

Dioxygen activation by a dinuclear nickel thiolate complex: structural characterization of the ligand oxidized product†

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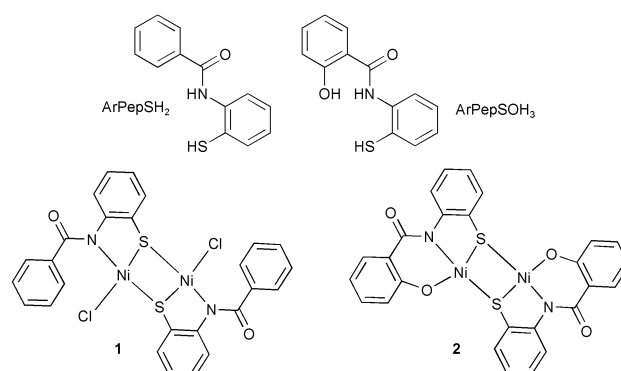
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A $(\mu\text{-SR})_2$ -nickel(II) dimer derived from a ligand with carboxamido nitrogen and thiolato sulfur donors reacts with O_2 to afford an oxidized product in which phenyl groups of the ligand frames are oxidized to nickel-bound phenolates.

The ability of transition metal complexes to bind and activate dioxygen (O_2) has been a topic of keen interest in the field of bioinorganic chemistry.¹ Amid several examples of oxygen-bound transition metal complexes, high-valent bimetallic bis($\mu\text{-oxo}$) $\text{M}(\mu\text{-O})_2\text{M}$ species have drawn much attention as possible reaction intermediates in oxygen metabolism.^{2–4} In the case of Ni complexes, the generation of the $\text{Ni(III)}(\mu\text{-O})_2\text{Ni(III)}$ motif has been reported with the nickel centers supported by pyridine,^{4a,c,d} pyrazolyl,^{4e} and thioether^{4b} ligand frames. In these complexes, inner-sphere reduction of O_2 at the metal center leads to generation of the Ni(III) centers and cleavage of the O–O bond. The mode of dioxygen activation by nickel complexes takes on several other distinct pathways. For example, outer-sphere electron transfer affording disulfide species is a common consequence of O_2 reactivity in nickel thiolate complexes. However, in the well characterized nickel amine/thiolate complex Ni(BME-DACO) , synthesized by Darensbourg and coworkers, nickel-bound sulfur oxygenates are formed as the sole products.⁵ In these latter complexes, the thiolate sulfurs are the sites of the highest nucleophilicity and hence no oxidation occurs at the metal center(s).

In recent years, several nickel complexes have been employed in catalytic oxidation and oxygenation of organic substrates. For example, mononuclear penta-coordinate nickel complexes of macrocyclic polyamine/carboxamide ligands have been shown to catalyze the aerobic oxidation of benzene to phenol.^{6,7} Although spectroscopic data indicate the intermediacy of $[(\text{Ligand})\text{Ni(III)}\text{-superoxide}]$ species in such reactions, a distinct mechanism of O_2 activation by these complexes is still missing.⁸ Inclusion of deprotonated carboxamido nitrogens in these ligands appears essential for complexes of this type to demonstrate any O_2 reactivity. In order to acquire more insight into the mechanism of O_2 activation by nickel complexes, we have synthesized a new ligand N-(2-mercaptophenyl)-benzamide (ArPepSH₂, Hs denote dissociable protons)⁹ that contains one carboxamide nitrogen and one thiolate sulfur in the ligand frame. Herein, we report the synthesis and reactivity of the dinuclear complex $(\text{Et}_4\text{N})_2[\text{Ni}_2(\text{ArPepS})_2\text{Cl}_2]$ (**1**) and the structural characterization of its ligand oxidized product $(\text{Et}_4\text{N})_2[\text{Ni}_2(\text{ArPepSO})_2]$ (**2**) obtained via oxygenation at room temperature. Our results demonstrate that, although the ligand apparently provides stabilization to Ni(III) , the process of O_2 activation eventually affords the Ni(II) complex **2** (and not any Ni(III) species) in which the phenyl ring of the ligand frame is hydroxylated. The reaction is clean and complex **2** is isolated in very high yield with no other oxidation products. This is the first example of a nickel complex supported by thiolate donors that activates O_2 at the metal center and causes ligand frame oxidation with no change at the S donor centers.



When a DMF solution of $(\text{Et}_4\text{N})_2[\text{NiCl}_4]$ is added to a solution of deprotonated ArPepS^{2-} in DMF under anaerobic conditions, the reaction mixture changes to a deep red color due to formation of **1** (*vide infra*). The red color of **1** is stable for weeks when kept in DMF or acetonitrile under dinitrogen. However, when O_2 or air is bubbled through a solution of **1** in acetonitrile for 5–10 s,¹⁰ the initial red color sharply turns to olive-green. Upon standing for several minutes, dark brown crystals, suitable for X-ray analysis, are obtained in the reaction flask in ~85% yield. Crystallographic study reveals that this crystalline product is the dinuclear complex $(\text{Et}_4\text{N})_2[\text{Ni}_2(\text{ArPepSO})_2]$ **2**, in which the benzene ring containing the carbonyl group of ArPepS^{2-} has been converted into phenolate and is coordinated to the nickel center.‡ Complex **2** is only formed when O_2 or dry air is allowed to react; addition of degassed water to the red solutions of **1** in acetonitrile or DMF does not bring about any change in color.

The structure of $[\text{Ni}_2(\text{ArPepSO})_2]^{2-}$, the anion of **2**, is shown in Fig. 1. The coordination geometry around both Ni(II) centers

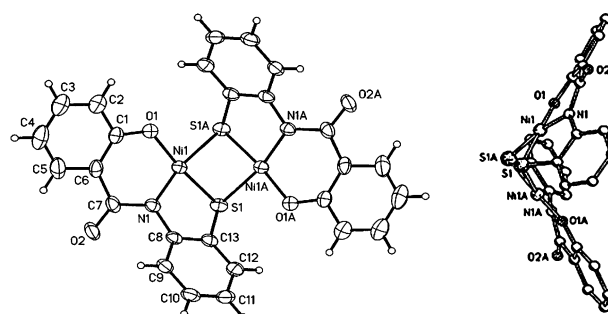


Fig. 1 (left) Thermal ellipsoid plot (50% probability level) of the anion of **2** and (right) its alternate view showing the V-shaped conformation and folding along the axis of the $(\mu\text{-SR})_2$ bridge. H atoms are omitted for clarity. Selected bond distances (Å): Ni(1)–N(1), 1.884(2); Ni(1)–O(1), 1.839(19); Ni(1)–S(1), 2.163(7); Ni(1)–S(1A), 2.212(7); Ni(1)–Ni(1A), 2.752(7); O(1)–C(1), 1.312(3); O(2)–C(7), 1.235(3); N(1)–C(7), 1.370(4); N(1)–C(8), 1.415(3); S(1)–C(13), 1.768(3); C(1)–C(2), 1.416(4); C(2)–C(3), 1.372(4). Selected bond angles (in deg.): O(1)–Ni(1)–N(1), 96.71(9); O(1)–Ni(1)–S(1), 173.34(6); N(1)–Ni(1)–S(1), 89.36(7); O(1)–Ni(1)–S(1A), 92.50(6); N(1)–Ni(1)–S(1A), 168.37(7); S(1)–Ni(1)–S(1A), 81.14(3); O(1)–Ni(1)–Ni(1A), 122.24(6); N(1)–Ni(1)–Ni(1A), 118.34(7); S(1)–Ni(1)–Ni(1A), 51.82(2); S(1A)–Ni(1)–Ni(1A), 50.22(2); C(13)–S(1)–Ni(1), 95.69(9); N(1)–C(7)–C(6), 117.6(2); O(2)–C(7)–C(6), 119.1(3); O(2)–C(7)–N(1), 123.2(3).

† Electronic supplementary information (ESI) available: Fig. S1: ^1H NMR spectrum of **2**. Fig. S2: Electronic spectrum showing conversion of **1** to **2**. See <http://www.rsc.org/suppdata/cc/b2/b211395n/>

is distorted square planar. One deprotonated ArPepSO³⁻ unit is bound to each Ni(II) ion and the two [Ni(ArPepSO)]⁻ units are fused together via a (μ-SR)₂ bridge. The unique mixed NOS₂ (where both sulfur donors bridge two metal centers) coordination sphere has been noted in a limited number of Ni(II) complexes.¹¹ The short Ni–N_{amido} distance in **2** (1.884(2) Å) is in accord with other Ni(II) complexes with bound carboxamido nitrogens.¹² The Ni–Ni distance (2.7527(7) Å) in **2** is among the shortest ones observed in similar dinuclear Ni(II) complexes.¹³ This arises from the small dihedral angle (106.4°) between the two NiNOS₂ planes (Fig. 1, right). Both the diamagnetism of **2** and its clean ¹H NMR spectrum (see ESI†) demonstrate the presence of Ni(II) centers in this complex.

Although we have not established the mechanism of O₂ activation unequivocally at this time, we propose the following working hypothesis based on spectroscopy, structure, and our current understanding of metal-amide chemistry. The dinuclear starting complex **1** is shown to contain a (μ-SR)₂ bridge and a chloride ligand coordinated at the fourth position¹⁴ completes the square planar geometry about each nickel center. The electronic absorption spectrum of **1** (band with λ_{max} at 556 nm) is typical of square planar Ni(II) complexes with a mixed nitrogen and sulfur donor set.¹² Also the mass spectrum and absence of O₂ reactivity at the sulfur centers support the presence of the (μ-SR)₂ core in **1**. We believe that it is the (μ-SR)₂ core that protects the thiolato sulfurs from O₂ attack and directs the oxidation chemistry toward a proximal phenyl ring of the ligand frame. The reaction of **1** with O₂ gives rise to a Ni(III)–O–O–Ni(III) unit stabilized by the presence of carboxamido nitrogens followed by homolysis of the O–O bond generating Ni(III)–O·(Ni(III)-oxyl) radicals. Internal attack of the Ni(III)-oxyl units to the phenyl ring of the two ArPepS²⁻ ligands followed by loss of two molecules of HCl affords the phenolate-bound Ni(II) dimer **2**. Similar oxidation of ligand and phenyl ring followed by coordination to the metal center occurs in several known copper complexes.³ However, this is the first example of such a transformation occurring in a nickel complex.

The reaction of **1** with O₂ to form **2** has been monitored by UV/Vis spectroscopy. The key features in the electronic spectrum of **1** in DMF are a band at 556 nm and shoulder at 430 nm. When O₂ is added, the spectrum of **2** is generated with absorption bands at 605 and 440 nm. Two isosbestic points are observed during this transformation indicating a clean transition from **1** to **2** upon oxygenation. We believe that the compressed nature of the (μ-SR)₂ core as well as the presence of Cl⁻ as the fourth ligand in **1** prohibits the formation of the well-established Ni(III)-(μ-O)₂ species during the **1**→**2** transformation.

The formation of **2** upon oxygenation of **1** is noteworthy for several reasons. First, this is the only example of a Ni(II) species supported by thiolato sulfur donors that undergoes oxidation of the ligand frame as opposed to the highly oxygen-sensitive sulfur centers. Second, regardless of the ligand to metal stoichiometry, only complex **2** forms when the reaction mixture is exposed to O₂ (or dry air). This indicates that the formation of the four-coordinate bis complex [Ni(ArPepS)₂]²⁻ is thermodynamically less stable than formation of the dinuclear species **1**. In contrast, the corresponding Schiff base form of ArPepSH₂ namely, 2-N-(phenylmethylideneamine)benzenethiol, forms a square planar bis complex with Ni(II) which shows no such reactivity toward O₂.¹⁵ Thus, the inclusion of carboxamido nitrogen in the coordination sphere is necessary for O₂ activation to occur seemingly as a result of stabilization of the Ni(III) state. Interestingly, there is a report of a Ni(III) complex with the preformed ligand ArPepSOH₃ namely (Me₄N)₃[Ni(ArPepSO)₂].¹⁶ Finally, the Ni complex **1** activates dioxygen at room temperature with air as the oxygen source to oxidize the ligand frame to form the nickel bound phenolate in **2**. The oxidation of **1** in air is clean and affords just one pure product in exceptional yields. The mechanism is under investigation.

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Notes and references

† Crystal data for **2**, Ni₂C₄₂H₅₆N₄O₄S₂, *M* = 862.45, orthorhombic, space group *Pbcn*, *a* = 13.0112(10), *b* = 13.8925(11), *c* = 22.1485(18) Å, α = 90°, β = 90°, γ = 90°, *V* = 4003.5(5) Å³, *Z* = 4, *D*_c = 1.431 Mg m³, μ(Mo-Kα) = 1.092 mm⁻¹, *T* = 91(2) K, Crystal size 0.25 × 0.20 × 0.03 mm³, 38325 reflections measured, 6376 unique (*R*_{int} = 0.066), final *R*₁ = 0.0467, *wR*₂ = 0.1041. Diffraction data were collected at 91 K on a Bruker SMART 1000 CCD diffractometer. Solution and refinement were solved by direct methods (standard SHELXS-97 package). CCDC 198289. See <http://www.rsc.org/suppdata/cc/b2/b211395n/> for crystallographic data in CIF or other electronic format.

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- Selected data for ArPepSH₂: ¹H NMR spectrum (298 K, CDCl₃, 500 MHz): δ (ppm from TMS) 8.94 (s, 1H), 8.47 (d, 1H), 7.97 (d, 2H), 7.60 (m, 2H), 7.55 (t, 2H), 7.38 (t, 1H), 7.08 (t, 1H), 3.18 (s, 1H); ¹³C NMR (298 K, CDCl₃, 500 MHz): δ (ppm from TMS) 116.9, 121.3, 124.6, 127.3, 129.0, 129.7, 132.2, 134.9, 135.5, 139.3, 165.3. Selected IR bands (KBr pellet, cm⁻¹): ν_{CO} = 1645, ν_{NH} = 3240, ν_{SH} = 2555.
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