Inorg. Chem. **2008**, *47*, 10832−10840

Inorganic Chemistry

Article

A Trinuclear Nickel(II) Enediolate Complex: Synthesis, Characterization, and O_2 Reactivity

Katarzyna Rudzka,[†] Atta M. Arif,[‡] and Lisa M. Berreau*[,†]

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300, and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received May 25, 2008

Using a new N_4-donor chelate ligand having a mixture of hydrophobic phenyl and hydrogen-bond-donor appendages, a trinuclear nickel(II) complex of the doubly deprotonated form of 2-hydroxy-1,3-diphenylpropane-1,3-dione was isolated, characterized (X-ray crystallography, elemental analysis, UV−vis, ^{1}H NMR, FTIR, and magnetic moment measurement), and evaluated for O_2 reactivity. This complex, $[(6\text{-NA-6-Ph}_2\text{TPANi})_2(\mu\text{-PhC(O)C(O)C(O)Ph})_2\text{Ni}](\text{ClO}_4)_2$ (**4**), has two terminal pseudooctahedral Ni^{II} centers supported by the tetradentate chelate ligand and a central square-planar Ni^{II} ion ligated by oxygen atoms of two bridging enediolate ligands. In CH_3CN, **4** exhibits a deep orange/brown color and $\lambda_{\text{max}} = 463$ nm ($\varepsilon = 16\,000$ $\text{M}^{-1}\text{cm}^{-1}$). The room temperature magnetic moment of **4**, determined by Evans method, is $\mu_{\text{eff}} = 5.3(2)$ μ_{B}. This is consistent with the presence of two noninteracting high-spin Ni^{II} centers, a diamagnetic central Ni^{II} ion, and an overall quintet ground state. Exposure of a CH_3CN solution of **4** to O_2 results in the rapid loss of the orange/brown color to give a green solution. The products identified from this reaction are $[(\kappa^3\text{-6-NA-6-Ph}_2\text{TPA})\text{Ni}(\text{O}_2\text{Ph})(\text{H}_2\text{O})]\text{ClO}_4$ (**5**), benzil [PhC(O)C(O)Ph], and CO. Identification of **5** was achieved via its independent synthesis and a comparison of its ^{1}H NMR and mass spectral features with those of the 6-NA-6-Ph_2TPA-containing product generated upon reaction of **4** with O_2. The independently prepared sample of **5** was characterized by X-ray crystallography, elemental analysis, UV−vis, mass spectrometry, and FTIR. The O_2 reactivity of **4** has relevance to the active-site chemistry of Ni^{II}-containing acireductone dioxygenase (Ni^{II}ARD).

Introduction

Acireductone dioxygenase (ARD) enzymes are found in a variety of species, including humans.[1−7] They are associated with the methionine salvage pathway, wherein they catalyze O_2-dependent oxidative aliphatic carbon−carbon bond cleavage reactions involving an acireductone intermediate.[1] The enzymes Ni^{II}ARD and Fe^{II}ARD′, which have the same protein component and differ only in the active site metal ion, have been shown to catalyze different reactions of the acireductone intermediate in *Klebsiella oxytoca ATCC 8724*. As shown in Scheme 1, the reaction catalyzed by Ni^{II}ARD is a shunt out of the methionine salvage pathway and gives carboxylic acids and CO as products. Carbon monoxide production via a similar reaction has also been identified in *Bacillus subtilis* and *Escherichia coli*.[8,9] The reaction catalyzed by Fe^{II}ARD′ gives a α-keto acid product that is a precursor to methionine in an “on-pathway”-type reaction. It is important to note that the activities of Ni^{II}ARD and Fe^{II}ARD′ can be interconverted by exchange of the metal ion.[10]

A recently deposited X-ray structure of a putative ARD from mouse (MmARD, PDB 1VR3),[11] combined with NMR

---

* To whom correspondence should be addressed. E-mail: lisa.berreau@usu.edu. Phone: (435) 797-1625. Fax: (435) 797-3390.

[†] Utah State University.

[‡] University of Utah.

[1] Pochapsky, T. C.; Ju, T.; Dang, R.; Beaulieu, R.; Pagani, G. M.; OuYang, B. In *Metal Ions in Life Sciences*; Sigel, A., Sigel, H., Sigel, R. K. O., Eds.; Wiley-VCH: Weinheim, Germany, 2007; pp 473−498.

[2] Qi, J.-L.; Zhang, W.-J.; Liu, S.-H.; Wang, H.; Sun, D.-Y.; Xu, G.-H.; Shi, M.-W.; Liu, Z.; Zhang, M.-S.; Zhang, H.-M.; Yang, Y.-H. *J. Plant Physiol.* **2008**, *165*, 1474−1482.

[3] Oram, S. W.; Ai, J.; Pagani, G. M.; Hitchens, M. R.; Stern, J. A.; Eggener, S.; Pins, M.; Xiao, W.; Cai, X.; Haleem, R.; Jiang, F.; Pochapsky, T. C.; Hedstrom, L.; Wang, Z. *Neoplasia* **2007**, *9*, 643–651.

[4] Akhunov, E. D.; Akhunova, A. R.; Dvorak, J. *Mol. Biol. Evol.* **2007**, *24*, 539–550.

[5] Gotoh, I.; Uekita, T.; Seiki, M. *Genes Cells* **2007**, *12*, 105–117.

[6] Lin, T.; He, X.-W.; Yang, L.; Shou, H.-X.; Wu, P. *Gene* **2005**, *360*, 27–34.

[7] Hirano, W.; Gotoh, I.; Uekita, T.; Seiki, M. *Genes Cells* **2005**, *10*, 565–574.

[8] Sekowska, A.; Denervaud, V.; Ashida, H.; Michoud, K.; Haas, D.; Yokota, A.; Danchin, A. *BMC Microbiol.* **2004**, *4*, 9.

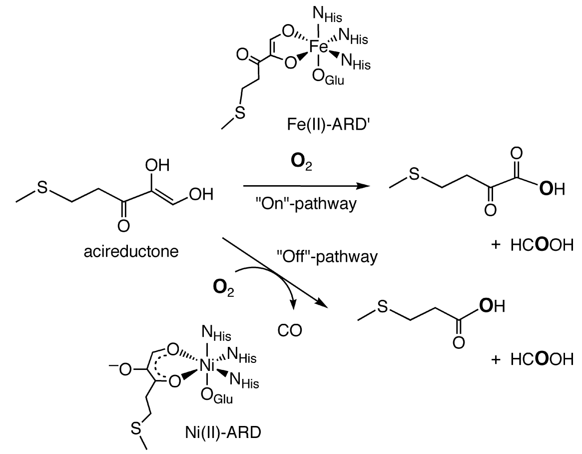
[9] Wray, J. W.; Abeles, R. H. *J. Biol. Chem.* **1993**, *268*, 21466–21469.

[10] Dai, Y.; Wensink, P. C.; Abeles, R. H. *J. Biol. Chem.* **1999**, *274*, 1193–1195.

10.1021/ic800947z CCC: $40.75

structural studies (PDB 1ZRR), conserved domain homology modeling, and X-ray absorption spectroscopic studies of *K. oxytoca* Ni^{II}ARD, indicates that the Ni^{II} center in this enzyme is ligated by a facial array of three histidine residues and a glutamate ligand from the protein.[12−14] The two remaining coordination positions of the Ni^{II} center are occupied by water/hydroxide ligands in the resting state. A histidine residue may be displaced from the nickel(II) complex in the enzyme/substrate complex.[15] The structural studies also revealed several important secondary residues that are located near the active site Ni^{II} center. These include Phe92, Phe142, Arg104, and Arg154 in *K. oxytoca* Ni^{II}ARD. The phenylalanine residues have been proposed to orient the substrate for reaction with O_2 and are close enough to exhibit paramagnetically shifted resonances.[12] Arg104 and Arg154 have been suggested to play a role in stabilizing substrate coordination via hydrogen bonding and/or may donate or accept a proton.[12,13] In Ni^{II}ARD, a 1,3-coordination motif is proposed for the acireductone dianion (Scheme 1) in the enzyme/substrate complex.[16,17] In this binding mode, Lewis acid activation of the C(1)−O(1) and C(3)−O(3) units is proposed to favor the formation of a five-membered cyclic peroxide upon reaction with O_2. Breakdown of this peroxide ring would then lead to the formation of the carboxylic acids and CO (Scheme 1).

Scheme 1



There is currently very little known about the coordination chemistry of acireductones and the O_2 reactivity of metal(II) acireductone species. As shown in Figure 1a, neutral acireductones have been proposed to adopt structures involving a six-membered ring.[18] However, the X-ray structure of the rubidium salt and neutral form of triose reductone ($R = R' = H$) revealed that all three oxygen atoms are positioned on one side of the carbon chain (Figure 1b).[19,20] Prior to 2005, one transition metal compound having a coordinated acyclic acireductone ligand had been characterized by X-ray crystallography. This compound, $[(Ru(bipy)_2)_2(\mu\text{-}C_4H_4O_3)](PF_6)_2$ (Figure 1c), was generated as a byproduct in reactions of $[Ru(bipy)_2Cl_2 \cdot 2H_2O]$ in ethylene glycol in the presence of NH_4PF_6.[21] Similar to the triose reductone structures, the acireductone ligand in $[(Ru(bipy)_2)_2(\mu\text{-}C_4H_4O_3)](PF_6)_2$ is coordinated with all three oxygen atoms of the enediolate on the same side of the carbon chain. Similar backbone carbon−carbon distances, and C(1)−O and C(3)−O bonds (1.29 and 1.30 Å, respectively) that are shorter than the C(2)−O bond (1.39 Å), indicate a delocalized enolate anion along the carbon backbone. No O_2 reactivity studies have been reported for this complex.

Of relevance to Ni^{II}ARD, we generated a nickel(II) *cis*-β-ketoenolate complex, $[(6\text{-}Ph_2TPA)Ni(PhC(O)C(OH)C(O)Ph)]ClO_4$ (**1**; Scheme 2), which can be isolated and characterized.[22] Treatment of **1** with 1 equiv of base followed by the introduction of O_2 results in the formation of a nickel(II) carboxylate complex, $[(\kappa^3\text{-}6\text{-}Ph_2TPA)Ni(O_2CPh)_2(H_2O)]$ (**2**), and CO, as well as benzil [PhC(O)C(O)Ph]. The formation of carboxylates and CO, as well as ^{18}O incorporation into one oxygen atom of each carboxylate ligand, is consistent with an ARD-type pathway. However, the formation of benzil suggests that an alternative reaction pathway is also operative. Complex **1** undergoes reaction with O_2 in the absence of excess base to give a nickel(II) monobenzoate complex, $[(6\text{-}Ph_2TPA)Ni(O_2CPh)]ClO_4$ (**3**), CO, benzil, and

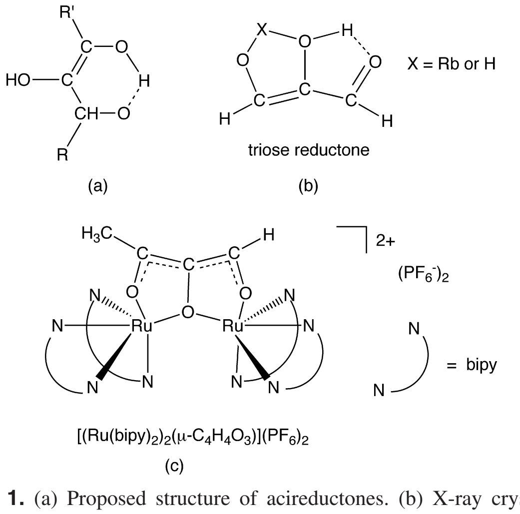


Figure 1. (a) Proposed structure of acireductones. (b) X-ray crystallographically determined structures of the neutral form and rubidium salt of triose reductone. (c) X-ray crystallographically characterized complex having acireductone dianion coordination to a transition metal.

---

(11) Xu, Q.; Schwarzenbacher, R.; Krishna, S. S.; McMullan, D.; Agarwalla, S.; Quijano, K.; Abdubek, P.; Ambing, E.; Axelrod, H.; Biorac, T.; Canaves, J. M.; Chiu, H.-J.; Elsliger, M.-A.; Grittini, C.; Grzechnik, S. K.; DiDonato, M.; Hale, J.; Hampton, E.; Han, G. W.; Haugen, J.; Hornsby, M.; Jaroszewski, L.; Klock, H. E.; Knuth, M. W.; Koesema, E.; Kreusch, A.; Kuhn, P.; Miller, M. D.; Moy, K.; Nigoghossian, E.; Paulsen, J.; Reyes, R.; Rife, C.; Spraggon, G.; Stevens, R. C.; van den Bedem, H.; Velasquez, J.; White, A.; Wolf, G.; Hodgson, K. O.; Wooley, J.; Deacon, A. M.; Godzik, A.; Lesley, S. A.; Wilson, I. A. *Proteins* **2006**, *64*, 808–813.

(12) Pochapsky, T. C.; Pochapsky, S. S.; Ju, T.; Mo, H.; Al-Mjeni, F.; Maroney, M. J. *Nat. Struct. Biol.* **2002**, *9*, 966–972.

(13) Pochapsky, T. C.; Pochapsky, S. S.; Ju, T.; Hoefler, C.; Liang, J. *J. Biomol. NMR* **2006**, *34*, 117–127.

(14) Pochapsky, S. S.; Sunshine, J. C.; Pochapsky, T. C. *J. Am. Chem. Soc.* **2008**, *130*, 2156–2157.

(15) Al-Mjeni, F.; Ju, T.; Pochapsky, T. C.; Maroney, M. J. *Biochemistry* **2002**, *41*, 6761–6769.

(16) Ju, T.; Goldsmith, R. B.; Chai, S. C.; Maroney, M. J.; Pochapsky, S. S.; Pochapsky, T. C. *J. Mol. Biol.* **2006**, *363*, 823–834.

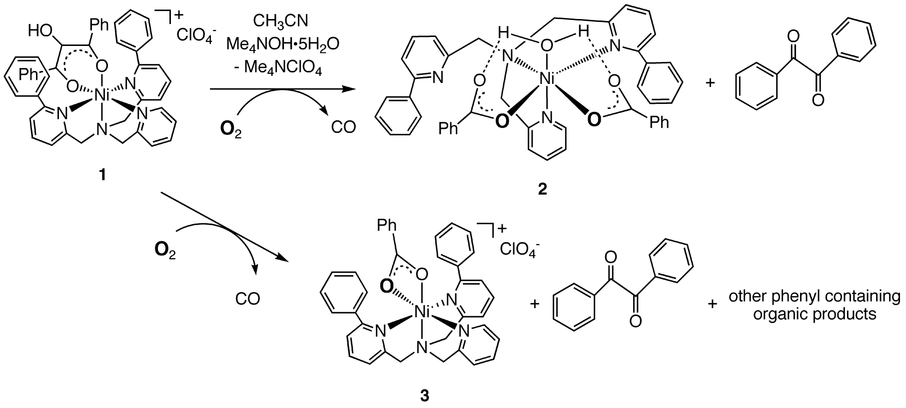
(17) Chai, S. C.; Ju, T.; Dang, M.; Goldsmith, R. B.; Maroney, M. J.; Pochapsky, T. C. *Biochemistry* **2008**, *47*, 2428–2438.

(18) Schank, K. *Synthesis* **1972**, 176–190.

(19) Aurivillius, B.; Lundgren, G. *Acta Chem. Scand.* **1955**, *9*, 912–916.

(20) Semmingsen, D. *Acta Chem. Scand. B* **1974**, *28*, 141–146.

Scheme 2



other phenyl-containing organic byproducts.[23] From these combined studies, we found that the O_2 reaction is cleaner, with a higher level of ^{18}O incorporation in the benzoate product, under conditions wherein the acireductone ligand can access a dianionic form, as is proposed to occur in the Ni^{II}ARD-catalyzed reaction.

Our initial approach toward modeling the active site chemistry of Ni^{II}ARD, as outlined in Scheme 2, was to use a tetradentate nitrogen-donor ligand having two hydrophobic phenyl appendages (6-Ph_2TPA). The phenyl groups were included to create a hydrophobic microenvironment that could have relevance to the possible role of active site phenylalanine side chains in Ni^{II}ARD. To model the acireductone ligand, we have used the deprotonated form of 2-hydroxy-1,3-diphenylpropane-1,3-dione. In the research outlined herein, we present the nickel(II) coordination chemistry of a new chelate ligand wherein a secondary amine hydrogen-bond donor has been incorporated to create a mixed hydrophobic/hydrogen-bond-donor microenvironment. This ligand, 6-NA-6-Ph_2TPA (Figure 2), is the reduced form of a previously reported amide-containing ligand.[24] Having a rigidly fixed hydrogen-bond donor, the 6-NA-6-Ph_2TPA ligand is appropriate for investigating the influence of a single hydrogen-bond donor on the chemistry of nickel(II) enolate or enediolate complexes. This investigation is relevant to evaluating the possible influence of hydrogen bonding involving an arginine side chain with a Ni^{II}-coordinated acireductone in the Ni^{II}ARD enzyme/substrate complex. Our results outlined herein demonstrate that use of the 6-NA-6-Ph_2TPA ligand enables the isolation and characterization of a trinuclear nickel(II) complex, $[(6\text{-NA-6-Ph}_2\text{TPANi})_2(\mu\text{-PhC(O)C(O)C(O)Ph})_2\text{Ni}](\text{ClO}_4)_2$ (**4**), wherein two enediolate ligands derived from 2-hydroxy-1,3-diphenylpropane-1,3-dione bridge between terminal pseudooctahedral Ni^{II} centers and a central square-planar Ni^{II} ion. Complex **4**, which is the first structurally characterized example of a nickel(II) enediolate complex of relevance to Ni^{II}ARD, reacts with O_2 to yield a 6-NA-6-Ph_2TPA-ligated nickel(II) benzoate complex, CO, benzil, and a nickel benzoate species.

Experimental Section

General Procedures. All reagents and solvents were purchased from commercial sources and used as received unless otherwise noted. Acetonitrile and diethyl ether were dried according to published procedures.[25] Air-sensitive reactions were performed in a MBraun Unilab glovebox or a Vacuum Atomospheres MO-20 glovebox under an atmosphere of purified N_2. $^{18}O_2$ was purchased from Icon Services, Summit, NJ. The ligand precursors 2-(pivaloylamido)-6-(aminomethyl)pyridine, 2-(chloromethyl)-6-phenylpyridine hydrochloride, and 2-hydroxy-1,3-diphenylpropane-1,3-dione were prepared according to literature procedures.[26-28] Qualitative CO detection was performed using the $PdCl_2$ method.[29]

Physical Methods. ^{1}H NMR spectra were recorded on a Bruker ARX 400 spectrometer, with the spectra for **4** and **5** being recorded under conditions as previously described.[30] Chemical shifts (δ) are referenced to the residual solvent peak in $CD_2\mathit{H}CN$ (^{1}H NMR: 1.94 ppm). UV−vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer. Mass spectrometry experiments were performed at the University of California, Riverside. Room temperature magnetic susceptibilities were determined by the Evans method.[31] Elemental analyses were performed by Canadian Microanalytical, Service, Inc., British Columbia, Canada, or Atlantic Microlabs, Inc., Norcross, GA.

Caution! *Perchlorate salts of metal complexes supported by organic ligands are potentially explosive.*[32]

2-(Neopentylamino)-6-(aminomethyl)pyridine. $LiAlH_4$ (1.02 g, 0.0268 mol) was added to 50 mL of freshly distilled Et_2O, and the resulting slurry was stirred under N_2 for ~10 min. This mixture was then added dropwise to 2-(pivaloylamido)-6-(aminomethyl)pyridine (0.69 g, 0.0033 mol). The resulting mixture was stirred at room temperature for 24 h. Distilled water (75 mL) was then added,

---

(21) Jeffery, J. C.; Liard, D. J.; Ward, M. D. *Inorg. Chim. Acta* **1996**, *251*, 9–12.

(22) Szajna, E.; Arif, A. M.; Berreau, L. M. *J. Am. Chem. Soc.* **2005**, *127*, 17186–17187.

(23) Szajna-Fuller, E.; Rudzka, K.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2007**, *46*, 5499–5507.

(24) Rudzka, K.; Makowska-Grzyska, M. M.; Szajna, E.; Arif, A. M.; Berreau, L. M. *Chem. Commun.* **2005**, 489–491.

(25) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Boston, MA, 1996.

(26) Berreau, L. M.; Mahapatra, S. M.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **1996**, *35*, 6339–6342.

(27) Makowska-Grzyska, M. M.; Szajna, E.; Shipley, C.; Arif, A. M.; Mitchell, M. H.; Halfen, J. A.; Berreau, L. M. *Inorg. Chem.* **2003**, *42*, 7472–7488.

(28) Plietker, B. *J. Org. Chem.* **2004**, *69*, 8287–8296.

(29) Allen, T. H.; Root, W. S. *J. Biol. Chem.* **1955**, *216*, 309–317.

(30) Szajna, E.; Dobrowolski, P.; Fuller, A. L.; Arif, A. M.; Berreau, L. M. *Inorg. Chem.* **2004**, *43*, 3988–3997.

(31) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005.

(32) Wolsey, W. *J. Chem. Educ.* **1973**, *50*, A335–A337.

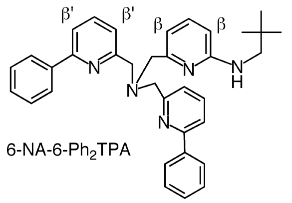


Figure 2. 6-NA-6-Ph$_2$TPA chelate ligand.

with the first 10 mL being added dropwise. The solution was then filtered, and the filtrate was extracted with ethyl acetate (3 × 50 mL), the combined organic fractions were dried over Na_2SO_4, and the solvent was removed under reduced pressure, yielding a pale-yellow oil (0.58, 90%). ^{1}H NMR (CD_3CN, 400 MHz): δ 7.32 (t, J = 7.7 Hz, 1H), 6.46 (d, J = 7.2 Hz, 1H), 6.31 (d, J = 8.3 Hz, 1H), 5.02 (br, 2H), 3.61 (s, 2H), 3.15 (d, J = 6.4 Hz, 2H), 0.94 (s, 9H) ppm.

6-NA-6-Ph$_2$TPA. 2-(Neopentylamino)-6-(aminomethyl)pyridine (0.58 g, 3.0 × 10^{-3} mol), 2-(chloromethyl)-6-phenylpyridine hydrochloride (1.44 g, 6.00 × 10^{-3} mol), Na_2CO_3 (3.18 g, 3.01 × 10^{-2} mol), and a catalytic amount of TBABr were combined in CH_3CN (150 mL). This mixture was refluxed under a N_2 atmosphere for 20 h. After cooling to room temperature, the reaction mixture was added to an equal volume of 1 M NaOH. Extraction with CH_2Cl_2 (3 × 80 mL) followed by drying of the combined organic fractions over Na_2SO_4 and removal of the solvent under reduced pressure yielded a yellow-brown oil. Purification by column chromatography (silica gel, 230−400 mesh; 1:1 ethyl acetate/hexanes) gave the product as a yellow oil (1.2 g, 74%). ^{1}H NMR (CD_3CN, 400 MHz): δ 8.05 (d, J = 8.5 Hz, 4H), 7.78 (t, J = 8 Hz, 2H), 7.69 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 7.7 Hz, 2H), 7.49−7.41 (m, 6H), 7.36 (m, 1H), 6.78 (d, J = 7.2 Hz, 1H), 6.35 (d, J = 8.3 Hz, 1H), 5.02 (br, 1H), 3.98 (s, 4H), 3.73 (s, 2H), 3.18 (d, J = 6.4 Hz, 2H), 0.94 (s, 9H) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 160.9, 160.4, 158.5, 157.0, 140.5, 138.4, 129.9, 129.7, 127.8, 122.5, 119.5, 111.8, 106.7, 61.0, 60.9, 53.5, 33.0, 27.9 (19 signals expected, 18 observed; overlap of two resonances in the aromatic region). FTIR (KBr, cm^{-1}): 3400 (ν_{N-H}).

[(6-NA-6-Ph$_2$TPANi)$_2$(μ-PhC(O)C(O)C(O)Ph)$_2$Ni](ClO$_4$)$_2$ (4). To a solution of 6-NA-6-Ph$_2$TPA (0.042 g, 0.080 mmol) in CH_3CN (2 mL) was added a CH_3CN solution (2 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.044 g, 0.12 mmol) and PhC(O)CH(OH)C(O)Ph (0.019 g, 0.080 mmol). After 15 min of stirring, this mixture was transferred to a new vessel containing $Me_4NOH \cdot 5H_2O$ (0.029 g, 0.16 mmol). The solution was stirred for 3 h at room temperature under a N_2 atmosphere, after which the solvent was removed under reduced pressure, the residue was redissolved in CH_2Cl_2 and filtered, and the filtrate was reduced to ~1 mL. The addition of excess Et_2O (~15 mL) resulted in the precipitation of an orange-brown solid, which was collected and dried under vacuum. Long needles were obtained by Et_2O diffusion into a CH_2Cl_2 solution of **4** (29 mg, 38%). Crystals suitable for X-ray crystallography were obtained by Et_2O diffusion into an aceonitrile/methanol solution of **1**. Anal. Calcd for $C_{100}H_{94}N_{10}O_{14}Ni_3Cl_2 \cdot 0.66CH_2Cl_2$: C, 61.58; H, 4.89; N, 7.13. Found: C, 61.50; H, 4.83; N, 6.75. (The presence of methylene chloride in the sample was confirmed by ^{1}H NMR.) UV−vis, nm (ε, M^{-1} cm^{-1}): 463 (16 000). μ_{eff} = 5.3(2) μ_B. FTIR (KBr, cm^{-1}): 3411 (br, ν_{N-H}), 1096 (ν_{ClO_4}), 624 (ν_{ClO_4}).

Independent Synthesis of [(6-NA-6-Ph$_2$TPA)Ni(O$_2$CPh)(H$_2$O)]ClO$_4$ (5). A solution of 6-NA-6-Ph$_2$TPA (0.028 g, 0.052 mmol) in CH_2Cl_2 was added to solid $Ni(ClO_4)_2 \cdot 6H_2O$ (0.019 g, 0.052 mmol). To this slurry was added a methanol solution of sodium benzoate (0.0075 g, 0.052 mmol). The resulting green solution was stirred for 1.5 h at room temperature. The solvent was then removed under reduced pressure. The green residue was redissolved in CH_2Cl_2 and filtered, and the filtrate was brought to dryness under vacuum. The solid was dissolved in methanol, and this solution was added to an equal volume of water. Slow evaporation of this mixture produced green crystals (0.029 g, 68%). Anal. Calcd for $C_{42}H_{44}N_5O_7NiCl$: C, 61.22; H, 5.39; N, 8.50. Found: C, 60.89; H, 5.44; N, 8.36. UV−vis, nm (ε, M^{-1} cm^{-1}): 600 (19), 1004 (18). FTIR (KBr, cm^{-1}): 3360 (ν_{N-H}), 1092 (ν_{ClO_4}), 621 (ν_{ClO_4}). FAB-MS (MeOH/NBA): m/z (relative intensity) 706 ($[M - ClO_4 - H_2O]^+$, 100%).

Product Isolation and Identification Following the Reaction of 4 with $^{18}O_2$. Compound **4** (57 mg, 0.030 mmol) was dissolved in CH_3CN (10 mL). It was degassed by two freeze/pump/thaw cycles, then exposed to $^{18}O_2$, and stirred for 12 h at room temperature. This resulted in the formation of a pale-green reaction mixture. After removal of the solvent under reduced pressure, to the remaining solids was added hexanes/ethyl acetate (a 4:1 mixture) and then CH_3CN dropwise until all solids had dissolved. The mixture was then transferred to a silica gel column, and fractions were collected. Using hexanes/ethyl acetate (4:1), benzil was eluted from the column. This product was identified by ^{1}H NMR and GC−MS. The yield of benzil from this reaction was consistently ~20% based on the formulation that one benzil molecule can form from each enediolate ligand of **4**. A control reaction indicated that an independent sample of benzil was recovered in ~85% yield using the column conditions outlined above.

Switching of the solvent to pure acetonitrile resulted in the elution of a pale-green band. Removal of the solvent from this fraction and analysis by ^{1}H NMR indicated the presence of **5** because the signals of this product in the 30−70 ppm region exactly matched those obtained for the independently prepared **5**. The isolated yield of this product from the column was variable (~50−75% based on producing 2 equiv of **5** from each 1 equiv of **4**). A control reaction indicated that an independent sample of **5** was recovered in ~75% yield using the column conditions outlined above. Thus, a portion of **5** is lost during the chromatographic separation. These combined results suggest that **5** is produced in nearly quantitative yield in the reaction of **4** with O_2, which is consistent with ^{1}H NMR spectra of the reaction mixture (Figure 5).

Switching of the column eluent to MeOH resulted in the elution of a yellow material. Following removal of the solvent under reduced pressure, the pale-yellow material was evaluated using ^{1}H NMR and FTIR. The ^{1}H NMR spectrum did not contain any resonances in the paramagnetically shifted region beyond 10 ppm, only broad peaks overlapping a few sharp resonances in the 5−8 ppm region. The IR spectrum of the solid yellow material shows carboxylate vibrations at 1554 ($\nu_{as(COO^-)}$) and 1405 cm^{-1} ($\nu_{s(COO^-)}$), respectively, and phenyl group vibrations at 1598 and 717 cm^{-1}. These combined results are consistent with the yellow compound being a nickel(II) benzoate species, such as $Ni(O_2CPh)_2 \cdot nCH_3OH$. Attempts were made to characterize this yellow compound using MS methods (FAB and MALDI). Unfortunately, this material, which has limited solubility in organic solvents, did not give clear spectral evidence for a particular formulation. The data from both methods exhibited only low-intensity m/z peak envelopes (e.g., <20% intensity relative to the peaks present for the nitrobenzyl acohol matrix in the FAB-MS spectrum) that could not be conclusively identified.

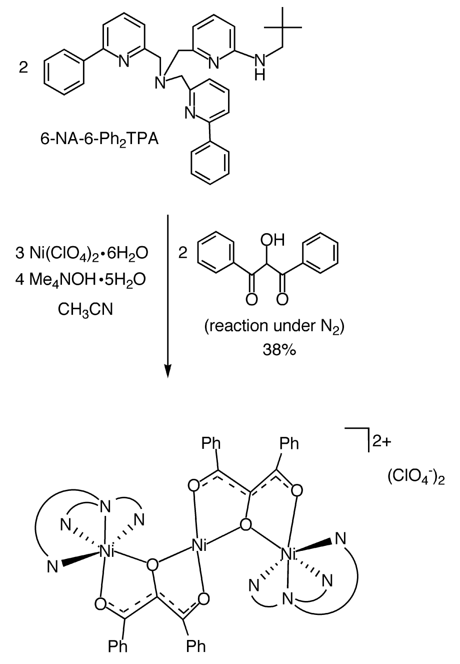
X-ray Crystallography. Single crystals of **4·2Et$_2$O·3CH$_3$CN** and **5·CH$_3$OH** were each mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius Kappa CCD diffractometer (Mo Kα, λ = 0.710 73 Å). A total of 10 frames of data were collected with an oscillation range of 1°/frame and an exposure time of 20 s/frame. Indexing and unit cell refinement based on all observed reflections from those 10 frames indicated a monoclinic *C* lattice for **4·2Et$_2$O·3CH$_3$CN** and a monoclinic *P* lattice for **5·CH$_3$OH**. A total of 17 358 reflections for **4·2Et$_2$O·3CH$_3$CN** and 17 258 reflections for **5·CH$_3$OH** were indexed, integrated, and corrected for Lorentz, polarization, and absorption effects using *DENZO-SMN* and *SCALEPAC*.[33] The structure was solved by a combination of direct methods and heavy atoms using *SIR97*.[34] All of the non-hydrogen atoms of **4·2Et$_2$O·3CH$_3$CN** and **5·CH$_3$OH** were refined with anisotropic displacement coefficients. The N(1)−*H* in **4·2Et$_2$O·3CH$_3$CN** was located and refined independently. All other hydrogen atoms were assigned isotropic displacement coefficients $U(\mathrm{H}) = 1.2U(\mathrm{C})$ or $1.5U(\mathrm{C_{methyl}})$, and their coordinates were allowed to ride on their respective carbons using *SHELXL97*.[35] One perchlorate anion and the *tert*-butyl methyl group exhibit disorder in **4·2Et$_2$O·3CH$_3$CN**. The perchlorate anion in **5·CH$_3$OH** exhibits disorder.

Results and Discussion

ARDs are fascinating metalloenzymes. The Ni^{II}ARD and Fe^{II}ARD′ enzymes represent the only example in biology wherein the simple change of a metal ion results in a different chemical reaction. The key issue that is proposed to determine ARD versus ARD′ reactivity is the coordination mode of the acireductone on the divalent metal center. Metal-centered reactivity with O$_2$ is not proposed in these systems. Instead, direct reaction between the coordinated acireductone and O$_2$ is proposed to result in the formation of a four- or five-membered peroxide species involving the acireductone from which the ARD and ARD′ products are generated, respectively.

Synthesis. A goal of our work is to prepare and characterize examples of divalent metal complexes of acireductone-type ligands and examine their reactivity with O$_2$. A recent Cambridge Crystallographic Database search (version 5.29, updated Jan 2008) revealed that structurally characterized examples of transition metal complexes having an acyclic acireductone-type ligand remain rare,[36] with the only examples to our knowledge being [(Ru(bipy)$_2$)$_2$(μ-C$_4$H$_4$O$_3$)](PF$_6$)$_2$ (Figure 1c) and **1** (Scheme 2). In the diruthenium complex, the acireductone is coordinated as a dianion in a coordination motif akin to that found in the neutral and rubidium salt forms of triose reductone (Figure 1). Complex **1** contains a *cis*-β-ketoenolate-type ligand of the monodeprotonated form of 2-hydroxy-1,3-diphenylpropane-1,3-dione (Scheme 2). The different coordination modes of these acireductone-type ligands could be due to their structural differences and/or the protonation level. Our investigations with the 6-NA-6-Ph$_2$TPA ligand started with an attempt to prepare an analogue of **1**, wherein one oxygen atom of the coordinated acireductone-type ligand could form a hydrogen-bonding interaction with the neopentyl substituent of the chelate ligand. From a reaction mixture comprised of a 1:1:1:1 stoichiometry (6-NA-6-Ph$_2$TPA, Ni(ClO$_4$)$_2$·6H$_2$O, Me$_4$NOH·6H$_2$O, and 2-hydroxy-1,3-diphenylpropane-1,3-dione) of reagents, we obtained a few small orange-brown needle-type crystals. This material was identified by single-crystal X-ray crystallography as the trinuclear complex **4**. The production of **4** under these conditions is interesting because it suggests that the presence of the internal hydrogen-bond donor may be important toward promoting dianion coordination. Adjustment of the reaction stoichiometry to that required for the formation of the trinuclear **4** (Scheme 3) gave an orange-brown crystalline solid in 38% overall yield. This relatively low yield appears to be due, in part, to the presence of at least one additional product in this reaction mixture as indicated by ^{1}H NMR.

Scheme 3



Core Drawing of **4**
Supporting chelate ligand abbreviated for clarity

X-ray Crystallography. A drawing of the cationic portion of **4·2Et$_2$O·3CH$_3$CN** is shown in Figure 3a. The two terminal pseudooctahedral Ni^{II} centers are equivalent via a C_2 rotation. A drawing of the trinuclear core and metal-coordinated atoms in **4·2Et$_2$O·3CH$_3$CN** is shown in Figure 3b, with the full ligand environments of the pseudooctahedral and square-planar Ni^{II} centers being shown in parts c and d of Figure 3. Details of the X-ray data collection and refinement are given in Table 1. Selected bond distances and angles are given in Table 2.

The Ni(1) center exhibits a pseudooctahedral coordination geometry. The Ni−N bonds vary in length over a range of ~0.3 Å, with the shortest Ni−N distance involving the tertiary amine donor of the chelate ligand [Ni(1)−N(3) 2.039(3) Å]. The longest Ni−N distance is found for one of the two phenyl-appended pyridyl donors [Ni(1)−N(4) 2.341(3) Å]. A survey of the nickel(II) complexes of chelate ligands

---

(33) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307–326.

(34) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(35) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(36) Several structurally characterized metal complexes of ascorbic acid, which contains the 1-oxo-2-ene-2,3-diol structural unit within a cyclic structure, have been reported. See: Zümreoglu-Karan, B. *Coord. Chem. Rev.* **2006**, *250*, 2295−2307; Davies, M. B. *Polyhedron* **1992**, *11*, 285–321.

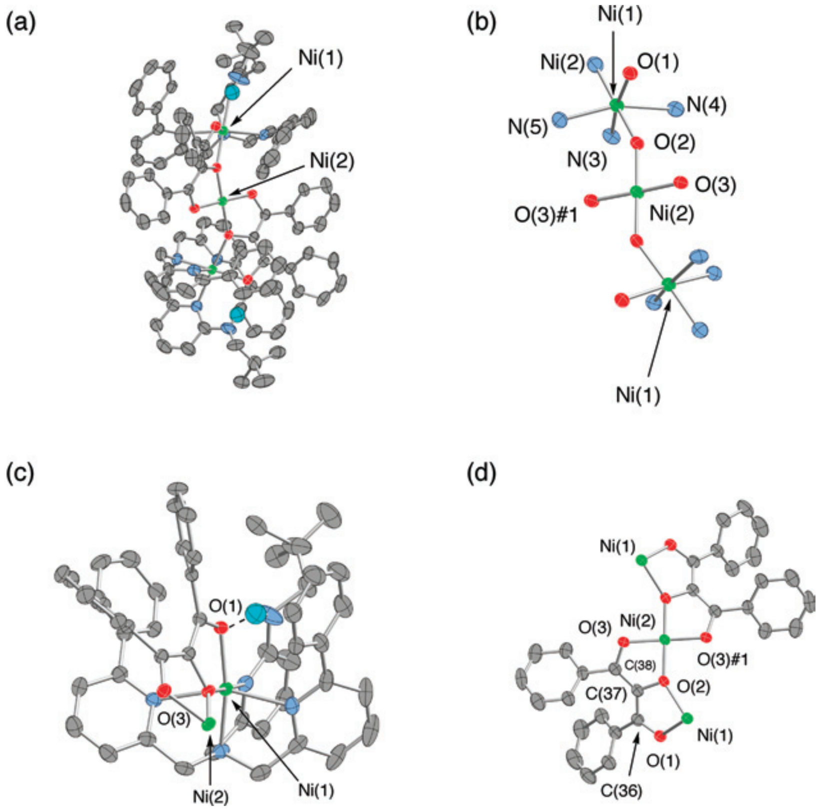


Figure 3. Thermal ellipsoid drawings (50% probability) of the cationic portion of $\mathbf{4\cdot 2Et_2O\cdot 3CH_3CN}$: (a) full cation; (b) trinuclear metal core; (c) pseudooctahedral Ni(1) center; (d) square-planar Ni(2) center. Hydrogen atoms except the neopentylamine proton have been omitted for clarity.

Table 1. Summary of X-ray Data Collection and Refinement for $\mathbf{4\cdot 2Et_2O\cdot 3CH_3CN}$ and $\mathbf{5\cdot CH_3OH}$

	$\mathbf{4\cdot 2Et_2O\cdot 3CH_3CN}$	$\mathbf{5\cdot CH_3OH}$
empirical formula	$C_{114}H_{123}N_{13}O_{16}Ni_3Cl_2$	$C_{43}H_{48}N_5O_8NiCl$
fw	2178.28	857.02
cryst syst	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$
a (Å)	24.4466(8)	11.6202(3)
b (Å)	18.6303(7)	23.7494(4)
c (Å)	23.8127(7)	15.1919(4)
α (deg)	90	90
β (deg)	96.160(2)	95.9420(11)
γ (deg)	90	90
V (Å^3)	10782.8(6)	4170.03(17)
Z	4	4
d_{calcd}, Mg/m^3	1.342	1.365
temp (K)	150(1)	150(1)
crystal size (mm^3)	0.23 × 0.13 × 0.08	0.30 × 0.25 × 0.20
diffractometer[a]	Nonius Kappa CCD	Nonius Kappa CCD
abs coeff (mm^{-1})	0.639	0.588
$2\theta_{\max}$ (deg)	50.72	54.96
reflns collected	17358	17258
indep reflns	9891	9480
variable param	721	685
R1/wR2[b]	0.0582/0.1174	0.0643/0.1487
GOF (F^2)	1.043	1.042
largest diff (e/Å^3)	0.609, −0.638	1.304, −1.026

[a] Radiation used: Mo Kα ($\lambda = 0.71073$ Å). [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/[\sum(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

Table 2. Selected Bond Distances (Å) and Angles (deg) in the Cationic Portion of $\mathbf{4\cdot 2Et_2O\cdot 3CH_3CN}$[a]

Ni(1)−O(1)	1.988(3)	Ni(1)−N(4)	2.341(3)
Ni(1)−O(2)	2.057(3)	Ni(1)−N(5)	2.188(3)
Ni(1)−N(2)	2.119(3)	Ni(2)−O(2)	1.864(2)
Ni(1)−N(3)	2.039(3)	Ni(2)−O(3)	1.856(3)
O(1)−Ni(1)−N(3)	170.32(13)	N(3)−Ni(1)−N(4)	75.40(13)
O(1)−Ni(1)−O(2)	80.00(10)	O(2)−Ni(1)−N(4)	81.86(11)
N(3)−Ni(1)−O(2)	100.27(12)	N(2)−Ni(1)−N(4)	99.46(12)
O(1)−Ni(1)−N(2)	97.44(12)	N(5)−Ni(1)−N(4)	157.36(13)
N(3)−Ni(1)−N(2)	82.43(13)	O(3)#1−Ni(2)−O(3)	175.39(18)
O(2)−Ni(1)−N(2)	177.24(13)	O(3)#1−Ni(2)−O(2)	94.20(11)
O(1)−Ni(1)−N(5)	106.66(13)	O(3)−Ni(2)−O(2)	85.77(11)
N(3)−Ni(1)−N(5)	82.97(14)	O(3)#1−Ni(2)−O(2)#1	85.77(11)
O(2)−Ni(1)−N(5)	95.69(11)	O(3)−Ni(2)−O(2)#1	94.19(11)
N(2)−Ni(1)−N(5)	84.03(13)	O(2)−Ni(2)−O(2)#1	179.06(17)
O(1)−Ni(1)−N(4)	95.13(11)		

[a] Estimated standard deviations in the last significant figure are given in parentheses.

containing an aryl-appended pyridyl donor reported to date indicates that a range of Ni−N$_{\mathrm{PhPy}}$ distances (2.15−2.36 Å) is possible depending on the other ligands present on the metal center.[22,23,27,30,37,38] The Ni(1)···Ni(2) distance is 3.73 Å.

The enediolate ligand in $\mathbf{4\cdot 2Et_2O\cdot 3CH_3CN}$ is coordinated as a cis-bridging ligand between Ni(1) and Ni(2), forming two five-membered chelate rings. This coordination motif is similar to that found in the rubidium salt and neutral forms of triose reductone (Figure 1) and in $[(Ru(bipy)_2)_2(\mu\text{-}C_4H_4O_3)](PF_6)_2$.[19−21] The Ni(1)−O distances differ only slightly, with the axial Ni(1)−O(1) distance being ~0.07 Å shorter than the bridging Ni(1)−O(2) bond length. The square-planar Ni$^{\mathrm{II}}$ center has shorter Ni−O bonds (~1.86

---

(37) Rudzka, K.; Arif, A. M.; Berreau, L. M. *J. Am. Chem. Soc.* **2006**, *128*, 17018–17023.

(38) He, Z.; Craig, D. C.; Colbran, S. B. *Dalton Trans.* **2002**, 4224–4235.

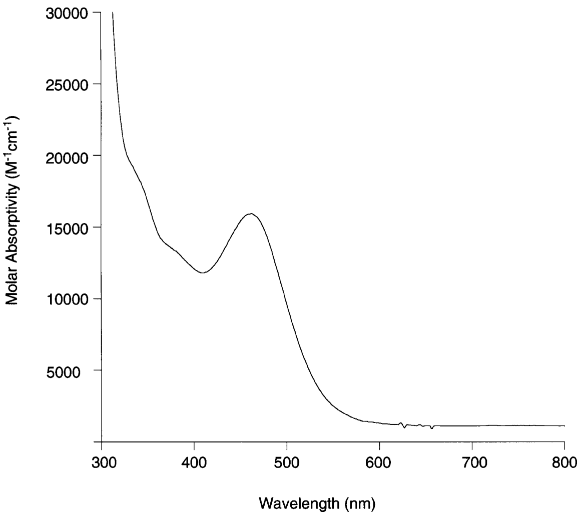


Figure 4. UV−vis spectrum of **4** in CH_2Cl_2 under a N_2 atmosphere.

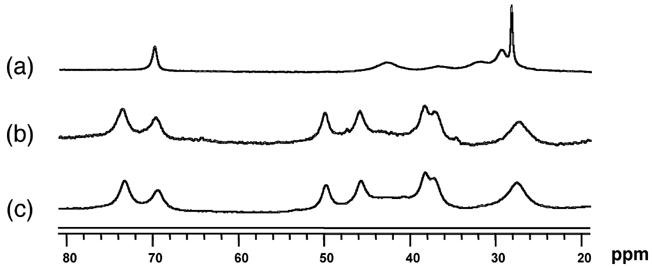


Figure 5. ^1H NMR spectra of (a) analytically pure **4**, (b) the reaction mixture produced from treatment of **4** with O_2, and (c) independently synthesized, analytically pure **5**.

Å).The C(36)−O(1) [1.287(5) Å] and C(38)−O(3) [1.310(4) Å] bond distances are shorter than the C(37)−O(2) [1.380(5) Å] bond, indicating more single-bond character in the latter. This is consistent with a localized anion at O(2) and a delocalized enolate anion in the O(1)−C(36)−C(37)−C(38)−O(3) backbone. Finally, at the Ni(1) site, O(1) accepts a hydrogen bond from the neopentylamine moiety of the chelate ligand [(N(1)···O(1) 2.838(5) Å; N(1)−H(1)···O(1) 163(5)°]. These parameters are consistent with the presence of a moderate hydrogen-bonding interaction.[39]

Overall, the isolation and structural characterization of **4** reveals that the enediolate form of the coordinated acireductone-type ligand can be stabilized via the recruitment of an additional Ni^{II} center, with a contribution from a hydrogen-bonding interaction. Stabilization of a Ni^{II}-coordinated acireductone dianion species in the active site of Ni^{II}ARD is proposed to involve hydrogen-bonding interactions with one or more arginine residues.[1]

Spectroscopic Properties. The solid-state IR spectrum of **4** in KBr contains a broad, intense feature at ~3420 cm^{-1} for the neopentylamine N−H moiety. Vibrations at 1096 and 623 cm^{-1} are consistent with the presence of the perchlorate anions.

The UV−vis spectrum of **4** in CH_2Cl_2 (Figure 4) contains a broad absorption band at 463 nm (ε = 16 000 M^{-1} cm^{-1}; Figure 4). This spectrum is notably distinct from that exhibited by **1** [λ_{max} = 399 nm (ε = 6800 M^{-1} cm^{-1}) in CH_2Cl_2].[23] The intensity of the absorption band in **4** is consistent with a charge-transfer-type transition.

The ^1H NMR spectrum of **4** contains several distinct paramagnetically shifted resonances in the region of 20−70 ppm (Figure 5a). Assignments of individual resonances in this region have not been made because the method typically employed to conclusively identify such signals (2D-COSY)[30] is not feasible because of the broad nature of several of the signals. However, on the basis of detailed NMR studies of several mononuclear nickel(II) complexes of the 6-Ph_2TPA ligand, many of these signals are likely for pyridyl ring protons.[30] Similar to histidine ring protons in the NMR studies of Ni^{II}ARD, the pattern of resonances in this region is affected by changes in the ligand environment of the Ni^{II} center.[12] The remainder of the resonances that can be identified for **4** are found in the region of 0−10 ppm (Figure S1 in the Supporting Information).

Magnetic Properties. Because of the extreme O_2 sensitivity of **4**, we have initially examined its magnetic properties via measurement of a magnetic moment. In acetonitrile, **4** exhibits a magnetic moment of μ_{eff} = 5.3(2) μ_B at room temperature as measured by the Evans method.[31] Because the cation contains two pseudooctahedral Ni^{II} centers and a central square-planar Ni^{II} ion, a quintet ground state is possible wherein the two noninteracting pseudooctahedral high-spin Ni^{II} centers each have two unpaired spins and the central Ni^{II} is diamagnetic. The observed magnetic moment is slightly higher than the spin-only value predicted for this electronic structure (μ_{so} = 4.9 μ_B), which could be due to orbital contributions to the magnetic moment.

O_2 Reactivity of 4. Product Identification. Exposure of an acetonitrile solution of **4** to O_2 results in the rapid loss of the orange-brown color to give a pale-green solution. The overall reaction that takes place is shown in Scheme 4. The methods used for product identification and/or isolation are outlined below.

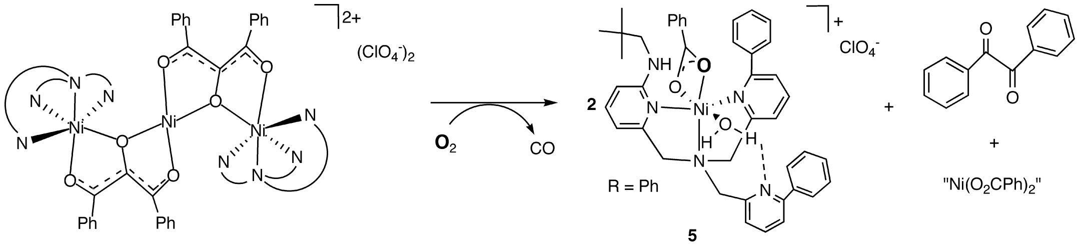
Analysis of the products generated in the reaction of **4** with O_2 by ^1H NMR revealed the presence of several new resonances in the region of 20−70 ppm (Figure 5b). MS analysis of the mixture revealed a parent ion at *m/z* 706. The complex associated with this ^1H NMR spectrum and parent ion was identified via an independent synthesis as **5**. This compound was prepared via an admixture of equimolar amounts of 6-NA-6-Ph_2TPA, $Ni(ClO_4)_2 \cdot 6H_2O$, and sodium benzoate in wet CH_2Cl_2/MeOH. Recrystallization of the product from MeOH/water yielded **5** as green crystals in 68% yield. The independently synthesized complex has been characterized by X-ray crystallography, elemental analysis, FTIR, mass spectrometry, and UV−vis. Compound **5** can be isolated from the reaction mixture of **4** with O_2 in ~50−75% yield by column chromatography. A less than stoichiometric amount is isolated because of the conditions employed (column chromatography) for separation of **4** from the other reaction products.

A drawing of the cationic portion of **5** is shown in Figure 6. Selected bond distances and angles of this cation are given in

---

[39] Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

Scheme 4



Core Drawing of **4**

Table 3. Complex **5** exhibits κ^3 coordination of the 6-NA-6-Ph_2TPA ligand, with the noncoordinated phenyl-appended pyridyl moiety serving as a hydrogen-bond acceptor for a metal-bound water molecule. This hydrogen-bonding interaction involves a N(5)···O(3) distance of 2.68 Å and a N(5)···H−O(3) angle of 172°. A similar hydrogen-bonding interaction, involving a noncoordinated phenyl-appended phenyl nitrogen, was identified in a nickel(II) acetohydroxamic acid complex, wherein the hydrogen-bond donor is the N−H moiety of the Ni^{II}-bound acid.[24] The Ni(1)−O(3) (water) distance in **5** is 2.061(3) Å, which is ~0.03 Å shorter than the average of the other five metal−ligand bond distances. The Ni(1)−N(4) distance [2.137(3) Å] is on the short end of the range of bond lengths previously identified for a phenyl-appended pyridyl donor to a pseudooctahedral Ni^{II} center (2.15−2.36 Å).[22,23,27,30,37,38] The benzoate ligand is coordinated in a bidentate fashion, with the O(1) atom of the benzoate ligand accepting a hydrogen bond from the neopentylamine moiety of the supporting chelate ligand.

In dry CD_3CN, **5** exhibits at least seven resonances in the range of 20−70 ppm (Figure 5c). Because all three pyridyl donors are inequivalent in this complex, at least six resonances can be expected in this range for the β/β'-H's (Figure 2). We note that methylene $-CH_2-$ resonances are also typically found in this region in mononuclear nickel(II) complexes of tripodal pyridyl ligands.[30]

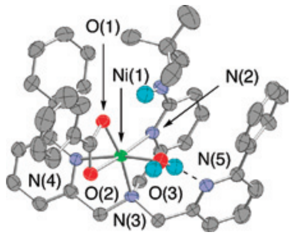


Figure 6. Thermal ellipsoid drawing (50% probability) of the cationic portion of **5**. Hydrogen atoms except the neopentylamine proton, and the water protons have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) in the Cationic Portion of **5·CH_3OH**[a]

Ni(1)−O(1)	2.075(3)	Ni(1)−N(2)	2.055(3)
Ni(1)−O(2)	2.163(3)	Ni(1)−N(3)	2.099(3)
Ni(1)−O(3)	2.061(3)	Ni(1)−N(4)	2.137(3)
N(2)−Ni(1)−O(3)	88.24(12)	O(1)−Ni(1)−N(4)	95.29(11)
N(2)−Ni(1)−O(1)	109.23(11)	N(3)−Ni(1)−N(4)	79.62(12)
O(3)−Ni(1)−O(1)	85.86(11)	N(2)−Ni(1)−O(2)	170.31(11)
N(2)−Ni(1)−N(3)	81.30(12)	O(3)−Ni(1)−O(2)	86.15(11)
O(3)−Ni(1)−N(3)	97.14(12)	O(1)−Ni(1)−O(2)	62.50(10)
O(1)−Ni(1)−N(3)	169.20(11)	N(3)−Ni(1)−O(2)	107.23(11)
N(2)−Ni(1)−N(4)	102.68(12)	Ni(4)−Ni(1)−O(2)	83.73(11)
O(3)−Ni(1)−N(4)	167.90(12)		

[a] Estimated standard deviations in the last significant figure are given in parentheses.

In the reaction mixture produced upon treatment of **4** with O_2, two additional products have been identified (Scheme 4). Exposure of a sample of the headspace gas of the reaction to an aqueous $PdCl_2$ solution resulted in the deposition of Pd^0, which is consistent with the presence of CO according to the equation[29]

$$PdCl_2 + CO + H_2O \rightarrow Pd^0 + CO_2 + 2HCl \qquad (1)$$

A second product, benzil, was isolated from the reaction mixture via column chromatography on silica gel with hexanes/ethyl acetate (4:1) containing trace CH_3CN as the eluent. This organic product has also been identified in the reactions of **1** as outlined in Scheme 2. The yield of benzil obtained in repeat reactions of **4** with O_2 is ~20%.

The column chromatography separation method used to isolate benzil also enables the separation of **5** from another fraction that is yellow in color. Pure acetonitrile is used to elute **5**, after which the addition of methanol results in the elution of the yellow product. When dissolved in CD_3CN, the yellow material exhibits several broad ^{1}H NMR resonances in the region of 5−8 ppm. In the portion of the spectrum from 7 to 8 ppm, the broad resonances are overlapped with at least two smaller, sharper signals (~7.5 and 8.0 ppm). The broad nature of the most intense resonances is consistent with a Ni^{II}-containing species. IR spectroscopic studies indicate that this material does not contain the 6-NA-6-Ph_2TPA ligand or a perchlorate anion but has vibrations, indicating the presence of one or more benzoate anions. Specifically, carboxylate vibrations are present at 1554 ($\nu_{as(COO^-)}$) and 1405 cm^{-1} ($\nu_{s(COO^-)}$), respectively, and phenyl group vibrations at 1598 and 717 cm^{-1}. These vibrations are similar to the major vibrations of sodium benzoate (1598, 1550, 1414, 706, and 681 cm^{-1}). Additional vibrations for the reaction product are found at ~3400 and ~2950 cm^{-1}. We propose that these vibrations may be due to the presence of methanol, suggesting a formulation such as $Ni(O_2CPh)_2 \cdot nCH_3OH$. A Cambridge Crystallographic Database search revealed that a series of nickel benzoate complexes having monodentate carboxylate ligands and four-coordinated water molecules of the empirical formula $[Ni(O_2CAr)_2(H_2O)_4] \cdot nH_2O$ [Ar = 3,5-dihydroxyphenyl (n = 3); 3,5-dinitrophenyl (n = 4); 4-formylphenyl (n = 4)] have been structurally characterized.[40−42] However, X-rayquality crystals of the yellow product have not yet been obtained.

Treatment of a CH_3CN (Acros extra dry, <10 ppm water) solution of **4** with $^{18}O_2$ results in ~86% ^{18}O labeling of one oxygen atom of the benzoate ligand of **5**. Reactions of this type performed using $^{16}O_2$, extra dry CH_3CN, and $H_2{}^{18}O$ did not result in ^{18}O incorporation into **5**. Thus, the ~14% of **5** that contains unlabeled benzoate must be generated from adventitious $^{16}O_2$ in the reaction mixture or via an alternative reaction pathway.

Comments on the O_2 Reactivity of 1 and 4. In the absence of added base, **1** reacts with O_2 to give a nickel benzoate complex, CO, benzil, and other phenyl-containing organic products.[23] This reaction occurs with only a modest level of ^{18}O incorporation (~50%) into one oxygen atom position of the benzoate ligand of **3**). Under conditions wherein the dianionic enediolate form of 2-hydroxy-1,3-diphenylpropane-1,3-dione is present, for example, **1** upon treatment with base or in **4**, the reaction is cleaner, with the only organic byproduct being benzil. These reactions also exhibit a higher level of ^{18}O incorporation into one of the oxygen atom positions in the product benzoate complex, **2** (67%) or **5** (86%), respectively. We note that these levels of ^{18}O incorporation are near that reported for the Ni^{II}ARD-catalyzed reaction (77.5%).[43]

Conclusions

The presence of a secondary hydrogen-bond donor in the 6-NA-6-Ph_2TPA ligand produces chemistry involving nickel(II) and 2-hydroxy-1,3-diphenylpropane-1,3-dione in the presence of a base that is distinctly different from that found for the 6-Ph_2TPA chelate ligand. Specifically, use of the 6-NA-6-Ph_2TPA ligand has enabled the formation and isolation of the trinuclear **4**, which contains a coordinated enediolate form of 2-hydroxy-1,3-diphenylpropane-1,3-dione. This indicates that the nickel(II) coordination chemistry of this acireductone-type ligand is strongly influenced by the nature of the supporting chelate ligand and secondary environment surrounding the metal center. Because the key factor in determining Ni^{II}ARD versus Fe^{II}ARD′ type reactivity has been proposed to be the coordination mode of the acireductone, which is likely influenced by the secondary environment of the metal center, additional investigations of ligand secondary environment modifications are clearly warranted.

Current efforts in our laboratory are also focused on kinetic and mechanistic studies of the O_2 reactions involving **1** and **4**. One avenue of investigation is directed at determining the pathway by which benzil is generated. We hypothesize that benzil may be formed via a reaction wherein the enolate or endiolate moiety of **1** or **4** is oxidized by O_2 to give 1,3-diphenylpropanetrione [PhC(O)C(O)C(O)Ph] and a hydroperoxide/peroxide anion.[44] A phenyl migration reaction involving this triketone could yield benzil and CO.[45] Because triketones have also been shown to undergo reaction with H_2O_2 to yield carboxylates and CO,[46] we hypothesize that the products generated in the reactions of **1** and **4** with O_2 could be generated via a "triketone" pathway or via a mechanism involving a Ni^{II}-coordinated cyclic peroxide species, as has been proposed for Ni^{II}ARD.[1] Efforts are underway to determine if one or both of these types of reaction pathways are occurring upon treatment of **1** and **4** with O_2.

Acknowledgment. We thank the National Institutes of Health (Grant 1R15GM072509) for financial support of this work.

Supporting Information Available: ^1H NMR spectral features of **4** in the 0−10 ppm region and X-ray crystallographic (CIF) files for **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC800947Z

---

(40) Deng, Z.-P.; Gao, S.; Ng, S. W. *Acta Crystallogr.* **2006**, *E62*, m2904–m2905.

(41) Chen, P.-G.; Gao, S.; Ng, S. W. *Acta Crystallogr.* **2006**, *E62*, m2623–m2624.

(42) Wang, H.-Y.; Gao, S.; Ng, S. W. *Acta Crystallogr.* **2006**, *E61*, m2639–m2640.

(43) Wray, J. W.; Abeles, R. H. *J. Biol. Chem.* **1995**, *270*, 3147–3153.

(44) Abe, Y.; Horii, H.; Taniguchi, S.; Kamai, K.; Takagi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 467–470.

(45) Roberts, J. D.; Smith, D. R.; Lee, C. C. *J. Am. Chem. Soc.* **1951**, *73*, 618–625.

(46) Dai, Y.; Pochapsky, T. C.; Abeles, R. H. *Biochemistry* **2001**, *40*, 6379–6387.