produced in 36% yield. However, when the same reaction was performed at -40°C , the IR spectrum exhibits an intense absorption at 1,629 cm⁻¹ attributable to an acyl CO stretch. X-ray structural analysis of brown crystals obtained at -40°C under a CO atmosphere



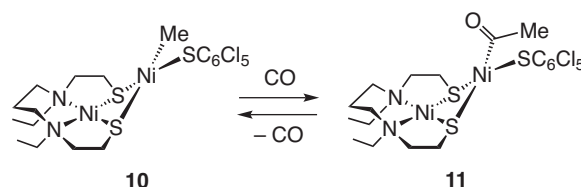
Scheme 4.

Fig. 4. ORTEP drawing of Ni(dadt^{Et})Ni(CO)₂ (**9**). Thermal ellipsoids are shown at 50% probability.

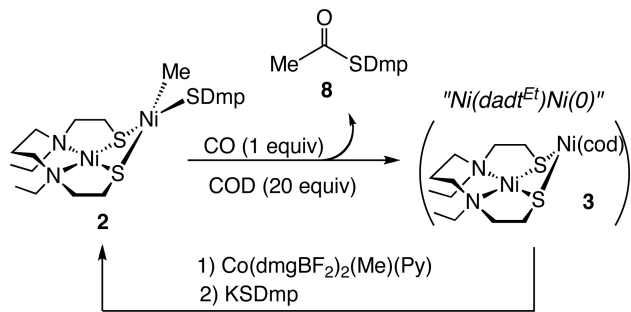
confirms the formation of the acyl complex Ni(dadt^{Et})Ni(COME)(SC₆Cl₅) (**11**) (see *SI Text*). Notably CO insertion is reversible in this particular case. The ν(CO) band in the IR spectra weakened and then disappeared upon evacuation of the solution at -40°C , from which complex **10** was recovered quantitatively (Scheme 5). In ACS catalysis, CO insertion into the Ni_p–Me species would be reversible, and the reductive elimination of acetyl-CoA would immediately occur when the CoA is coordinated to Ni_p site.

Because complex **9** obtained after treatment of **2** with excess CO does not react with methyl cobaloxime, the acetylthioester formation reported here is stoichiometric. However, the active Ni(II)–Ni(0) complex such as **3** can be regenerated when complex **2** is treated with 1 equiv of CO in the presence of 20 equiv of 1,5-cyclooctadiene. This significantly suppresses the formation of **9** and Ni(CO)₄, and complex **2** and CH₃C(O)SDmp (**8**) were obtained in 46% and 93% yields, respectively, upon treatment with methylcobalamin **5** and KSDmp (Scheme 6). According to these results, CO addition to the Ni_p site in ACS catalysis must be strictly regulated to prevent the formation of inactive Ni(0)-carbonyl species, such as **9**, and therefore CO transfer may perhaps be controlled by opening and closing the tunnel connecting CODH and ACS (5, 6). The cystein thiolate of the [4Fe-4S] cluster located at the Ni_p site may be important for the regulation of CO coordination and promotion of reductive elimination of acetyl-CoA, a role played by 1,5-cyclooctadiene in our model reaction.

Concluding Remarks. We have synthesized the dinuclear nickel complex Ni(dadt^{Et})Ni(Me)(SDmp) (**2**), having a methyl group and a thiolate, which is a good mimic of the structure of the dinuclear nickel site of the A-cluster, although the diamidodithiolate Cys-Gly-Cys ligand of the A-cluster is different from the diaminedithiolate dadt^{Et} ligand. Complex **2** has been synthesized from the Ni(II)–Ni(0) species such as [Ni(dadt^{Et})Ni(cod)] (**3**) via methyl transfer from Co(dmgbF₂)₂(Me)Py (**5**), which models the reaction of the active state of the A-cluster with methylcobal-



Scheme 5.



Scheme 6.

amin. Notably an ACS model reaction was found to take place on the Ni_p site of **2**, featuring CO insertion into the Ni–Me bond, successive reductive elimination of the acetylthioester, $\text{CH}_3\text{C}(\text{O})\text{SDmp}$ (**8**), and generation of such $\text{Ni}_d(\text{II})\text{--Ni}_p(0)$ species. These results are consistent with an ACS mechanism, in which the Ni_p site in the A-cluster first takes up a Me moiety and CO insertion follows (12). However, the alternative mechanism,

which involves initial CO coordination at $\text{Ni}_p(\text{I})$ and subsequent reaction with Me, remains to be examined (13). In either case, Ni_d is not the catalytic site but plays a structural role to hold the 2 bridging cysteinyl sulfurs of the Cys–Gly–Cys backbone in a favorable and perhaps flexible position for coordination to Ni_p (33–35).

Materials and Methods

All reactions and the manipulations were performed under nitrogen or argon atmospheres by using standard Schlenk techniques. Solvents were dried, degassed, and distilled from CaH_2 (CH_2Cl_2), or from Mg turnings (methanol) under nitrogen. Hexane, ether, toluene, THF, and CH_3CN were purified by columns of activated alumina and a supported copper catalyst supplied by Hansen.

All experimental procedures and details of characterization of complexes are given in *SI Text*. Molecular structures of **4**, **6**, **7**, **10**, and **11** are given in Figs. S1–S5, and selected bond distances and angles for **2**, **4**, **6**, **7**, **9**, **10**–**11** are listed in Tables S1–S5, respectively. Crystal data are summarized in Table S6.

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